afa

الإتحاد العربي للأسمدة
Arab Int'l Organization هيئة عربية دولية
Arab Fertilizer Association
Since 1975

AFA
WORKSHOP
Water Treatment and Water Quality in
Fertilizer and Petrochemical Industries

PAPERS

23 – 25 December, 2013
Aswan, Egypt

AFA
WORKSHOP

Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Arab Int'l Organization
Arab Fertilizer Association
Since 1975

Program

DAY 1: Monday: Dec. 23 th, 2013

08:00   Registration
09:30   Welcome Address:
10:00   **Session I**

- Overview of Water Treatment
  Dr. Faiza Abou Zeid
  General Manager – AQUA Trust for Water Treatment – Egypt

12:00   **Networking Coffee / Tea**

12:30   **Session II**

- Applying Statistical Techniques in Decision Making
  Dr. Abdel Hakim EL–Menhawy
  AQUA Trust for Water Treatment – Egypt

- Water conservation intiatives
  Eng. Mohamed Abu Taleb
  Utipities Dept. Manager
  Fertil – UAE

- Case Study « effect of scale inhibitor addition in cooling water of synthesis gas compressor inter cooler
  Eng. Hassan mostafa Ahmed
  Head of Mechanical Engineering Sector– KIMA – Egypt

14:00   **Networking Lunch – Isis Island Hotel**

09:30 **Session III**

- Pretreatment technology for Surface water and well water.
- Membrane technology for ultra–filtration and desalination process.
  Dr. Abdel Aziz Konsowa
  Chairman –Environmental Engineering Consultants (ENCO).
  Prof. of Environmental Engineering, Chemical Engineering Dept., Alexandria Univ. – Egypt

- Membrane Technology for Water Production from Surface water

- Membrane Technology for Waste Water Recycle
  Eng. Wissam El Mahgoub
  Eng. Alaa Ali
  Pall Corporation – France

11:30 **Networking Coffee / Tea**

12:30   **Session IV**

- Role of Electrochemical Techniques in the Treatment of Wastewater Generated From Fertilizer
  Dr. Ahmed Elshazly
  Chairman of the Chemical and Petrochemical Department, School of Energy,Environmental and Chemical Engineering, E–JUST – Egypt

- An Online Cleaning System to Reduce Demister Fouling in MSF Sidi Krir Desalination Plant
  Chemist Mohamed A. Ismail
  Senior Chemist – Sidi Krir – Egypt

- Oxygen Control in Steam Boilers
  Eng. Osama Khalil
  Power Plant Chemical Supervisor
  Eng. Fouad Alzoubi
  Power & Energy Manager
  APC, Jordan

- Advances in Corrosion Monitoring
  Prof. Essam Khamis Ibrahim
  Director, City of Scientific Research and Technological Applications(SRTA CITY) – Egypt

14:30   **Networking Lunch – Isis Island Hotel**

09:30   **Session V**

- Approaching Zero Liquid Discharge with Cleaner Production
  Dr . Samia Massoud Mohamed
  Environmental & Water Engineering Consultant (EWATEC) – Egypt

- Case Study «Zero liquid Discharge»
  Eng. Amr Saber
  Abu Qir Fertilizer Co. – Egypt

- Case Study «Zero liquid Discharge Unit in NCIC»
  Eng. Ahmed Samir
  Head Production Sector
  NCIC – Egypt

- Startup and 7 years post experience in water treatment units in Alexfert complex
  Eng. Ibrahim A. Elshibiny
  Alexfert Co. – Egypt

Day 1: Monday: December 23rd, 2013

Session I

AFA
WORKSHOP
Water Treatment and Water Quality in
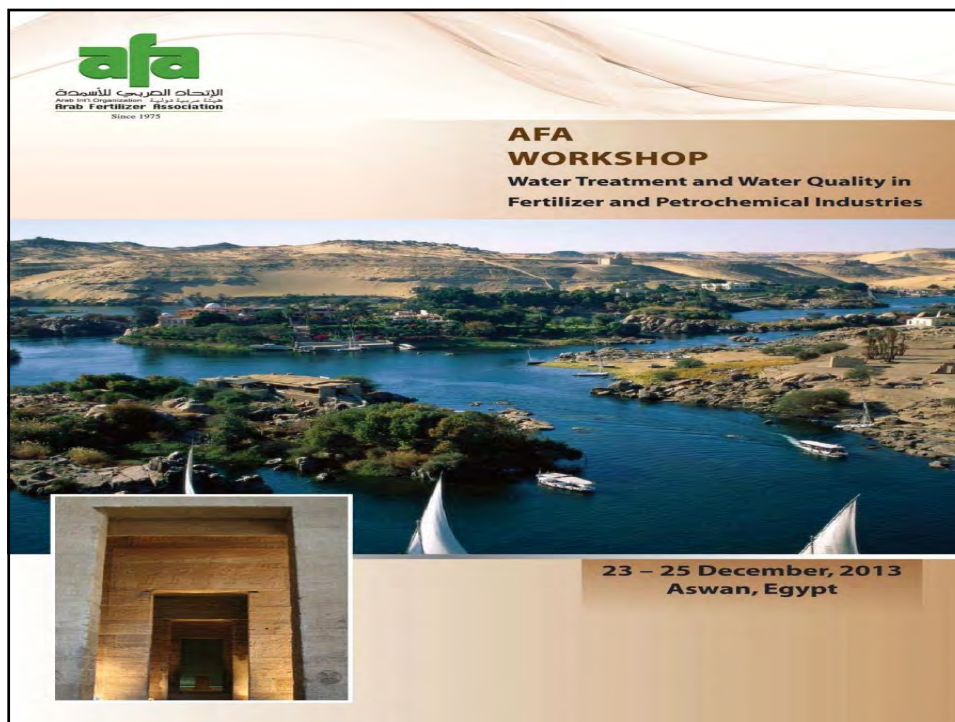**Fertilizer and Petrochemical Industries**

Overview of Water Treatment

Dr. Faiza Abou Zaid

General Manager
Aqua Trust For Water Treatment ~ Egypt

W.H.R.S.G
And Auxiliary Boiler
Treatment For Optimum
Efficiency and Corrosion control

Presented by:

Eng. Faiza Abou Zeid

General Manager

AQUA TRUST FOR WATER TREATMENT LTD. Co.

Abstract

➢ Since the industry is always looking for more energy- efficient ammonia plants and also higher plant capacities are in demand. The engineering companies are offering this new technology to fulfill this requirements.

➢ During the last few years the Ammonia production Engineering companies such as Topose-Uhde and Lurgi-Casal presenting new technology for a production capacity from 2000 MTPD up to 4000 MTPD by one train, this is called MEGAMMONIA plants.

➢SAFCO:- Saudi Arabia has a plant producing 3300 MTPD ammonia- one train **the largest in the world**.

➢ The ammonia plants consist of a combination of energy consuming and energy producing process units.

➢Energy is mainly required for initial conversion of feed stock natural gas or refinery residues by steam reforming.

➢Energy is also required for generation of process steam, for preheat of natural gas, process air, boiler feed water and for regeneration of solvents (or potassium bicarbonate solution) in carbon dioxide removal unit.

➢Furthermore motive power is required for pumps, blowers, compressors and turbines.

➢The energy for this purpose is obtained by Recovery of Waste Heat from process units, by using WHRSG and Super Heaters to produce high pressure steam.

➢The total steam production is about 4 ton steam /one ton of ammonia at temp. 510 °C, 110 kg/cm2 steam pressure.

This paper will illustrate the effect of boiler feed water and boiler water conditions on the Waste Heat Recovery Steam Generators and Super Heaters and on the turbine condition, and on the production efficiency of the ammonia plant.

Megammonia Steam Production Optimization

Introduction:

The new technology makes it possible to construct a single-line units with a higher capacities than currently operation is possible.
More than 3000 MTPD Ammonia will be produced which is looking for more energy efficient operation.
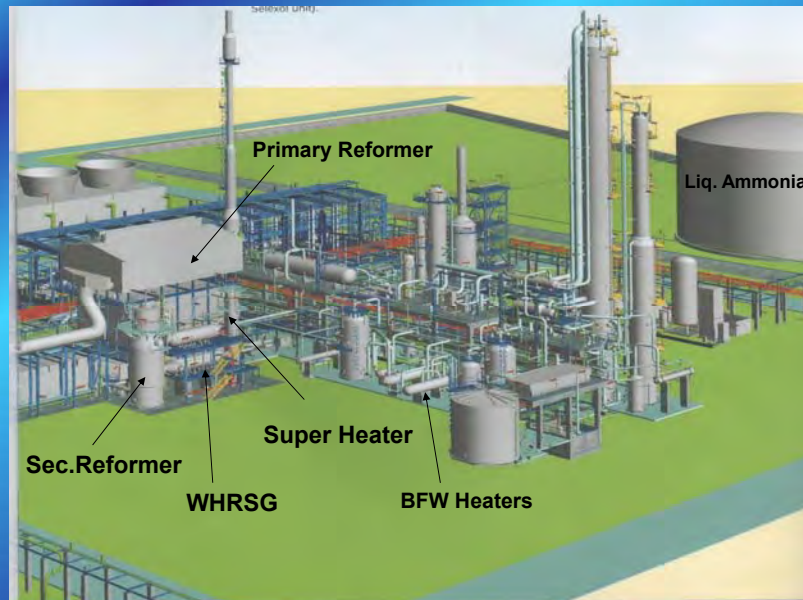
Integration between the process and steam production is optimized, since all waste heat down to below 160 °C is utilized for the production of high pressure steam by Heat Recovery Steam Generators (HRSGs) and super heated.

In ammonia plant, steam generation depend totally on the recovery of waste heat.
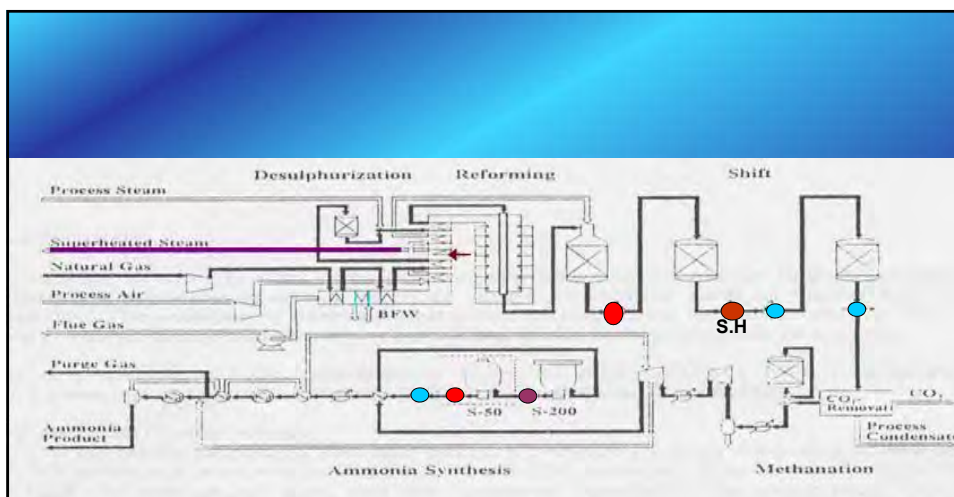
AMMONIA AND STEAM CO-PRODUACTION

➢The ammonia plants consist of a combination of energy consuming and energy producing process units.

➢Energy is mainly required for initial conversion of feed stock natural gas or refinery residues by steam reforming.

➢Energy is also required for generation of process steam, for preheat of natural gas, process air, boiler feed water and for regeneration of solvents (or potassium bicarbonate solution) in carbon dioxide removal unit.
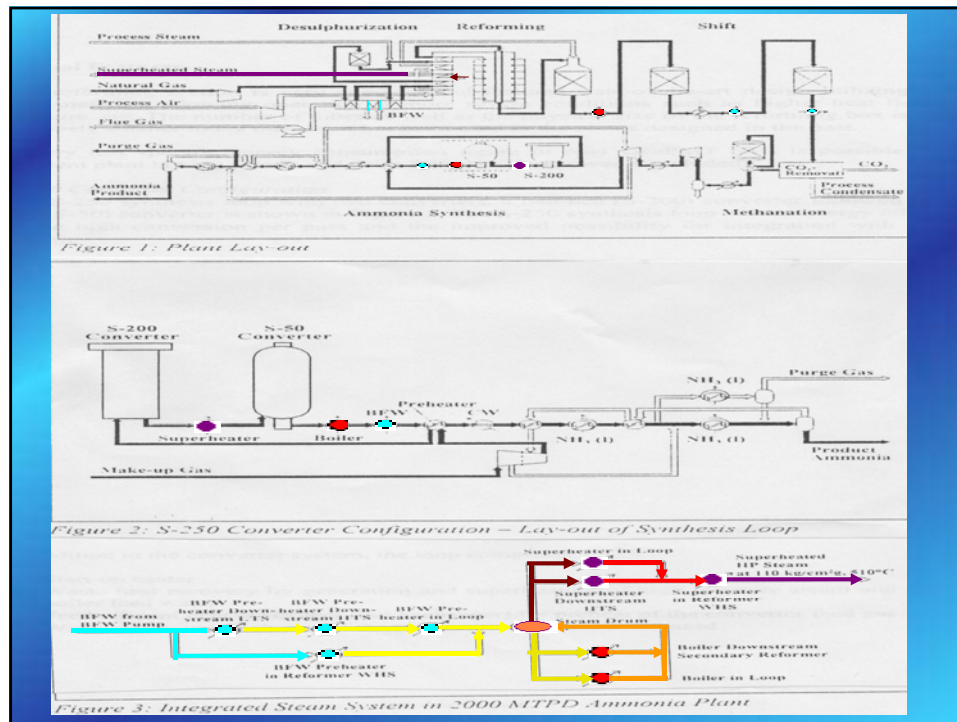
➢**Furthermore motive power is required for pumps, blowers, compressors and turbines.**

➢**The energy for this purpose is obtained by Recovery of Waste Heat from process units, by using WHRSG and Super Heaters to produce high pressure steam.**

➢**The total steam production is about 4 ton steam /one ton of ammonia at temp. 510 °C, 110 kg/cm2 steam pressure.**

Gas Steam Reforming and Ammonia Production Loop

Megammonia Plant Lay-out

Figure 1: Plant Lay-out

Figure 2: S-250 Converter Configuration – Lay-out of Synthesis Loop

Figure 3: Integrated Steam System in 2000 MTPD Ammonia Plant

PRODUCTION OF HIGH PRESSURE STEAM:

Steam production plant has three distinct areas:

1 - Preheating of boiler Feed water (BFW cycle)

➤ The flow diagram illustrate the boiler feed water long trip from the pretreatment plant to the boiler feed water pump to start the Feed water cycle (which is considered the economizer section in normal operation of fossil fuel fired boilers).

The BFW will be divided into two streams,
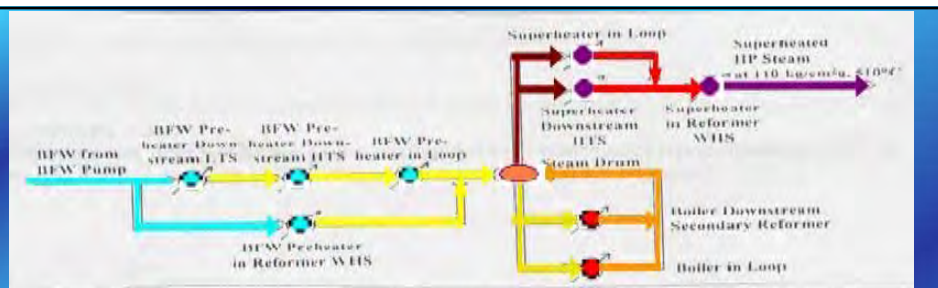
Integrated Steam System in 2000 MTPD Ammonia Plant
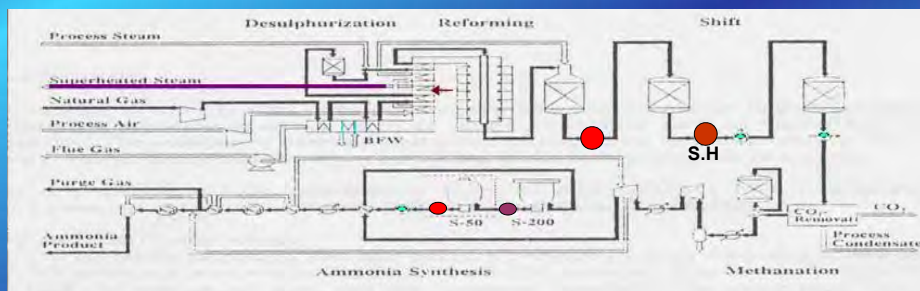
Megammonia Plant Lay-out

-**The first stream will exchange heat with the process gases in three preheaters as follow:**

1. **BFW is pumped to a preheater down stream the low temperature shift LTS to exchange the heat with the process gas. (gas cooler)**

2. **The BFW preheated down stream the LTS, enter a preheater down stream HTS heat exchanger to exchange heat with the exit gas from HR boiler down stream HTS.**

BFW Heaters - Economizers

3. The BFW exit the HTS heat exchanger will enter another preheater which is the heat exchanger down stream the ammonia converter loop which is the final BFW pre-heater of the first stream.

4. The second stream of the BFW will be preheated in a preheater in the WHS in the reformer which is the fourth preheater.

The preheated two BFW streams will be mixed in a common feed water header connected to the common steam drum.

II –Boiler section- Production of Saturated Steam

There are two boilers in that process:

1. The first boiler down stream the secondary reformer.

2. The second boiler down stream the S-50 synthesis converter.

Both boilers are gas coolers where the gas moving in the tubes and boiler water in the shell - It is similar to fire tube boiler.

Both two boilers are connecting to a common steam drum where the steam is produced and leave through one steam header.

Process of Steam production in HRSG:

➤When preheated BFW enters the steam drum, will move down in down comer connected to the gas cooler shell.

➤The boiler water sweep around the tube bundle and steam forms with the hot water which will have a lower density than the water.

Waste heat recovery boiler
Process gas cooling train downstream
of the reforming section
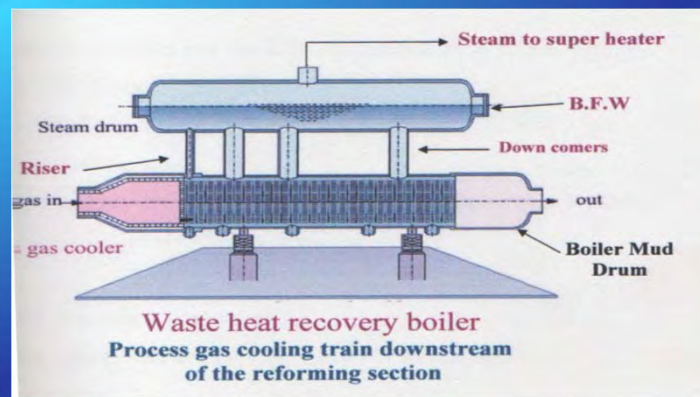
➤ **The mixture of steam and water will rise up in the riser tubes to the steam drum.**

➤**In the steam drum, steam is separated through special engineering mechanism called steam-separators to separate steam from boiler water and to prevent carry over of any water bubbles to the after boiler section.**


Waste heat recovery boiler
Process gas cooling train downstream
of the reforming section
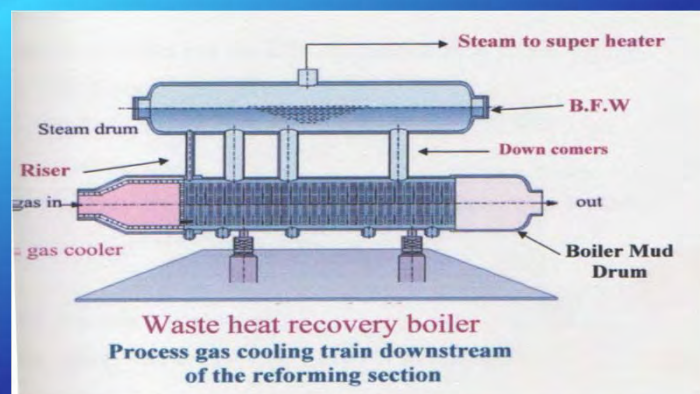
III – Super Heaters

❑ To super heat the saturated steam it has to be heated up separately from water.

❑ The steam will leave the steam drum to the steam header from the common steam drum and will be divided into two streams to feed two separate super heaters installed in parallel.
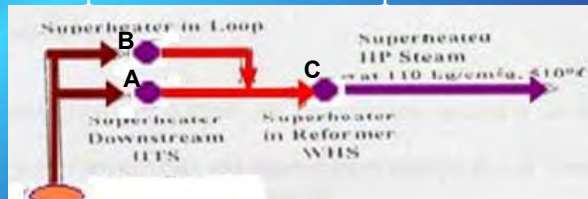
A. Super heater down stream the HTS.

B. Super heater in ammonia converter loop between the S-200 and the S-50 converter.

C. Final super heater in the reformer waste heat section WHS to produce super heated HP steam with temp 510 °C, pressure110 kg/cm^2.
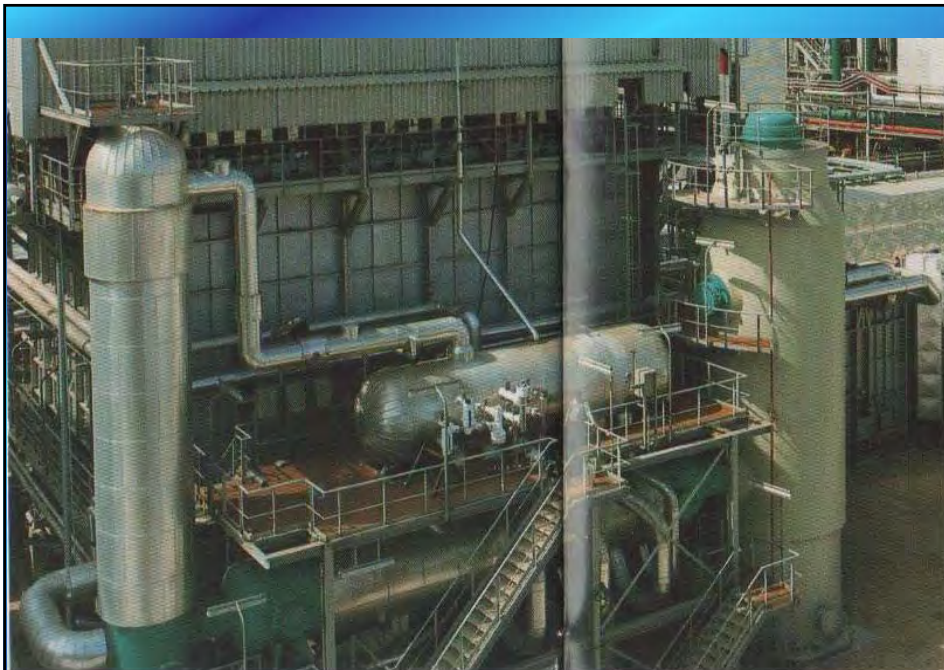
Steam Capacity of Megammonia Plant:

Around 341 ton per hr of high pressure steam ($110Kg/cm^2$ and 510 °C) is produced in the megammonia plant producing 2000 MTPD.

Users of produced steam:

The steam is used for the process in the reforming section and for power generation.
Also could be transported to another use as electric power generation.

❑ All the major compressors as well as the large pumps are steam turbine driven.

The synthesis gas compressor and the refrigeration compressor are driven by high pressure steam.

IV – Recycling of Steam Condensate:

◈ The turbines exhaust steam is condensed by two condensers to be recycled as boiler feed water after polishing and treatment.

◈ Condensate and Makeup water start again the same mentioned above trip to produce super heated steam.

◈ During this trip there will be the very well known boiler water problems which are

    A. **Deposition.**

    A. **Corrosion**.

    A. **Carry over.**

➢Industry is still searching for the perfect chemical treatment.

➢Many surveys performed by EPRI [The Electric Power Research Institute] of boiler tube failures.

➢The most recent survey done in 2001 found that the number of plants with chemically related boiler tube failure increased significantly from the previous survey, done in 1997, which prove that the industry is still searching for the perfect chemical treatment.

◈The table illustrate the results of two EPRI surveys.
◈Source is power magazine – volume 148, issue 7-2003.

PROBLEMS	2001 Survey	1997 Survey
Had chemically influenced boiler tube failures in the past year	81%	61%
Hydrogen damage	57%	37%
Corrosion fatigue	45%	43%
Pitting	40%	7%
Phosphate gouging	25%	17%
Stress-corrosion cracking	28%	18%
Caustic gouging	11%	11%

From the table above, of even more concern were significant increase in the incidence of failure due to under-deposit corrosion mechanisms such as hydrogen damage in the figure, phosphate gouging and pitting.

Hydrogen damage

Choose your treatment:

◈In chemical treatments, as with shoes, one size doesn't fit all.

◈The key is to understand the basics and prerequisites of each general treatment and device a program that provides the best fit for your unit in its current configuration.

◈The goal should be to passivate water-touched surfaces in a way that prevents corrosion, regardless of the boiler and feed water treatment program used.

◈Steam cycle chemistry determines the extent to which passive oxide films can form on metal surfaces.

◈Corrosion occur when such a layer becomes unstable or when chemicals are allowed to come between it and the base metal.

◊Corrosion in one part of the cycle typically results in deposits some where else in the cycle.

◊It is useful to think of the feed water treatment chemicals and boiler water chemicals working together as a package when we think of chemical treatment for steam cycle.

◊Feed water chemistry affects boiler and steam chemistry.

◊It is also important, regardless of the chemical treatment used, it must be consistent.

Key parameters during the selection of a treatment program:

➤**Metallurgy –** The presence of copper alloys in your (or your steam users) equipment requires that the chemistry exclude oxygen at all times.

➤**Mode** – Every time the unit comes offline and starts again, there is a potential for contamination and oxidation of otherwise passivated surfaces.

◊One day of poor lay up practices can ruin months of excellent chemistry control.

➤**Make-up / condensate purity –** the two major sources of chemical contamination due to:

◊Malfunctioning of water treatment equipment.
◊Condenser tube leaks and air in-leakage.

Every step you take to improve make up water quality and to prevent contamination from the condenser improves your chances of having an excellent feed water and boiler water chemistry program.

➢**Monitoring** – Regardless of how good a program it is sooner or later, you-know-what-happens.

◈There is no substitute for reliable and accurate monitoring of critical boiler, feed water and steam parameters.

◈There must be a commitment to watch for problems, respond when something is out of line and train operators so they know what to do.

Generally speaking in chemical treatment of steam cycles, less is more. Adding just what you need in the simplest form to get the job done is a good rule of thumb.

I - Conventional boiler water treatment:

1. Phosphate – about 60% of the fossil-fire-fueled boilers in the U.S still using some form of phosphate chemistry for their boiler treatment.

◈In lower pressure industrial boilers that produce process or heating steam the concentration of phosphate in the boiler (20 – 40 ppm) is sufficient to precipitate minor amounts of contaminant (hardness from water softener leakage, for example).

◈However, the few ppm of phosphate carried in large utility boilers (high pressure boilers > 900 psig) is primarily to stabilize the pH of the boiler water, not to precipitate hardness.

◈Although both disodium and trisodium phosphate have historically been used in boiler treatment, more and more utilities have decided to rely on trisodium phosphate alone.

◇This is due to the concerns about phosphate hideout and the potential to form iron phosphate deposits that maybe corrosive.

◇Traditional (congruent) phosphate program relies on combinations of disodium and trisodium phosphate to produce in the boiler sodium to phosphate ratio 2.2 to 2.8

➤Disodium phosphate has ratio of Na to PO4 = 2
➤Trisodium phosphate has ratio of Na to PO4 = 3

◇The ban of phosphate treatments has been a phenomenon known as phosphate hide out.

◇Operating mode, pressure and heat flux all can limit the solubility of sodium phosphate in the boiler.

◇At the boiler conditions, sodium phosphate can react with the magnetite layer on the boiler tubes to form sodium hydroxide and at least two different sodium-iron-phosphate compounds.

◇When the boiler water solution has a sodium to phosphate ratio of less than 3, the sodium-iron-phosphate compounds formed are more acidic have a lower sodium to phosphate ratio than the original water solution.

◇When boiler conditions change, these sodium-iron-phosphate compounds return to solution and can lower pH and increase phosphate concentration.

◇Many phosphate programs were applied such as EPT Equilibrium Phosphate Treatment to prevent phosphate hideout. The EPT added sufficient tri sodium phosphate and caustic to maintain solid alkali.

◇Originally applied in a 2600psig boiler and control its water pH at 9.0-9.5. EPT does not specify a phosphate control range, instead it requires each unit determine its own equilibrium point for phosphate.

Final conclusion of phosphate treatment:

EPRI placed EPT as an additional phosphate treatment philosophy on the pH/phosphate control chart along with the other phosphate regime and EPT phosphate limits at 0-2.5 ppm.

EPRI RECOMMEND THAT TRISODIUM PHOSPHATE IS THE ONLY PHOSPHATE USED IN ANY PHOSPHATE TREATMENT REGIME.

Although both disodium and trisodium phosphates have historically been used in boiler treatment, more and more utilities have decided to rely on trisodium phosphate alone. This is typically due to concerns about phosphate hideout and the potential to form iron phosphate deposits that may be corrosive.

➢**Caustic.** Caustic is the other form of solid alkali added to the boiler. In the past it had an undeserved reputation for causing gouging-type corrosion. But it is now being used more frequently in conjunction with trisodium phosphate in phosphate treatments.

➢Caustic was used successfully as a stand-alone boiler treatment in the UK for many years and a caustic-based treatment will be included in the next version of EPRI's Guidelines on Phosphate Treatment.

➢**Ammonia.** Added to the condensate after the condensate pumps, Ammonia's job is to increase the pH of the feed water to minimize the amount of iron corrosion in feedwater heaters and piping.

❑ If there are copper alloys in the cycle, the amount of ammonia needs to be controlled to minimize copper corrosion.

❑ More important than the amount of ammonia alone is the combined amount of ammonia, carbon dioxide and oxygen.

❑ Unless air in-leakage is minimized, copper corrosion will result and pH control will be difficult.

❑Ammonia has no effect on pH in the boiler at boiler operating conditions because the ammonia is not hydrolyzed but exists as NH_3.

❑However, by the time samples are cooled, analyzed by an on-line pH meter or collected and analyzed in a lab, the ammonia does contribute to their pH.

❑ For phosphate treatment, this is particularly important: The contribution of ammonia to the boiler water pH must be subtracted out before an accurate sodium-to-phosphate ratio can be determined.

➢**Amines.** Amines are used to increase the pH of the feedwater and the pH of the condensate in utility and industrial steam systems.
❑There are a number of different amines, and they vary in basicity and volatility.
❑Among the amines in common use in the utility industry are cyclohexylamine, morpholine, and diaminoethanol.
❑Determining which amine to use is in part a function of what equipment you want to protect and where it is in the condensate cycle.

♯There is today a lively discussion about the positive and negative effects of amines in the utility steam cycle.
▪All amines eventually break down into organic acids. At a minimum, these acids contribute to the cation conductivity of the feed water and steam.
▪For some water-treatment experts, the inability to differentiate between a small condenser tube leak and an **over dose** of amine is sufficient reason to preclude their use in the cycle.
▪ Those in favor of using amines point to their ability to condense more quickly than ammonia and thus provide a greater increase in the pH of condensate and a lower corrosion rate.

➢**Oxygen scavengers** (reducing agents).
❑ For units with copper alloys in the cycle the feedwater must remain in a reducing condition at all times to prevent copper corrosion.
❑Besides eliminating dissolved oxygen mechanically in the deaerator.
❑ Chemical oxygen scavengers or reducing agents typically are added after the condensate pump discharge to passivate the copper and form more-stable cuprous oxides.
❑Some common oxygen scavengers are hydrazine, carbohydrazine, diethylhydroxyamine and hydroquinone.
Draw backs of oxygen scavengers:
◊The strong reducing conditions created these chemicals, decrease the stability of magnetite,
 thereby increasing the rate of flow-accelerated corrosion in areas of the feedwater piping.
▪This is why many units with all-ferrous metallurgy have discontinued the use of oxygen scavengers altogether.

❑If oxygen scavengers are used the feed must be consistent.

❑ Recent research indicates that although copper corrosion and corrosion product transport (the release of copper oxide into the feedwater) is higher under oxidizing conditions than under reducing conditions, it is far higher in the transition from the latter to the former.

❑Conditions such as a broken vacuum on the condenser or open vents on feedwater heaters can cause such a transition in copper chemistry.

❑All oxygen scavengers except hydrazine contain carbon and will breakdown into organic acids, raising the same cation conductivity issue as the use of amines.

II - THE ALL VOLATILE OPTION
ALL-VOLATILE TREATMENT (AVT).

➤All – volatile treatment (AVT) uses ammonia to adjust the pH of the feedwater and adds nothing to the steam drum.

➤AVT has been around at least as long as supercritical units, which must use only volatile treatment chemicals because all feed water becomes steam.

➤Supercritical units were also routinely equipped with full-flow condensate polishers as another barrier against contamination from the condenser.

➤ Often, operators who tried to use AVT without condensate polishers wound up with hydrogen damage.

➤Until recently, all AVT units added hydrazine even if the unit had no copper alloys.

➤Many of these units also had considerable accumulations of magnetite on the boiler tubes, which required frequent chemical cleaning.

➤This iron was generated in the feed water piping and collected on the boiler.

➤Feed water piping failures due to flow-accelerated corrosion, and the successful application of oxygenated treatment (see below) in the U.S. begged the question of why operators were so intent on operating all ferrous boilers using AVT under reducing conditions.

VI – New trend for boiler water treatment

Recently, two different forms of AVT have emerged.

1. If a boiler's tubes contain copper alloys, an oxygen scavenger (reducing agent) typically, hydrazine –is added to the feed water together with the ammonia. This treatment has been dubbed AVT (R) (The R indicates reducing).

2. If a boiler has all-ferrous metallurgy, no oxygen scavenger is added.

   ◊ The deaerator removes enough dissolved oxygen to prevent oxygen pitting but does not create the reducing environment that a chemical treatment would.

   ◊ This treatment is referred to as AVT (O) (for oxidizing).

   ▪ AVT (O) is preferred treatment for HRSGs with all-ferrous metallurgy.

◊With either flavor of AVT, the tolerance for contamination is nil.

▪To a boiler, AVT is like no treatment at all.
▪At boiler operating temperatures and pressures, ammonia dose not hydrolyze and therefore, cannot contribute to the pH of the boiler, **ONLY** solid alkalis such as trisodium phosphate or caustic can do that.

◊Therefore, if a condenser tube leak or similar contamination occurs in a boiler on AVT, the pH of its water will drop.

◊Depending on the extent of contamination, the drop may or may not be apparent when the pH of the boiler blowdown is measured (and the ammonia once again hydrolyzes).

◊This why measuring of the cation conductivity of boiler water is critical for drum units operating on AVT.

Oxygen opportunity.

◊Oxygenated treatment (OT) was introduced in the U.S. in 1991 as a treatment for supercritical units
And is currently in use by more than 100 such domestic units.

◊Internationally, some 80 drum units also use the technique.
◊It requires that there be no copper alloys in the cycle and the plant have full-flow polishers to ensure consistent purity of feed water.

◊Ammonia is used to control the pH of the feed water, to which the oxygen gas is added such that the dissolved oxygen at the economizer inlet is 30 to 150 ppb for a supercritical unit, and 30 to 50 ppb for drum units.

◊Units on OT in the U.S. have had an excellent operational history, characterized by significantly fewer or no tube failures.

◊One of the reasons that adding oxygen has become popular
 is that doing so, eliminates flow accelerated corrosion (FAC) in feedwater piping.

◊FAC (Figure) has been responsible for a number of catastrophic failures in the utility industry. Some newer HRSG units also experienced problems with FAC.

Figure.

OT to the rescue. Oxygenated treatment eliminates flow-accelerated corrosion, a problem most recently seen in heat-recovery steam generators.

➢As it turns out, even a few ppb of dissolved oxygen in feedwater significantly reduces the rate of FAC, but the levels associated with OT essentially eliminate single-phase FAC.

➢There have been some units that have experienced problems with two-phase FAC in drain lines and deaerators.

➢The cause of these problems has been identified as incorrect venting of the deaertor during operation.

➢(Figure 3) compares the pros and cons of OT, AVT(R), AVT(O) and EPT/PT water treatment regimes, as well as their impact on feedwater's tolerance for contamination
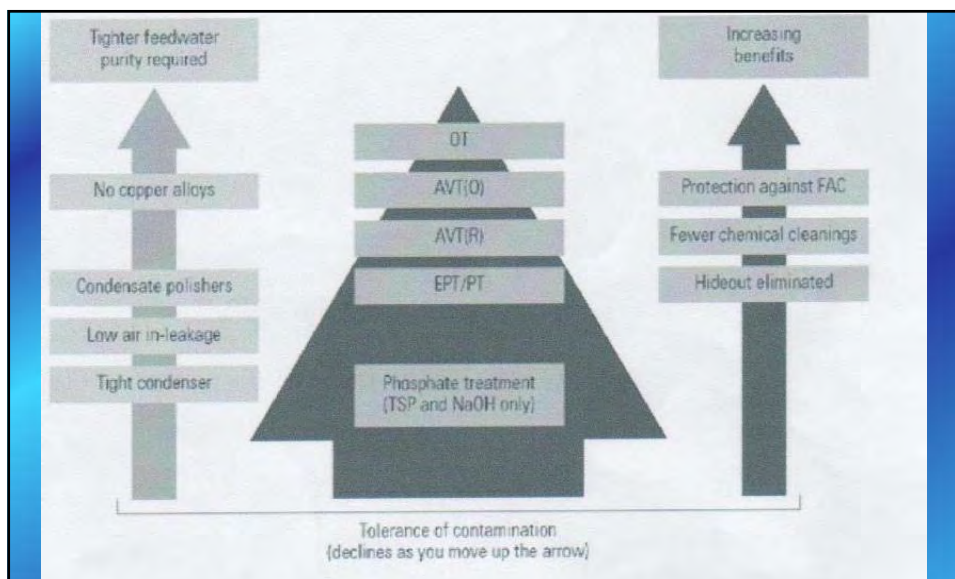
Chose your weapon.
The tolerance of feedwater for contaminants is a function of the technique used to treat it.

Conclusion :

1- Application of stable corrosion inhibitor which protect the system and the use of carboxylic & sulfonated polymers work efficiently at alkaline pH, keeping the system free of any deposits , also it help in keeping the zinc soluble at this pH , when the zinc product is applied for pitting control .

2-   Prevent the use of phosphate based corrosion inhibitors and the use of acids for pH control .

3 - The use of organic phosphate corrosion inhibitor in the ammonia cooling water to prevent the formation of sludge of calcium phosphate due to the high pH of the water.
Some formulations of organic and inorganic phosphate proven good results because the organic phosphate and polymer will keep the inorganic phosphate in solution.

4 - Application of some mechanical modification for the heat exchangers and cooling towers such as .

a - Using a booster pump to increase the water flow .

b - Side stream filtration of the cooling water .

c - Air or nitrogen pumping for shell side coolers and back flushing to remove any debris.

d - Installation of double screen at the succsion line of the cooling water pumps for alternative cleaning for each screen .

e - Injection quills for dosing of antiscalant installed at the water inlet to a problematic coolers.

AFA WORK SHOP

Corrosion Problems In Industry

23 – 25 December 2013

Aswan – Egypt

Water ruse – key to the future

Presented by:

Eng. Faiza Abou Zeid

General Manager

AQUA TRUST FOR WATER TREATMENT

LTD.

Water reuse – key to the future

The management of our water resources involves many basic elements, which appear on the flow diagram below. Sources must be developed and water supplies treated to make them suitable for use. Intelligent utilization must be encouraged and wastewater treatment handled to limit pollution. We are making progress in all of these areas, but a dramatic improvement in the overall water supply situation can be made now by greatly expanding the amount of water that is reclaimed and reused by industry and by municipalities.

Water survey. In the case of an industrial plant this means undertaking a complete engineering survey of water use to develop an accurate water balance for peak and average operating conditions. In fact, a complete inventory of all plant operations using water and producing wastes is needed.

Then, with this data in hand, take a fresh look at plant and process operations and see if changes can be made to reduce the amount of water used or decrease the flow of waste-water produced. A simple process adjustment is often all that's required to lower the concentration of pollutants. Perhaps there are valuable chemicals that can be recovered.

Is there an alternate approach that will change the nature of the waste entirely and make it easier to handle?

Sometimes the simple step of segregating a contaminated process water from the rest of the waste discharge can reduce the size of the wastewater treating system.

The survey will uncover applications where water can be recycled for repeated reuse. Some wastewater, now discharged to the sewer, may be well suited for cooling or boiler feed. Take another look at the economics of using cooling towers to replace once-through cooling systems.

Sewage effluent. Finally, when evaluating alternate sources of supply for a new plant or a plant expansion, don't ignore the waste-water available from municipal sewage treatment plants. Of all the sources of water available to industry, sewage plant effluent is the one most reliable at all seasons of the year and only one that is actually increasing in quantity and improving in quality.

Every day our cities literally throw away millions and millions of cubic meters of basically good, thoroughly treated, slightly used water. In Cairo area alone, huge volume of fresh water is used once, treated and discharged into the sewer. Similar situations exist in many cities elsewhere. Since the regulations will require complete treatment in communities that may not have it now, reclaimed water quality will be constantly upgraded with time.

Complete sewage treatment in most communities produces an effluent that's well suited for cooling and other industrial reuses. With proper treatment, such as any other alternate source would require, reclaimed

water can be used for boiler feed, steel-quenching, rayon fiber manufacture, etc.

The treatment of municipal waste-water for direct and deliberate reuse is inevitable. In some areas, water shortages will require direct recycle of renovated waste-water into the community water supply. Recreational use of waste-water will also become popular in the drier areas of the world.
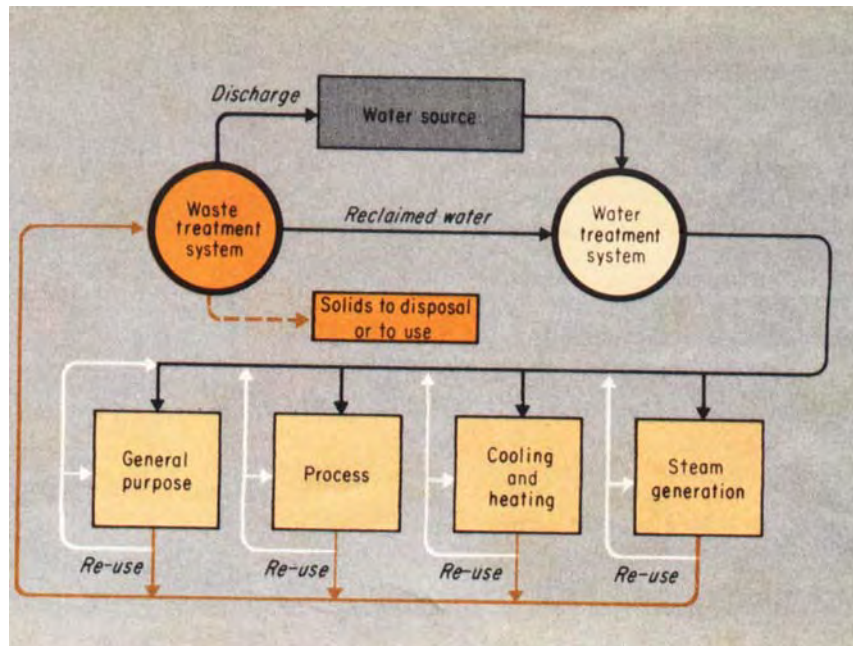
The goal in water pollution control

Is to secure and maintain, water for a quality suitable for specific uses, what are those uses?

Listed alphabetically they are:
1. Animal watering
2. Boating
3. Domestic water supplies
4. Fish propagation-and shell fish culture
5. Industrial water supply
6. Irrigation
7. Swimming
8. Waste transportation and dispersion
9. Water power and navigation

For any individual of water, the relative importance of these uses is geared to the economy of the area and the wishes of the local people. Some uses like domestic water supplies and industrial process for example are compatible within a narrow range of water quality, others are obviously not.

Water sources classification:

The regulatory authorities recognize the beneficial use concept in classifying water sources and developing water quality standards according to the required usage.

Following are some ideas of classifying water sources standards.

Standards: when quality standard are agreed upon they may take the form:

1. **Effluent standards**: will state precisely what is allowed in wastewater discharged from municipality or industrial plant. It might require removing a given percentage of suspended solids for set limits or color.
   Or:
2. **Receiving water standards**: says nothing about composition of wastewater discharge provided stream quality is maintained within specified limits. This approach leans on the self-purifying and dilution capabilities of rivers, lakes and seawaters.

The states of California and Washington are an example. Where it is forbidden to discharge waste that will: -
1. Drop dissolved oxygen of the stream below 5 PPM.
2. Produce a pH outside the range of 6.5 - 8.5.
3. Generate toxic conditions harmful to fish or water potability.

The specific treatment required for a given waste depends on many things.

Naturally it is linked to the quality and quantity of pollutants present, dilution that can be called upon in the receiving body of water, capacity

of the water supply to assimilate waste and quality of water required for other water uses.

Yet the understanding of any specific treatment starts with knowledge of wastewater chemistry, which is illustrated on the following pages.

The California interstate water pollution control commission has set up 4 Classifications:

1.   Class A - is water suited for general use, including drinking water with proper sterilization.

2.   Class B - waters are set aside for bathing, recreation, irrigation and general agriculture use. They have good ethetic value, are suitable for fish and with filtration and disinfection are acceptable for public supply.

3.   Class C - supplies are suited for recreational, boating and irrigation of crops normally cooked before eating.
Most industrial process and cooling needs can be met by class -C water, which is also suitable for wildlife and game fish.

4.   Class D - waters are suited for the transportation of swage and industrial waste without nuisance, and for power, navigation and some industrial use.
Once water supplies are classified, the next step is setting water quality criteria we shall list below the many pollutants that must be considered.
The effect of pollutant on the water quality as shown on the following curve.
This hypothetical curve of water quality illustrates how water becomes polluted with respect to established criteria for example to maintain water quality for fish, there must be sufficient dissolved oxygen, the ideal amount is 10 PPM. Established criteria might consider the pollution threshold at 5 PPM.
The zone of gross pollution with resulting fish kills would not be reached until dissolved oxygen dropped below the lower limit say 3-PPM.

While pollutants fall into three basic categories......

..They can further classified by unwanted properties and chemical or biological origins

Floating materials

Oils, greases, foam and other solids that are lighter than water, in addition to making the stream or lake unsightly, retard plant growth by blocking the passage of the sunlight through the water. Oil in particular, interferes with natural reaeration of the stream, destroys natural vegetation along the banks and is toxic to fish and aquatic life. A fire hazard is also created when there are excessive amounts of oil on the surface.

Suspended matter

Insoluble materials such as mineral tailings either wash up on the banks as unsightly slime and sludge, or slowly settle to the bottom of the stream. If the bottom coating is dense enough, it smothers useful purifying microorganisms and ruins the spawning and breeding grounds of fish. When suspended matter is organic in nature, it progressively decomposes, using up dissolved oxygen to produce noxious gases, odors.

Dissolved impurities

Acids, alkalines, heavy metals, insecticides, cyanides and other toxics make water undrinkable and destroy aquatic life. Traces of phenols cause objectionable taste and odor. Organic matter is attacked by oxygen-consuming microbes. Oxygen is also depleted by chemical reducing agents such as sulfite and ferrous compounds. Nitrogen, phosphorus spur unsightly algae growth. Without enough dissolved oxygen, fish and vegetation die

Temperature

Discharge of hot wastewater raises temperature of the receiving stream. This lowers the solubility of oxygen in the water and increases rate at which oxygen consuming microbes attack organic waste. The result is accelerated depletion of dissolved oxygen and disruption of aquatic life. Problem is worst when stream flow is low, ambient temperature high.

Color

Color is mainly objectionable from an esthetic standpoint. Even though it isn't harmful for most water uses, color does interfere with biological activity by retarding transmission of sunlight into the stream. Color also indicates the presence undesirable dissolved and suspended solids. For example, dissolved chromate ions are yellow; copper is blue

Taste and odor

Odors are offensive when pronounced enough to pollute the air over a sizeable area. For most waters, taste and odor are important indicators of undesirable impurities. The wastewater itself may contain the chemicals responsible, such as phenolic compounds or hydrogen sulfide. Odors also come from septic decomposition of organic wastes.

Radioactivity

Highly concentrated solid or liquid radioactive wastes are disposed of under carefully controlled conditions. But some dilute or low-level radioactive waste invariably reaches sewer and streams. Maximum allowable limits of radioactivity have been established for drinking water and for waste water from institutions using radioactive materials.

Chemical compound

An extremely wide variety of chemical impurities (organic and inorganic) are added by man or are naturally present in ground and surface waters. All must be considered potential pollutants since, if sufficiently concentrated, they can adversely affect water for one or more beneficial uses. However, if these impurities are diluted sufficiently, the water will be harmless for all uses. Following are typical impurities in water supplies and wastewater.
Acids, alkalines and hydroxides, arsenic, barium, boron, cadmium, cesium, chlorides, chromium, copper, cyanides, dissolved gases, detergents, dyes, fluorides, fungicides, hardness, hydrocarbons, hydrogen sulfide, insecticides, iron lead, manganese, nitrates, nickel, Organic chemicals, Organic agents, Phenols, Potassium, Sulfites, Tars, Urea, Zinc

Biological matter

Living matter, both plant and animal, directly affect water quality and use. Bacteria, the simplest form of plant life, can produce odors and may attack and destroy other plants and animals. Under controlled conditions bacteria help stabilize organic matter and play a major role in wastewater treatment. Fungi are similar to bacteria. Algae in excess amount use up oxygen and bring taste and odor problems. Microscopic animals such as protozoa are valuable as bacteria scavengers.

When is a water supply polluted?

Pollution is the downgrading of water quality by sewage or other wastes to the point where it unreasonably affects water use for domestic, industrial, agricultural, navigational or other beneficial uses. Pollution exists only when the impurity concentration is high enough to "adversely and unreasonably" harm water usage.

This concept is shown in the next graphical representation.

For each beneficial water use there are two critical water quality values: the threshold concentration and the maximum concentration, of pollutants. The area in color- above the established criteria for the threshold value-represents the zone of safe water use. At the lower criteria limits-maximum allowable pollutant concentrations- water use for all practical purposes is inhibited or destroyed.

Beyond this lower level, water enters the zone of gross pollution, shown black. Pollutant concentrations in the danger zone, between threshold and limiting criteria, can be tolerated safely for limited periods.
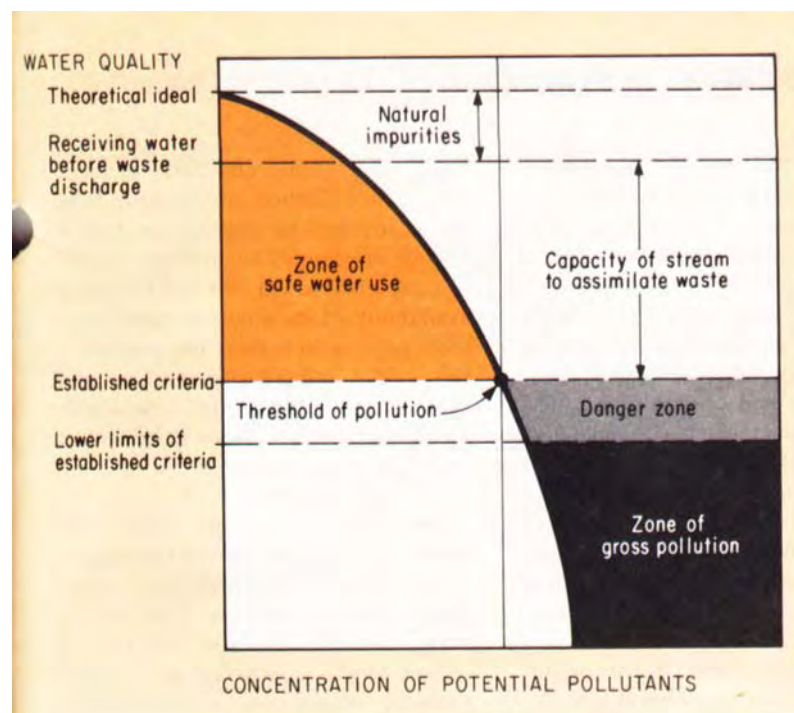
What is the significance of BOD and COD in waste-water?

The oxygen demand of wastewater is created by:

1.   Organic compounds that act as sources of food for microorganisms.

2.   Oxidizable nitrogen produced by nitrite, ammonia and organic nitrogen compounds, which also serve as food for bacteria.

3.   Chemical reducing compounds such as ferrous iron, sulfite, sulfide that readily combine with dissolved oxygen.

BOD (biochemical oxygen demand) is the quantity of oxygen used by bacteria in consuming organic matter in a sample of waste water over a five-day period at a temperature of 20 ^{o} C (68 F). The BOD test is widely used to measure the pollutional strength of waste water since it gives results in terms of dissolved oxygen that would be consumed if the waste water were discharged into a natural body of water.

Essentially complete biological oxidation of organic matter takes about 20 days. However, experience shows that BOD from the standard five-day test is satisfactory and equals about two-thirds of the total BOD.

BOD may be measured directly if the sample has a BOD under 7 mg/1. But since most wastewater has a much higher BOD, dilution of the sample is needed.

Otherwise there would not be sufficient dissolved oxygen in the sample to run the test to completion. For example, a 10 % dilution will use oxygen at one-tenth the rate of a full-strength sample. Since samples strength is generally unknown, BOD is usually run with dilutions to extend range of measurable BOD.

Everything that affects the rate at which organic matter is consumed must be closely controlled, including pH, nutrients, temperature, toxic materials, dilution water and nature of the microorganisms.

COD (chemical oxygen demand) measures the total organic content that can be oxidized by potassium dichromate in a sulfuric acid solution. Most organic compounds can be oxidized to carbon dioxide and water under these conditions.

The main limitation of COD is that it does not reveal whether the organic matter is biodegradable or non-biodegradable. Neither does it give any idea of the rate at which biologically active material would be stabilized in a stream. It also includes the effect of any chemical-reducing compounds that may be present.

Main advantage of COD is that the test can be run in three hours. Used with BOD it helps spot toxic conditions and nonbiodegradable materials.

Following are some of the terms commonly used in waste-water chemistry:

Biodegradable organics are those that can be broken down by microorganisms to form stable compounds such as CO_2 and water.

BOD (biochemical oxygen demand) is the amount of oxygen in mg/1 used by microorganisms to consume biodegradable organics in wastewater under aerobic conditions.

COD (chemical oxygen demand) is the amount of oxygen in mg/1 to oxidize both organic and oxidizable inorganic compounds.

Pathogenic bacteria are those microorganisms capable of producing diseases in man, animals and plants.

Coliform bacteria are nonpathogenic microbes found in fecal matter that indicate the presence of water pollution: are thereby a guide to the suitability of water for potable use.

E-coli (Escherichia coli) is also one of the nonpathogenic coliform organisms used to indicate presence of pathogenic bacteria in water.

MPN Index (most probable number) is used to report results of coliform test for bacteria. It represents the number of coliform bacteria in the water which-probably more than any other number-gives the results shown by lab examinations.

Digestion is the prolonged solution or reaction of a liquid with a solid.

Effluent is the liquid, solid or gaseous product discharged or emerging from a process.

Organic nitrogen is the nitrogen combined in organic molecules such as proteins, amines and amino acids.

Suspended solids are those that can be removed by filtration.

Total solids equal the sum of suspended solids and dissolved solids.

Turbidity is the amount of suspended matter in wastewater, obtained by measuring its light scattering ability.

Settleable solids are those in suspension that will pass through a 200-micron sieve and separates by flotation for an hour.

ORP (oxidation-reduction-potential) indicates the degree of completion of the chemical reaction by detecting the ratio of ions in the reduced form to those in the oxidized form as variations in electrical potential from an orp assembly.

# Waste-water chemistry and microbiology:

Waste - water chemistry is a logical extension of basic water chemistry both involves the analysis and treatment of very dilute solution of impurities or pollutants in water.

However, to effectively tackle wastes - water problems, a basic knowledge of organic chemistry and microorganisms are also required.

You do not have to know all the ways of preparing a given organic compound and how to calculate the expected yield but it is important to be familiar with the chemical characteristics of organic compounds found in waste - water and understand how they serve as a source of energy - or are the cause of death for various living organisms.

I- Organic chemistry is the chemistry of organic carbon:

All organic compounds contain carbon combined with one or more other elements such as hydrogen, oxygen, nitrogen, phosphorous and sulfur.
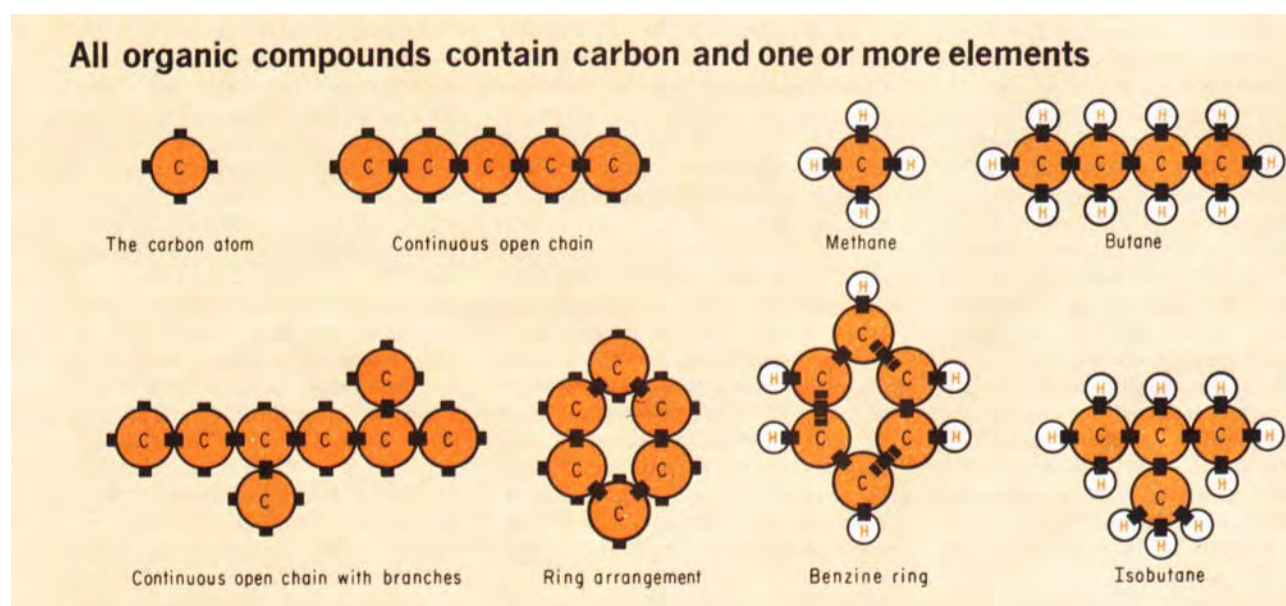
Carbon atom with four electrons (in black) and a valence of four uniquely combines with itself in a continuous open chain or chain with branches or in a ring. Together with other elements, it forms an infinite number of compounds.

Hydrogen atom joins carbon to form methane and benzene. Alternate carbon atoms in benzene have double bonds. Butane with the molecular formula C_4H_{10} represents two separate compounds (isomers) formed by the same atoms.

Most organic compounds are drived from three basic sources:

a-   Nature gives us fibers, animal oils and fats, vegetable oils, starch, sugars, etc.

b-   Fermentation produces alcohols, acetone, glycerol, etc. Through the action of microorganisms on organic matter.

c-   Finally, synthetic compounds and materials come from various chemical processes.

Properties of organic compounds differ from inorganic compounds in a number of ways. The organic compounds generally serve as food for bacteria.

The carbon cycle:

Can be considered the most important cycle in the operation of the world, As we know it. Plants take carbon dioxide (inorganic carbon) and convert it to organic carbon using the energy from sunlight for photosynthesis.

Animals consume the resultant plant tissue containing organic carbon and convert part of it to animal tissue. At the same time they oxidize some of organic carbon back to carbon dioxide (inorganic carbon).

Since animals can not consume all the plant tissue, and the animal tissue it self has limited life, microscopic plants have developed which oxidize the residual organic carbon back to carbon dioxide.

Find below some of the organic compounds.

All organic compounds contain carbon and one or more element. The carbon atom has a valence of four, which mean that each carbon atom can accept four electrons from other atoms and form a stable compound. Carbon atoms also have the ability to link together, in a wide variety of ways.

The following tables show some typical organic compounds. The simplest organic compounds are the Hydrocarbons, containing only carbon and Hydroxen. Although most of the emphasis in waste - water chemistry is on organic compounds, basic water chemistry also plays an important role. Fortunately, the inorganic impurities in water are relatively simple and follow definite patterns. The effect of pH is extremely important. Low pH tends to keep metallic ions in solution while high pH tends to precipitate them. Both are detrimental to biochemical reactions.

The monovalent ions such as sodium, potassium, lithium, ammonium, chloride, nitrite, nitrate, and bicarbonate are extremely soluble in water and difficult to remove from waste - waters. Fortunately, Na^+ K^+ Li^+ chloride, are not toxic except in a very high concentrations.

Nitrites and nitrates can be both good and bad. In drinking water, these impurities can produce blue babies, when the amount exceeds 40 PPM. Yet they are a good source of oxygen or nitrogen for microorganism growth. While divalent ions as Ca and Mg. react to from insoluble compounds and trivalents as Fe. and Al. And P is most reactive ions aside from H_2 and OH. All the naturally occurring metallic compounds are
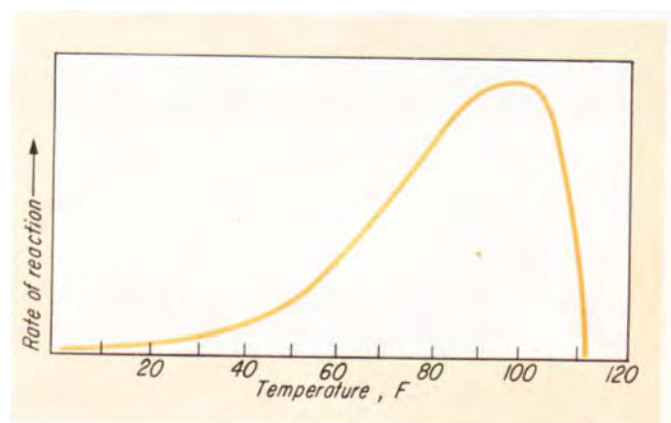
important as enzyme activators in biological systems in free form at trace levels. All are toxic at high concentration.

Wastewater disposal problems involve a wide range of organic compounds

classification	Typical compounds	classification	Typical compounds
Hydrocarbons compounds of carbon and Hydrogen classified as saturated or unsaturated	Saturated methane(CH_4), propane(CH_3-CH_2-CH_3) butane(C_4H_{10}) Unsaturated Ethylene series (olefins, alkanes) Polyenes, Acetylene series	**Mercaptans** Similar to alcohols with oxygen replaced by sulfur	Butyl mercaptan
Alcohols created by adding oxygen to hydrocxarbons	Methyl (CH_3OH), ethyl($CH_3CHOHCH_3$), Butyl, Hexadecanol, Ethylene glycol, Glycerol(glycerine)	**Amines and amides** Simple compounds containing nitrogen. Amines are alkyl derivates of ammonia; amides are made from organic acids and ammonia	Primary amine (R-NH_2) urea
Aldehydes and ketones Oxidation products of primary, secondary alcohols	Formaldehyde acetone	**Aromatic compounds** Benzene (C_6H_6), parent of the aromatic series, forms a multitude of compounds similar to the straight chain or aliphatic compounds	Benzene (C_6H_6) Napthalene ($C_{10}H_8$) Phenol (C_6H_5OH) Cresols, Benzyl alcohol, Benzoic acid
Acids Highest oxidation state an organic compound can reach; further oxidation forms carbon dioxide and water. All contain the carboxyl group (COOH)	Formic, acetic, acrylic, oleic(fatty acids), oxalic, glycolic, citric, and tartaric acid	**Carbohydrates** Compounds of carbon, hydrogen and oxygen containing two atoms of hydrogen for each of oxygen. Includes: (1) simple sugars or monosaccharides, (2) complex sugars or disaccharides, and (3) polysaccharides	pentoses($C_5H_{10}O_5$) (ribose) Hexoses ($C_6H_{12}O_6$) (glucose) sucrose, Lactose ($C_{12}H_{22}O_{11}$) starch, Cellulose, Hemicellulose
Esters formed by reaction of acids and alcohols. Correspond to salts in inorganic chemistry	Butyl acetate	**Fats, oils and waxes** Esters produced by long chain fatty acids	Glycerol tristearate beeswax
Ethers produced by treating alcohols with strong dehydrating agents	Diethyl ether	**Proteins and amino acids** Proteins are complex compounds of carbon, hydrogen, oxygen, and nitrogen. Amino acids are the building blocks from which proteins are constructed	**Typical composition** Carbon, 51-55% Hydrogen, 6.5-7.3% Oxygen, 20-24% Nitrogen, 15-18% Sulfur and phosphorus, 0-3.5%
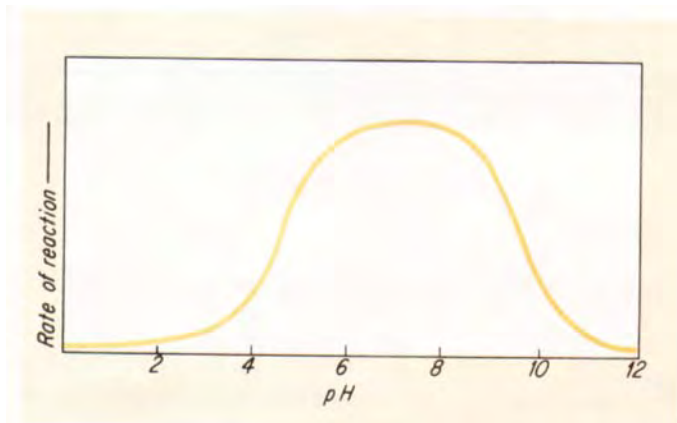
Ideal pH: range for bacteria is 6.5 to 8.5   Temperature change of 20 F
Death occurs below 4.3 or above 10.5   alters microbe metabolism rate   fungi
will predominate at pH below 6   by a factor of two. As 32 F approaches
                                             Rate near zero.

II-Microorganisms: They are classified to:

A-Plants as:

1. **Bacteria:** are classified as plants because they can eat only soluble food, insoluble organic must be hydrolyzed or dissolved in the cell wall prior to metabolism. Some bacteria are aerobic.

2. **Fungi:** are multicellular and like the single cell bacteria, can feed on all types of soluble organics, but unlike bacteria they are strict aerobes - in other words fungi must have dissolved oxygen to survive and grow.

3. **Algae:** are photosynthetic plants, in both single and multiple-cell form - which take energy from sunlight although inorganic compounds are the main source of nutrients, some types in the absence of sunlight can feed on organics. Oxygen is an important by-product of algae metabolism.

B- Animals as:

1. **Protozoa:** single celled microscopic animals. There are four basic groups of protozoa important to waste-water chemistry

    1)   sarcodina(amoebae)
    2)   mastigophora
    3)   ciliata
    4)   suctoria

    They eat bacteria and algae.

2. **Rotifers:** multicellular animals they eat bacteria and algae and need excess dissolved oxygen.

3. **Crustaceans:** are complex multicellular animals with hard shell, microscopic, feed on higher forms of microbes in an aerobic environment.

    Optimum development of microorganisms requires close control of their environment. They need just the right amount of nutrients, trace

elements metals and oxygen, temperature and pH must be also at the proper levels.

Careful control of the environment is essential for microbe survival and growth.
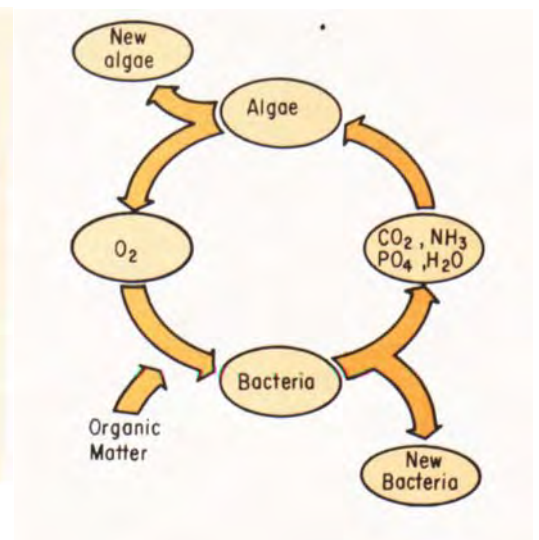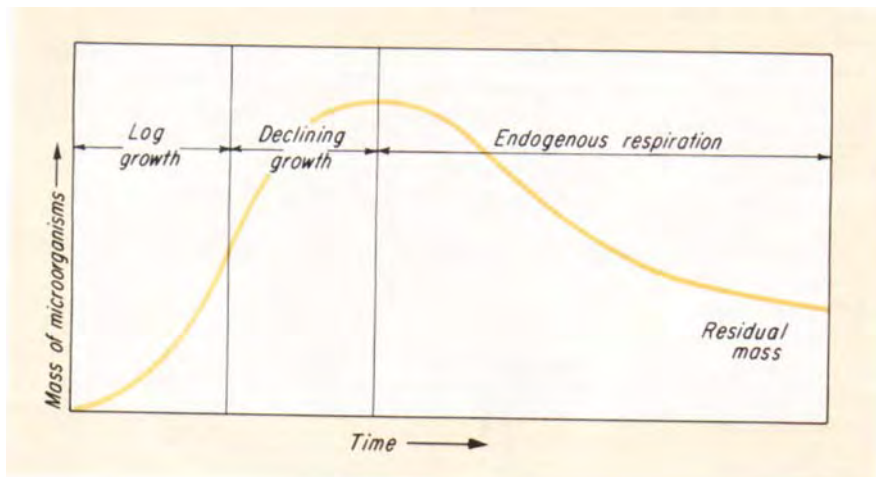
Microorganisms growth starts off at start rate, called log growth, When there is an excess of organic matter for food. As microbes Multiply, the food concentration drops and the rate of growth declines.
Endogenous phase begins when there is not enough Food for continued growth: microbe population starts to decline

Algae and bacteria help each other grow,
Bacteria uses oxygen to metabolize organics to co_2 and H_2O.
Algae uses co_2 releases oxygen for Bacteria.

The most important aspect of biological growth is the chemical characteristic of individual organic compounds, Their nature determines which microbes can grow and the magnitude of such growth. A mixture of organic compounds produces a mixed population of the optimum microbes for a given set of operating conditions. This population can be changed only by changing the environment.

Therefore, the quality of the waste - water will control the optimum development of micro - organisms, because they need just the right amount of nutrients, trace metals and oxygen temperature and pH must also be at the proper levels.

Nitrogen and phosphorous are key element in producing the microbial protoplasm.

Bacteria need C: N ratio of 5:1 and C: P ratio of 25:1.

Endogenous metabolism releases some of these nutrient elements and permits their reuse. With less Nitrogen Fungi predominate over bacteria.

Waste-water treatment system

    The best approach to design a treatment system for waste water, is to make a comprehensive survey that will:

1.   Determine the waste-water quantity discharged.
2.   Locate the major sources of waste with in the plant.
3.   Determine waste-water composition.
4.   Explore in-plant of process changes to minimize the waste problem.
5.   Establish the basis for waste-water treatment.
6.   Evaluate effect of wastes on the receiving stream.

A waste water treatment systems may include the following equipment, and methods to maintain the required standard criteria of the effluent discharged from the plants to the receiving streams.

Chemicals and chemical processes play a role in waste-water treatment. Chart below lists some of the major treatment systems and their present applications.

Operating results range from removal of organic pollutants to recovery of valuable materials.

Treatment	Chemicals used	Typical applications	results
Adsorption	Activated carbon	Clarified wastewater containing phenols, insecticides, detergents	Removes organic compounds not responsive to clarification or biological treatment
Coagulation	Aluminum sulfate(alum) sodium aluminate ferric chloride(ferrichlor) ferric sulfate(ferrisul, ferrifloc) ferrous sulfate (copperas) clay, activated silica polyelectrolytes (synthetic polymers)	Clarifiers Thickeners Digesters Vacuum filters filters	Removes colloidal turbidity, speeds up setting rates, improves water clarity, helps eliminate carryover, increase efficiency of thickeners and filters
Dialysis	Special membranes	Wastewater containing valuable chemicals	Recovery of sodium hydroxide from textile wastes. Acid recovery.
Electrodialysis	Ion exchange membranes	Treated wastewater	Reduction of dissolved solids
Ion exchange	Cation and anion exchange resins sulfuric acid, calcium hydroxide	Wastewaters containing chromium salts. Treated wastewater.	Recovery of both chrome and water of reuse. Reduction of dissolved solids
Neutralization	Carbonic acid, sulfuric acid, sodium hydroxide, sodium carbonate, lime, dolomitic lime	Alkaline or acid wastewaters	Wastewater pH approaches 7
Oxidation reduction and precipitation	Oxidizing agents: chlorine, hypochlorites, ozone Reducing agents: ferrous sulfate, sodium sulfate compounds, sulfur oxide	Wastewaters containing chromium salts, cyanides	Chromate is precipitated as insoluble hydroxide. Cyanide is oxidized to carbon dioxide and nitrogen.

Waste-water analysis

Waste-water analysis plays a vital role. The accurate measurement of impurities present in wastes is one of the most critical problems facing engineers in the design of waste-water treatment systems.

Limitations imposed on waste-water discharge to receiving streams and the expanding variety and complexity of pollutants makes it imperative to analyze the impurities quickly and accurately and at reasonable cost.

If the cost of the test is too high it limits the amount of data collected and therefore weakens the basis of the treatment systems design.

Composition of waste-water varies with the amount of impurities initially present in water and the chemical analysis of any pollutant that added.

While the domestic sewage has a fairly uniform composition, industrial wastes have an almost infinite variety of characteristics

Most waste-waters should be analyzed for at least:

BOD, COD, Color, total solids (suspended and dissolved solids), pH and turbidity.

Other impurities of interest will vary with the source and type of wastewater for example nitrogen content and urea and ammonia and phosphate.... etc. for fertilizer plants.

The concentration of pollutants must be correlated with average values, minimum and maximum-flows of waste-water encountered.

The analysis program must also take effluent water quality standards into account and the BOD reduction required to meet them.

Any toxic or unusual impurities in the wastewater that might adversely affect quality must be brought to light.

Starting point in any wastewater survey: is an effective program of sampling and flow measurement. To be useful, a sample of waste-water must accurately represent the source from which it is collected and be large enough to run all the laboratory tests are required.

This means that the method of sampling must be tailored to the type of waste-water flow. A close check of each waste source will reveal whether flow is continuos or intermittent and any wide swing in flow rate. It is also important to know if the concentration of pollutant widely changes or fairly constant.

If the flow and pollutant concentrations are fairly uniform a simple-sampling system will do.

The sampling systems are:

1.   Manual system: spot or grab sample is a manually-collected single portion of waste -water. It provides a useful spot check of operating condition.

   A series of grab sample makes it possible to keep track of variations in impurities. A composite of these correlated with flow shows average conditions. These data enable the analyst to compute the amount of the pollutants discharged over a specified time period.

   When the flow rate is constant, uniform samples collected at regular intervals make up the composite. When the flow rate varies a weighted composite should be collected.

   The continuous sampling is called for when a running record of conditions at a given location is required. An automatic system provides more data than is practical by manual system and it avoids human errors.

Sampling points: should be located at points of thorough mixing where the velocity is high enough to prevent deposition of solids.

Flow measuring: it is a critical part of waste-water survey. These usually done at point of discharge to receiving waters.

1. The open channel flow: or flow in a partly filled pipe can be measured with head area meters. These operate on the principle that a special barrier in the flow channel, such as weir, will back up the liquid and create a higher level above the barrier.

   The difference in level or head is a function of liquid velocity and therefore, flow rate.

2. **Measuring flow rate of water under pressure:** can be measured by a wide variety of standard meters, including differential head devices.

   A complete analysis of waste-water is a job for an experienced chemist.
   But every engineer should have a basic knowledge of testing methods in order to interpret waste-water analysis, select treatment systems and make operating adjustment on equipment. The analytical results may be expressed as mg/liters or PPM. One PPM in water equals 1 mg/liter.

   The critical need for water quality data to properly manage our water resources and design and control waste-water treatment systems, will accelerate the development and application of the type of analytical instrumentation.

Complete instructions on all phases of waste-water testing are contained in:

1.   Manual on industrial water and waste-water published by ASTM and
2.   Standard methods for the examination of water and waste-water published jointly by American Public Health Association and American water works Association and the water pollution control federation.

AFA WORK SHOP

Corrosion Problems In Industry

23 – 25 December 2013

Aswan – Egypt

Steam generators

Problems and treatment

Presented by:

Eng. Faiza Abou Zeid

General Manager

AQUA TRUST FOR WATER TREATMENT LTD.

Steam generators - Problems and treatment

Table of content:

The following presentation will illustrate:

1. Steam power generating plant

WATER TREATMENT
BOILER WATER TREATMENT
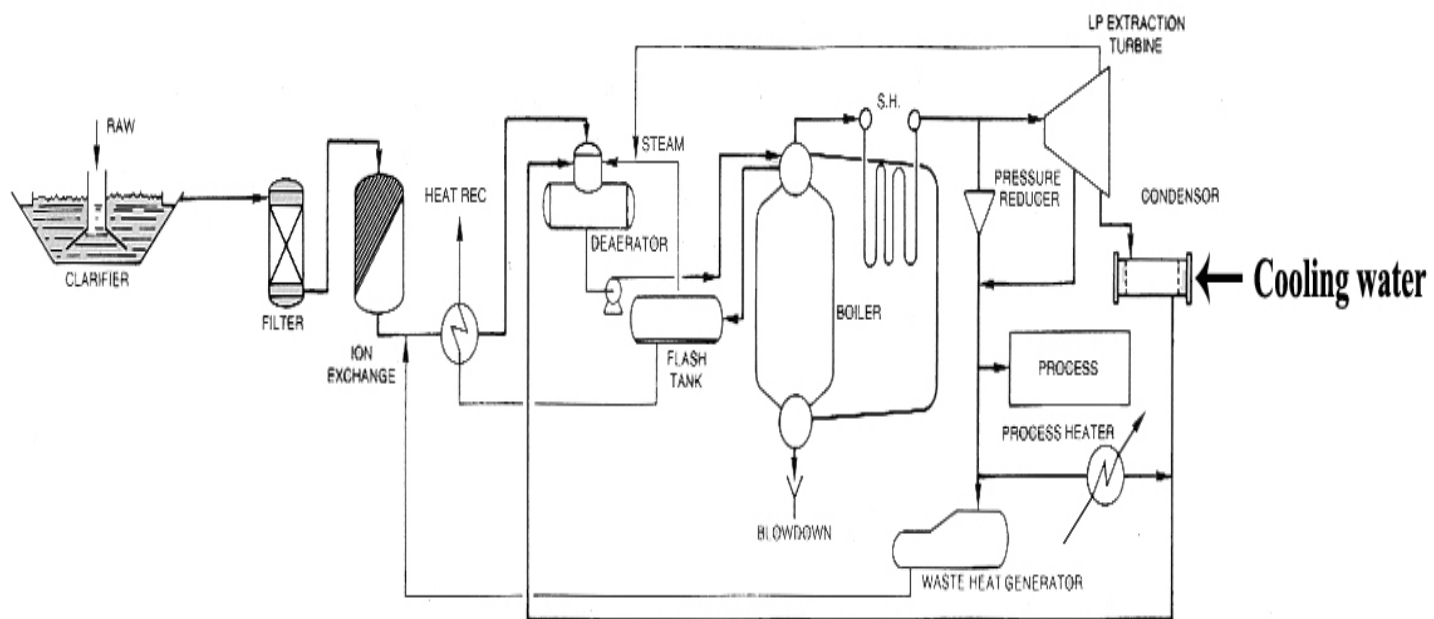
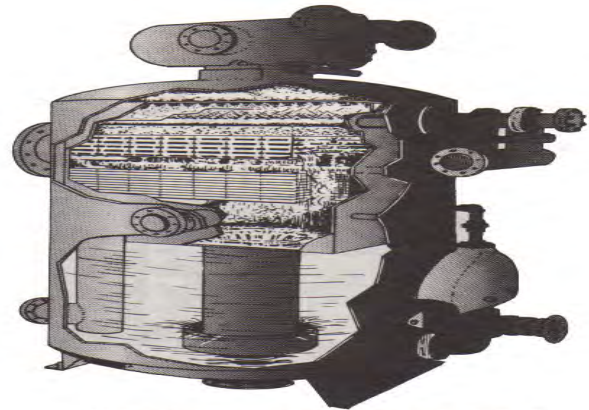← **Pretreatment system** →←Boiler→←Superheater→←Turbine→←Condenser→←Cooling water→

I . A . Pretreatment system

Demineralization plant

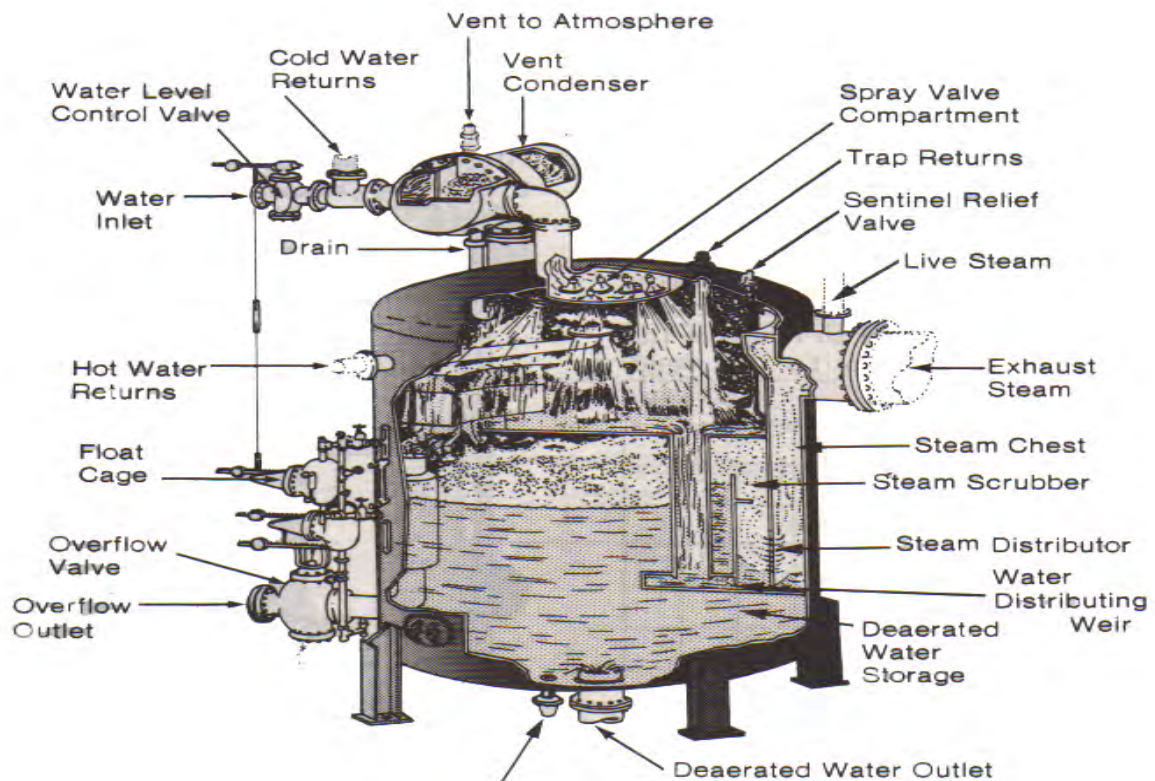**Deaerating heater**

Tray type

Tray heater design providing for primary
and secondary deaeration.

Spray type

- Water Level Control Valve
- Cold Water Returns
- Vent to Atmosphere
- Vent Condenser
- Water Inlet
- Drain
- Hot Water Returns
- Float Cage
- Overflow Valve
- Overflow Outlet
- Spray Valve Compartment
- Trap Returns
- Sentinel Relief Valve
- Live Steam
- Exhaust Steam
- Steam Chest
- Steam Scrubber
- Steam Distributor
- Water Distributing Weir
- Deaerated Water Storage
- Deaerated Water Outlet

I.B. Boiler system :
- Boiler types
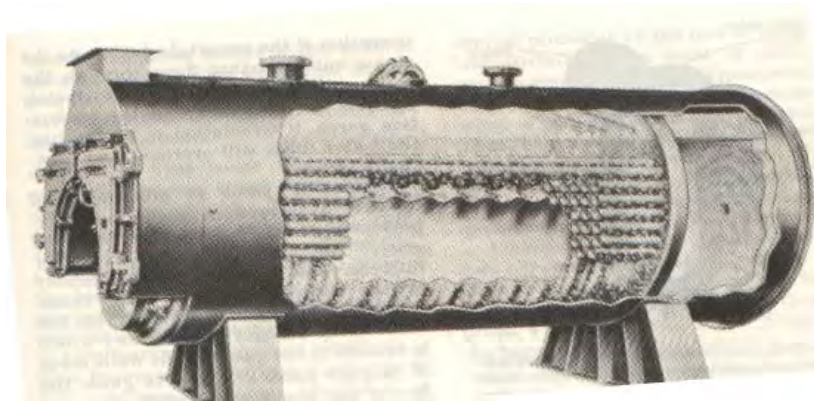I.B.1. Fired boilers
      I.B.1.a. Fire tube boilers
      I.B.1.b. Water tube boilers
I.B.2. Unfired boilers : HRSG
      Waste heat recovery boilers – Heat recovery steam generator
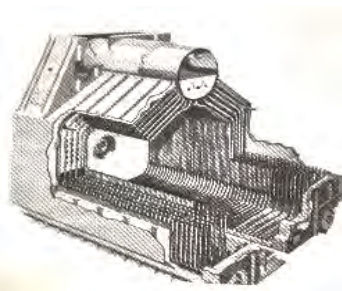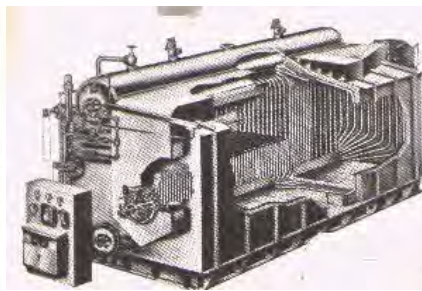

I.B.1.a. Fire tube boilers

It is a fired boiler where the combustion gases passes through tubes surrounding by water . Maximum operating pressure about 12 bar.

I.B.1.b. Water tube boilers
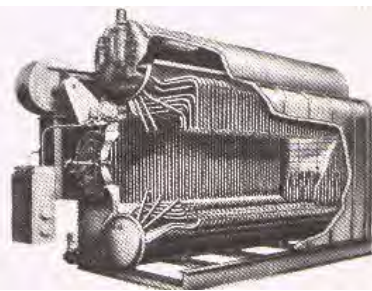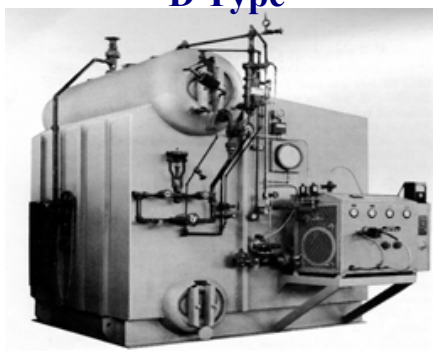
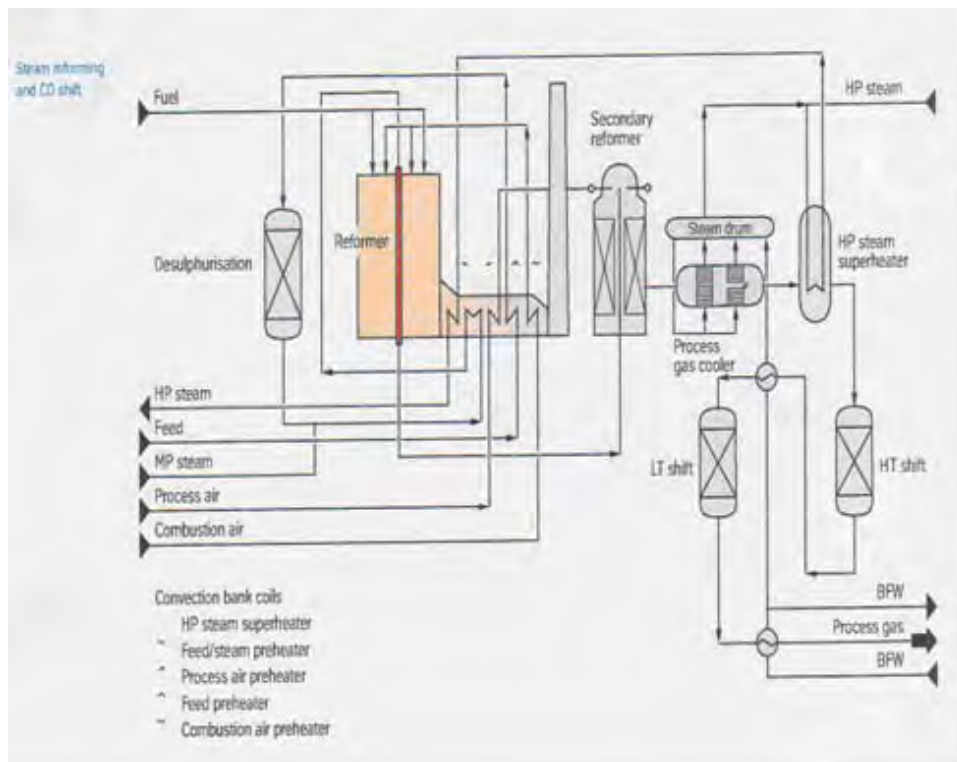**A Type**   **D Type**   **O Type**

D Type

Steam drum
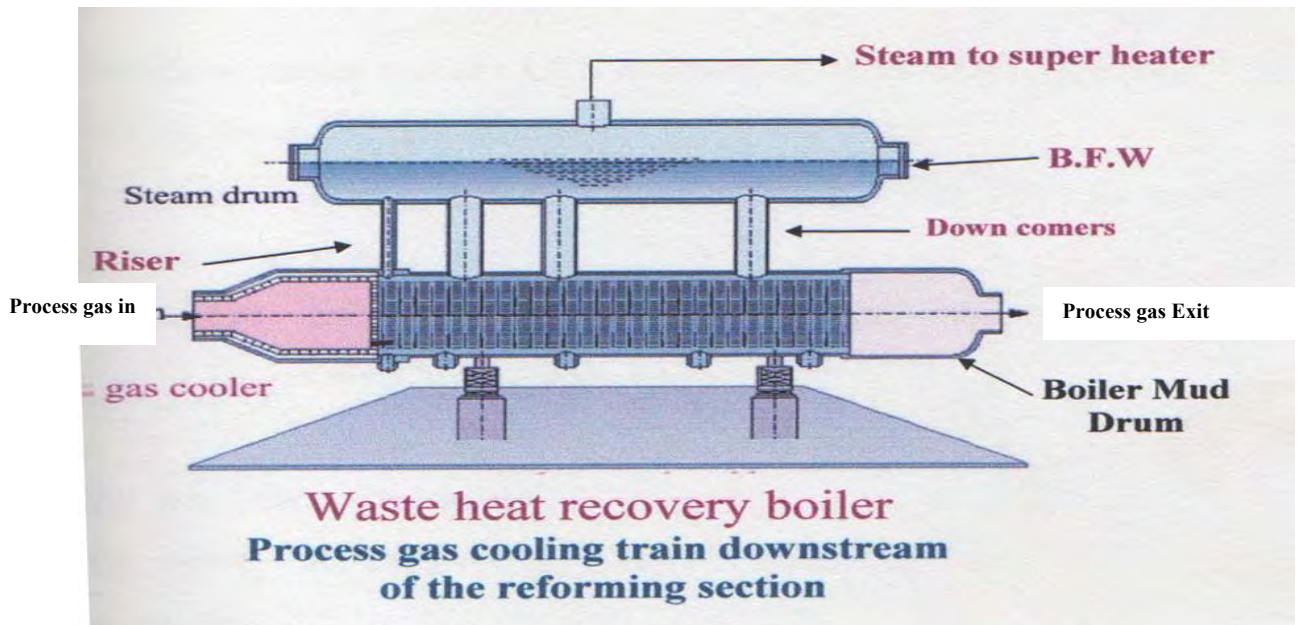
I.B.2. Unfired boilers – Heat exchangers

Waste heat boilers – Heat Recover Steam Generator – HRSG

Waste heat recovery boiler
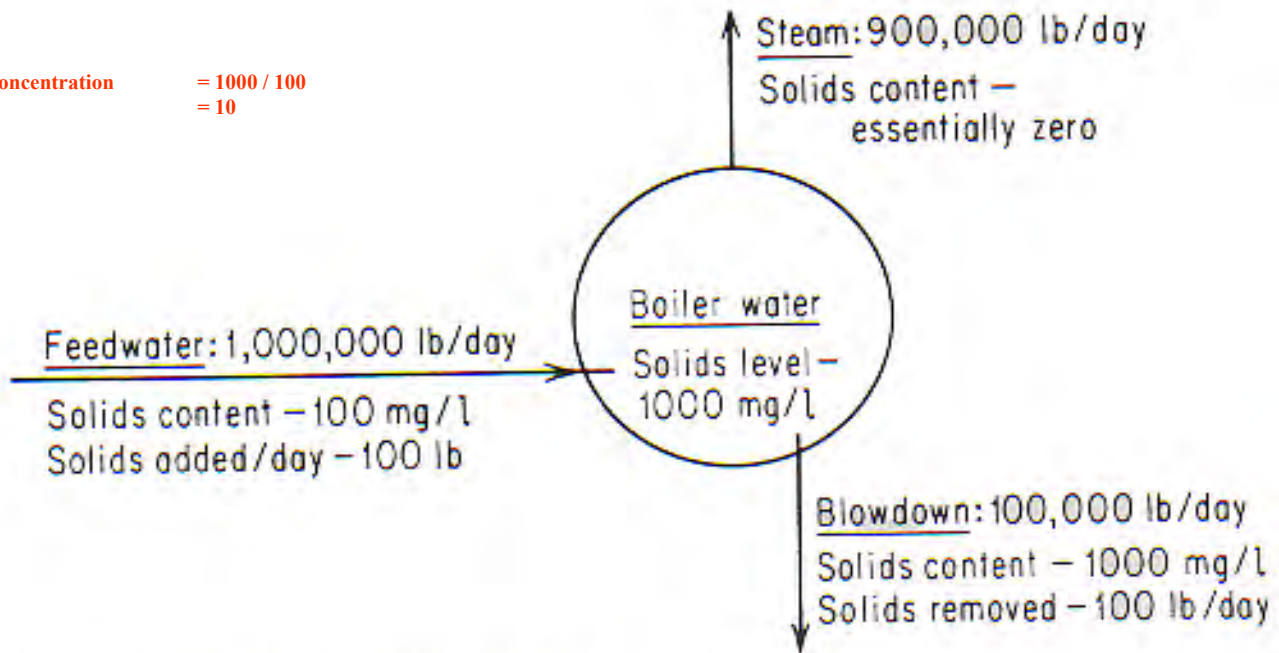Process gas cooling train downstream
of the reforming section

Catalytic steam reforming of natural gas by primary and secondary reformers for the
production of syngas for the ammonia production plant

The process gas cooler is used as a waste heat boiler

Blow down system :

- Continuous blow down from steam drum removes only TDS.
- Intermittent blow down from mud drum to remove sludge and TDS.

Steam: 900,000 lb/day
Solids content —
essentially zero

Boiler water
Solids level —
1000 mg/l

Feedwater: 1,000,000 lb/day
Solids content – 100 mg/l
Solids added/day – 100 lb

Blowdown: 100,000 lb/day
Solids content – 1000 mg/l
Solids removed – 100 lb/day
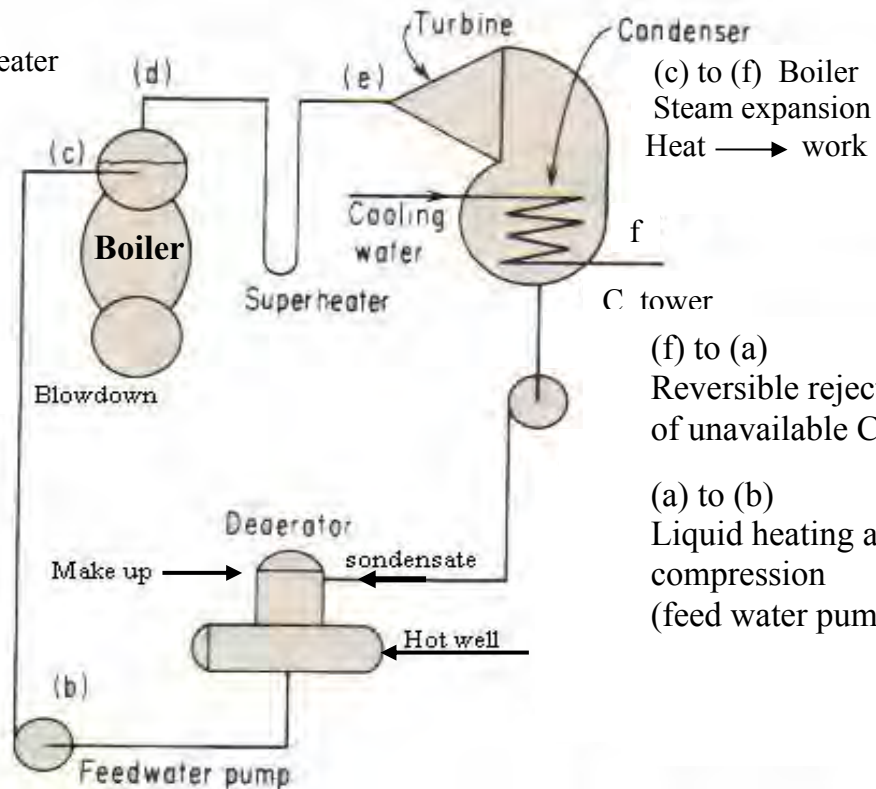
How boiler water solids are controlled by blow- down.

Blow down boiler water

$$\text{Blowdown rate} = \frac{\text{Feed water rate}}{\text{Cycle of concentration}}$$

$$\text{cycle of concentration} = \frac{\text{TDS of boiler water}}{\text{TDS of feed water}}$$

(c) to (d) Boiler
(d) To (e) Super heater

(d)

(c)

Boiler

Superheater

Turbine

(e)

Condenser

Cooling water

f

C. tower

(c) to (f) Boiler
Steam expansion
Heat ⟶ work

(f) to (a)
Reversible rejection
of unavailable C.W

(a) to (c)

feed water
heating

Blowdown

(a) to (b)
Liquid heating and
compression
(feed water pump)

Deaerator

Make up ⟶

sondensate

Hot well ⟵

(b)
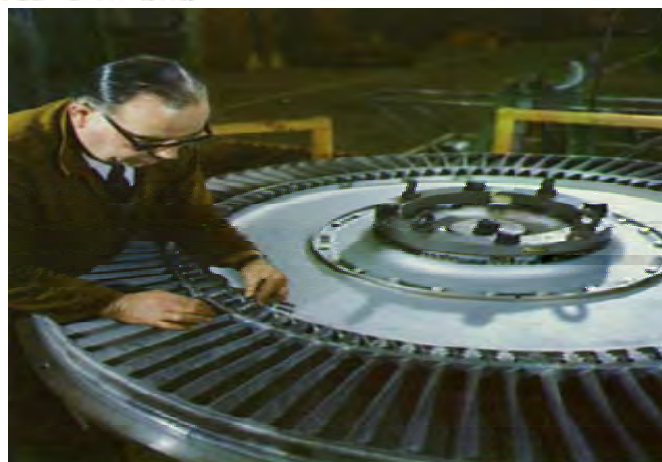
Feedwater pump

Turbine
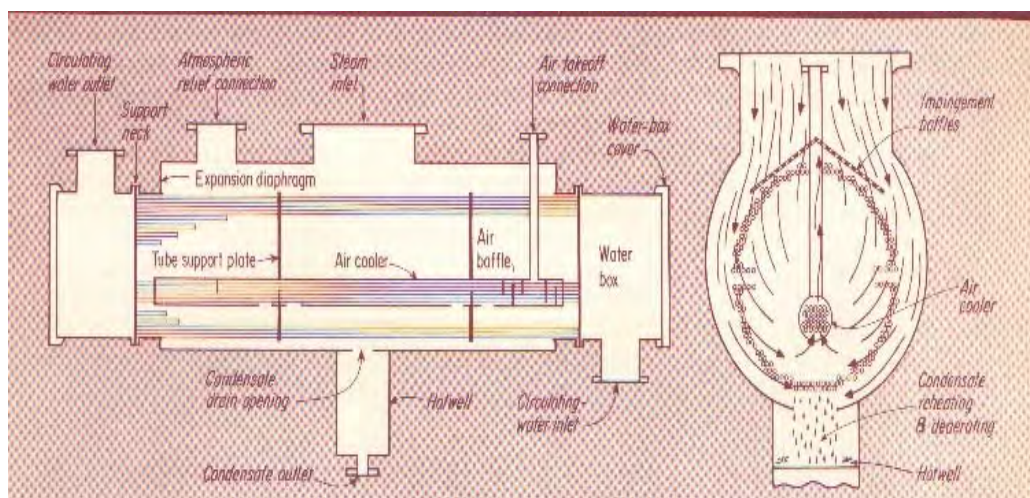
Surface condenser

2. BOILER WATER PROBLEMS :

Boiler feed water , regardless of the type and extent of external treatment may contain contaminants that can cause the following problems.

I – DEPOSITIONS :

Deposition are most serious problem in the pre boiler , boiler and after boiler.

Deposits of calcium salts.
Deposits of Mg salts.
Deposits of other contaminants.
- Directly reduce heat transfer
- Higher metal temperature and over heating and eventually tube failure.
- Cause higher fuel consumption

II – CORROSION PROBLEMS :

1 - Oxygen – O2
2 - Carbon dioxide CO2
3 - Caustic attack
4 - Stress corrosion cracking (SCC)
5 - Hydrogen damage
6 - Acid attack
7 - Caustic embitterment
8 - The ductile gouging

Both longitudinal and transverse stress-corrosion cracks on a brass heat exchanger tube that had been exposed to ammonia. Note the branching of the cracks.

Condenser Tube

A pattern of erosion spots on the external surface facing the turbine exhaust inlet.

Severe grooving on the internal surface of a copper pipe carrying condensate. Grooves were cut by condensing vapors running down pipe walls. Note the vivid blue corrosion products and deposits near the bottom.

Smooth attack on carbon steel by carbonic acid. Note the vivid red color of hematite, indicating high oxygen concentrations.

A brass condenser tube severely wasted by condensing vapors containing ammonia.

Note the fine grooves resembling cracks.

A large, ragged perforation in a region of severe internal wastage on a copper pipe. Corrosion was caused by ammonia-containing condensate.

III – CARRY - OVER :

- Results in super heater deposits and failure.
- Results in turbine deposits and corrosion and / or erosion problems.
- Condensate system deposits and corrosion.
    - Carry over even at extremely low levels may cause failure and complete system outages.
    - The more serious problems is the selective carry over , like the supplement of silica which is volatilized from the boiler water and dissolved in the steam , the pure silica deposits is hard glassy deposit on the turbine blades which can not be removed by condensate washing.
    - They removed by grit or sand plasting or by chemical cleaning using HF.
    - Sometimes soluble silicate may form due to volatile silica and non-selective carry over of boiler water containing sodium ions.

A typical tube failure caused by overheating.

Turbine shaft   Rust patches surround small pits on a stainless steel shaft. The rust is formed by oxidation of ejected ferrous ion from the tiny pits. Pits were initiated by chloride and sulfate ions concentrated by evaporation.

3. Boiler water treatment programs :

The treatment program that should achieve the following
1. Prevent deposition and scaling.
2. Minimize and control corrosion.
3. Carry over control.

The new and modem treatment program for boiler water include the following items:

1 - Antiscalant by terpolymer of acrylate and natural polymer as lignin . This may be used with both precipitating or solubilizing programs.

2- Phosphonate complex the hardness salts keeping them fluidized by threshold effect in the boiler water and also work as corrosion inhibitor.

3- Catalysed Hydrazine or other organic oxygen scavengers. are more efficient scavengers for high pressure boilers.

4- Volatile amines , filming and neutralizing amines to protect the after boiler section from corrosion by the carbonic acid.

5- Antifoam to prevent carry over or entrainment which cause deposition and under deposit corrosion in the after boiler section and also cause steam contamination,

The antifoam chemicals based on poly alkylene glycol which is also working as after boiler corrosion inhibitor.

There are two different types for deposit control programs

1. Precipitating program based on phosphate product for high press boiler TSP is used for pH control using the ratio of 2.6 for Na : PO4 which called the congruent program .

- The coordinate program based on a ratio of 3 of $Na : PO_4$

    This ratio may lead to free NaOH.

2. The solubilizing program for medium pressure boilers

a. Based on chelants .

b. Based on terpolymer and phosphonate .

Carryover control

- The control of chemical carry over :
- By the use of chemical antifoam.
- By maintaining the TDS , Alkalinity and silica at the desired recommended level.
- Control of mechanical carry over :
- Adjustment of the steam drum internals.
- Adjustment of water level in the steam drum .
- Operation at steady loads.

Conclusion:

Importance of boiler feed water treatment

Main objective of feed water treatment is to eliminate troubles caused by scale , corrosion , carry over and caustic embrittlement . Today's subcritical and supercritical pressures call for complete makeup treatment in the form of evaporation or demineralization . In addition , condensate in these systems is treated or " polished " by filtration , demineralizing or a combination of both. Minute traces of metal picked up by water or steam must be removed to prevent damage to boilers or steam turbines .

Chemical treatment programs are also employed with considerable success in preventing corrosion both morpholine and hydrazines are effective under normal operating conditions.

Mainly the new technology of the boiler water treatment based on organic materials such as natural and synthetic anionic and non-ionic polymers with catalyzed Hydrazine and organic phospate , and blend of amines with antifoam , this program is solvbilizing program which keep the entire system under control .

Reference :

- Drew Principles of industrial water treatment .
- Power special report – Jun 1964.
- Beecher , Jess S. corrosion and deposit control in industrial and utility boilers – Metropolitan New York section of the national association of corrosion engineers (NACE).
- Bell , W.E Rice , R.C. and Clark , R.J.
- Chelating agents in treatment of boiler feed water presented at 54th annual meeting of international water conference (1995).
- Denman , wayne L. Eldelson,
- Boiler scale control in carbonate cycle with synthetic polymers.
- Dessman , and Salutsky,
- Boiler scale control with polyacrylate and polymethacrylate power (1968).
- Procedure of industrial water treatment , J.n.tanis.
- Encyclopedia Americana.
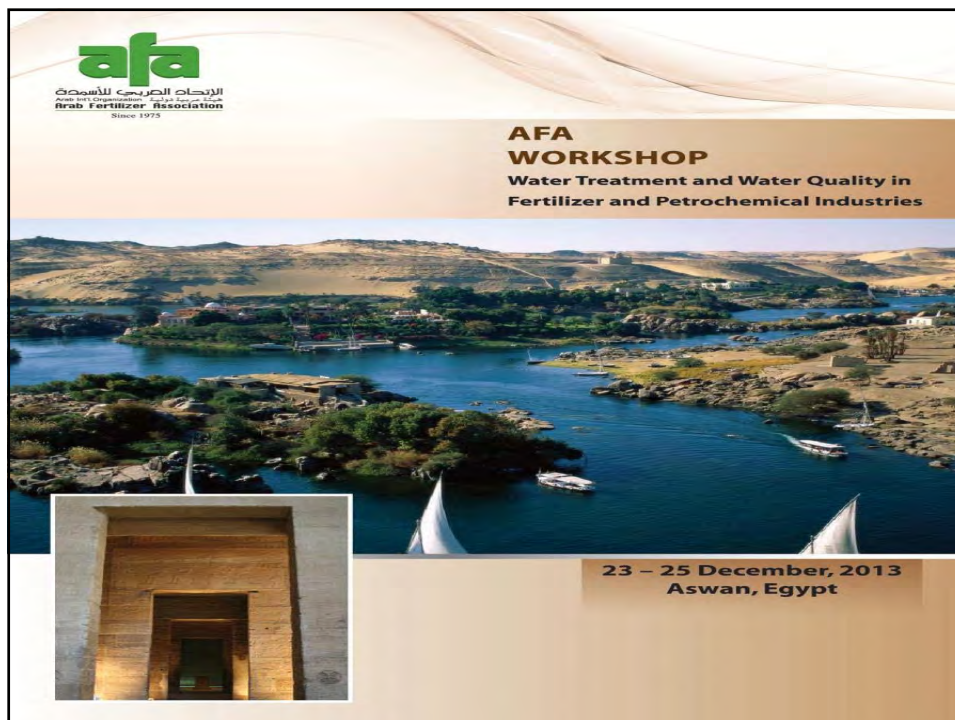
COOLING TECHNOLOGY INSTITUTE
MAINTAINING CLEAN COOLING SYSTEMS

Technical Paper Number TP 05-21

Faiza Abou Zeid
AQUA TRUST FOR WATER TREATMENT

The studies and conclusions reported in this paper are the results of the author's own work . The report has been presented before and reviewed by members of the Cooling Technology Institute , and approved as valuable contribution to cooling tower literature , and presented by the author at the Annual meeting of CTI.
Copyright 2005 . All rights reserved
Presented at the 2005 Cooling Technology Institute Annual Conference
San Antonio, TX – February28 – March 3, 2005

2

MAINTAINING CLEAN COOLING SYSTEMS

Cooling Technology Institute (CTI)
Annual conference 28 Feb – 3 Mar 2005
San Antonio - Texas

Presented by :
Aqua Trust General Manger
Eng .Faiza Abou Zeid
With compliment of Aqua Trust for water treatment

CTI Annual conference 2005   Aqua Trust For water Treatment
3

Table of content :

I   . Introduction .
II . Cooling systems are utilizing the following plants .
III . Types of cooling systems and towers .
IV . Water related problems of cooling systems .
V   . Results of water related problems .
VI . Control methods .
VII. Recommended cooling water treatment programs .

CTI Annual conference 2005   Aqua Trust For water Treatment
4

I. Introduction:

This presentation will discuss newly developed Green Chemical additives corrosion inhibitor and scale prevention of cooling water systems with minimum environmental impact and the application of some mechanical modification such as air bumping and side stream filtration of cooling water also the use of double mech screen before the suction line of water pumps , back flushing and blow down Ports for shell side heat exchangers also making some holes at the base of the baffles .

The all-organic treatment program together with the mechanical modifications achieved the required goal which is

" Maintaining a clean cooling system "

CTI Annual conference 2005   Aqua Trust For water Treatment

5

II. Cooling systems are utilizing the following plants

➢ Ammonia production.
➢ Weaving and Spinning mills
➢ Power generating stations.
➢ Chemical plants .
➢ Fertilizer manufacturing plants.
➢ Petroleum refineries.
➢ Steel and Aluminum mills.
➢ Commercial refrigeration plants.
➢ Central air – conditioning systems.
➢ Cement plants .
➢ Sugar industries.
➢ Food industries.
➢ Air liquefaction and oxygen plants.
➢ Soda / Chlore plants .
And many other industries.

CTI Annual conference 2005   Aqua Trust For water Treatment

6

III . Types of cooling systems

1- Once – through
   systems

2- Closed recirculation systems-
   Closed Circuit cooling towers

3- Open recirculating evaporative systems –
   Open cooling towers

Open Cooling Towers

An evaporative piece of equipment that exposes water directly to the cooling atmosphere , thereby transferring the source heat load directly to the air .

Induced Draft

Type of mechanical draft tower in which one or more fans are located in the air outlet to induce air through the air inlets .

Forced Draft

Type of mechanical draft tower in which one or more fans are located at the air inlet to force air into the cooling tower .

Counter flow

In a counter flow cooling tower , the air enters at the base of the tower , flows upward and interfaces counter currently with the falling hot water .

Crossflow

In a cross flow cooling tower , the air flows horizontally through the cooling tower and interfaces perpendicularly with the falling hot water .

Forced draft – cooling tower – counter flow

Ammonia plant cooling tower – counter flow

CTI Annual conference 2005

Aqua Trust For water Treatment

13

Induced draft – counter flow

Hyper bolic – forced draft

CTI Annual conference 2005

Aqua Trust For water Treatment

14

IV . WATER RELATED PROBLEMS OF COOLING SYSTEM

a-Deposition

b- Corrosion

c- Microbiological fouling

Ammonia condenser

Surface condenser

Turnaround of the ammonia plant for mechanical cleaning of the ammonia condenser and surface condenser of the turbine

Inter stage cooler of CO$_2$ compressor

Oil cooler of compressor

Ammonia and Nitric Acid plants experienced sever scaling problems using Ortho-phosphate based treatment .

CTI Annual conference 2005

Aqua Trust For water Treatment

17

Fouled tube and cleaned tube

Plate coolers in the Nitric acid plant having heavy scales of calcium phosphate and calcium carbonate

CTI Annual conference 2005

Aqua Trust For water Treatment

18

Open Tower Packing (Fill) :

- Scale , Solids and bio-fouling restrict air & water passages .

- Capacity diminishes rapidly with increased fouling .

- Extra weight can damage fill and structural supports .

Typical fill clogging from

biofilms and suspended solids.

CTI Annual conference 2005   Aqua Trust For water Treatment
19

Deposits Accelerate Corrosion

Corrosion Inhibitor film does not reach the metal surface

Pits
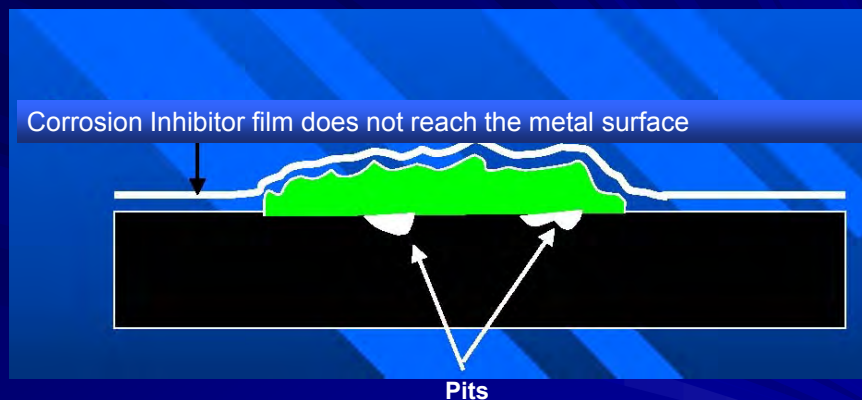
BACTERIA METABOLISM LOWERS pH UNDER BIOFILM WHICH CORRODES METAL

CTI Annual conference 2005   Aqua Trust For water Treatment
20

Under Deposit Corrosion

Deposit layer

Pits

OXYGEN DIFFERENTIAL CELL LEADS TO PITTING WHICH CORRODES METAL

V . Results of water related problems

- Lost heat transfer,

- Accelerated corrosion,

- System deterioration,

- Increased costs of repair and replacement.

VI . Control Methods

■ **Inhibitors** to protect Metals from Corrosion.

By carboxylic Phosphonate and HEDP(free pH).

■ **Anti scalant** to prevent Scale
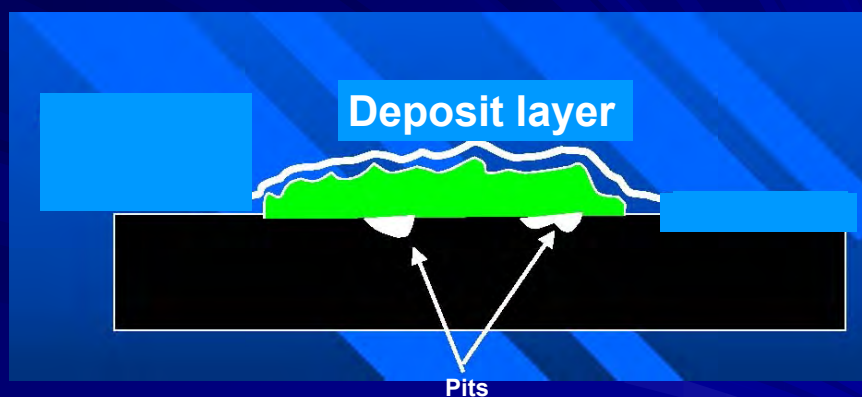Precipitation.   By poly Acrylic acid and
poly Maleic acid polymers.

■ **Antifoulant** to prevent fouling matters from deposition.
By anionic sulfonated polymers and nonionic glycol polymer.

■ **Biocide** to reduce Microbe and Biofilm Growth.
[corrosion and scaling effect]
By quats or organo sulfer compounds and chlorination.
- 0.2 to 0.5 ppm free chlorine residual control range typical .

■ **Anti-foam** to Reduce visible effect of some biocide.

CTI Annual conference 2005   Aqua Trust For water Treatment
23

VII . Recommended cooling water treatment program

1- Phosphonate maintained at 2.0 – 3 ppm .
2- Poly carboxylic polymers at 10 – 20 ppm .
3- Zinc as zinc 1.5 – 2.2 ppm , zinc product may be used due to the high chloride ions in the make up and cooling water to control pitting corrosion.
4- Non-ionic surfactant and sulfonated polymers at 5 – 10 ppm .
5- Microbiocide based on isothiazoline at 1 – 2 ppm once per week and Cl_2 every day .

CTI Annual conference 2005   Aqua Trust For water Treatment
24

Determination of antiscalant and dispersant action in cooling water by

DISPERSION LEVEL

D L

25

$$D L = \frac{Ca \text{ or } S.S \text{ IN COOLING WATER}}{Ca \text{ or } S.S \text{ IN M.u. water}} \times Cn$$

Cn = cycle of concentration based on TDS

$$= \frac{\text{measured TDS ppm} - \text{ppm of treatment}}{\text{TDS of M.u water}}$$

26

INTERPRETATION

D L = 1   i.e.   No deposition   - good

D L < 1   i.e.   Deposition   - bad

D L > 1   i.e.   Deposit removal - excellent
                    means cleaning of the
    cooling   system is taking
    place .

Determination of corrosion control by :

➢ Instantenious corrosion rate measurement
    by corrater .

➢ Coupon type corrosion rate measurement by
    weight lost of 30 days duration.

➢ Corrosion rate of mild steel should be below
    5 mils per year.

Microbiological control

- Chlorination once a day.
- Microbiocide – wide spectrum biodegradable type -

➢ **To control the TBC below 20 thousand colony /ml of cooling water.**
➢ **To keep the cooling tower clean free from algae and fungi.**

The most important point to make a cooling water systems efficiently operate lies in the area of deposit control which on the other hand minimize corrosion and pitting .

By a three – step method of treatment based on new technology keeps cooling systems clean through the use of environmentally compatible dispersants , penetrants and antifoulant formulated with organic phosphonates is maintaining optimum efficiency of the cooling water system .

Phosphonate compounds
corrosion inhibitor and Fe sequestrant
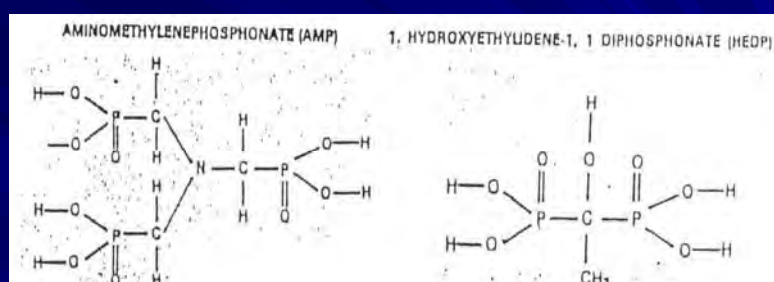
These compound has (C-P-O) bond
which is a strong bond .

Types of polymers for scale and deposite prevention

1- Anionic polymers

Functional groups :
Carboxylic and sulfonic groups

$$O$$
$$| $$
$$—S—OH$$
$$| $$
$$O$$

Polyacrylic acid

CH_2 CH_2 CH_2
CH CH CH
$COOH$ $COOH$

Polymaleic acid

$COOH$ $COOH$
CH CH
CH CH
$COOH$ $COOH$
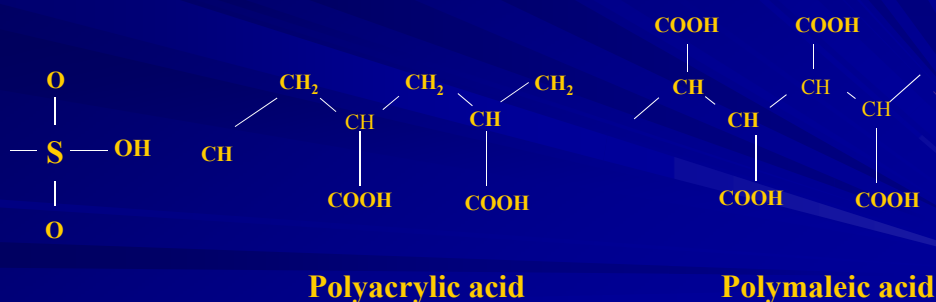
CTI Annual conference 2005   Aqua Trust For water Treatment
33

2- Nonionic polymers - Antifoulant

Functional groups :
Amides and alcohols
Such as polyamides and polyalkylene glycols

$$O$$
$$—C$$
$$NH_2$$

AMIDES

$$CH—OH$$

HYDROXYL

CTI Annual conference 2005   Aqua Trust For water Treatment
34

3- Cationic polymers

Functional groups :

Amines $R \!-\! NH_2$

Quats

$$CH_3$$
$$| $$
$$-\!\!-\,N\!-\!CH_3$$
$$|$$
$$CH_3$$

Conclusion :

1- Application of stable corrosion inhibitor which protect the system and the use of carboxylic & sulfonated polymers work efficiently at alkaline pH, keeping the system free of any deposits , also it help in keeping the zinc soluble at this pH , when the zinc product is applied for pitting control .

2-   Prevent the use of phosphate based corrosion inhibitors and the use of acids for pH control .

3 - The use of organic phosphate corrosion inhibitor in the ammonia cooling water to prevent the formation of sludge of calcium phosphate due to the high pH of the water.
Some formulations of organic and inorganic phosphate proven good results because the organic phosphate and polymer will keep the inorganic phosphate in solution.

4 - Application of some mechanical modification for the heat exchangers and cooling towers such as .

a - Using a booster pump to increase the water flow .

b - Side stream filtration of the cooling water .

c - Air or nitrogen pumping for shell side coolers and back flushing to remove any debris.

d - Installation of double screen at the succsion line of the cooling water pumps for alternative cleaning for each screen .

e - Injection quills for dosing of antiscalant installed at the water inlet to a problematic coolers.

CTI Annual conference 2005   Aqua Trust For water Treatment
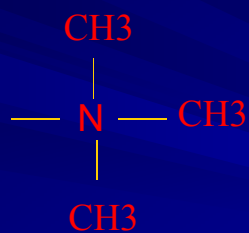   37

Acknowledgments :

The above descriped cooling water treatment program was applied and currently applied in ammonia , urea , nitric , nitrates , sulfuric and power plants , sulfates , gas liquifaction , oxygen plants , chlor/alkalin and chemical production and meneral oils production plants the program proven wery successful control results , those results were achieved by the co-operation between Aqua Trust technical staff and following clients technical stuff.

CTI Annual conference 2005   Aqua Trust For water Treatment
                                                                                          38

It would be difficult to acknowledge all dedicated personnel who diligently participate in the work however we wish to thank the following companies and their chairmen for the very good opportunity given and the ethical support to Aqua Trust ,

would like personally to thank prof . Dr.Bashir Abd ElNaby – head of chemistry department – faculty of science , Alex . For his revision of this presentation.

CTI Annual conference 2005   Aqua Trust For water Treatment
39

- **Thanks to Aqua Trust clients :**

- **Rolls – Royce peebles electric company – Eng Ignatius Tight**
- **Delta fertilizer and chemicals company – Talkha.**
- **El Nasr fertilizer and chemicals company - Suez.**
- **General fertilizer company.**
- **El Nasr for intermidiat chemicals co. - NICC.**
- **Kima – Egyptian Chemical Industries Aswan.**
- **El Nasr for coke and basic chemicals co. – Helwan.**
- **Alexandria mineral oils company – Amoc.- Alex.**
- **Abu Qir fertilizers and chemicals co. – Alex.**

Many thanks for the opportunity given to Aqua Trust.

Faiza Abou Zeid

CTI Annual conference 2005   Aqua Trust For water Treatment
40

MAINTAINING OPTIMUM EFFICIENCY
OF COOLING SYSTEM BY
ALL-ORGANICS / LOW ZINC
HYBRID PROGRAM

2013 Annual Convention and Exposition - Uncasville, CT
October 30-November 2, 2013 - Mohegan Sun

Presented by:
Eng. Faiza Abou Zeid
General Manager
And
Eng. Samar Yassin
Quality control Manager
Aqua Trust for Water Treatment

Table of content :

1

I . Abstract:

This presentation will discuss newly developed HYBRID program of

A-ORGANIC Chemical

Additives corrosion inhibitor blend of HEDP and PBTC phosphonates and scale prevention based on sulfonated acrylic acid co polymers has anti foul ant based on nonionic surfactant for cooling water treatment

B-LOW ZINC

According to chloride concentration when exceeds 100 ppm in cooling water and a liquid zinc product is applied to maintain zinc at very low concentration(1.0-1.5 ppm)in cooling water to supplement pitting corrosion control by equipotentialization.

This program with no or little environmental impact

(Direct injection of the anti scalant to the problematic coolers

to remove and prevent depositions was recommended)

The HYBRID program of ALL-ORGANIC and low Zinc Adebt and achieved the required goal of treatment which is

Maintaining optimum efficiency by keeping cooling system clean free from deposition and corrosion.

2

II. Cooling systems are utilizing such industries

- Ammonia production.
- Power generating stations.
- Chemical industries.
- Fertilizer manufacturing.
- Petroleum refineries.
- Steel and Aluminum mills.
- HVAC &R systems.
- Cement industries.
- Sugar industries.
- Food industries.
- Air liquefaction and oxygen.
- Sodium hydroxide / Chlorine.
- Weaving and Spinning mills and many other industries

3

Induced draft

14 - 12 2004

Counter - flow Type

4

Induced draft

Cross – flow Type

5
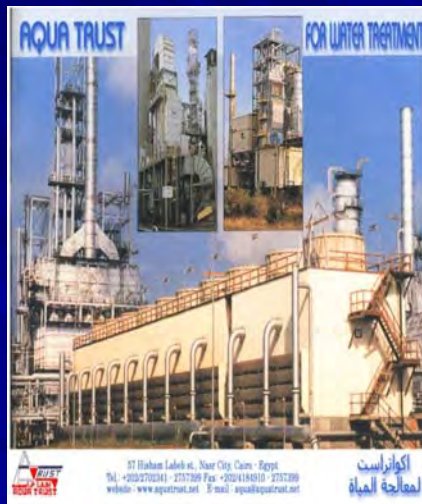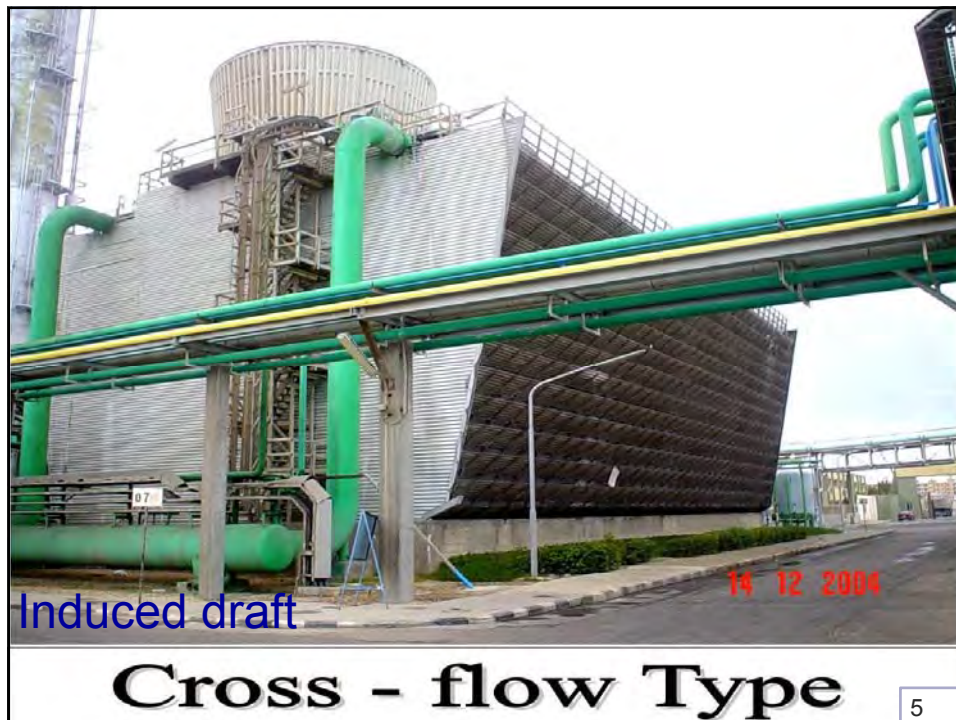
III . TYPES OF COOLING SYSTEMS

1- Open evaporative systems

2- Closed Circuit cooling towers

3- Once – through systems

6

IV . WATER RELATED PROBLEMS OF COOLING SYSTEM

a-Deposition

b- Corrosion

c- Microbiological fouling

7
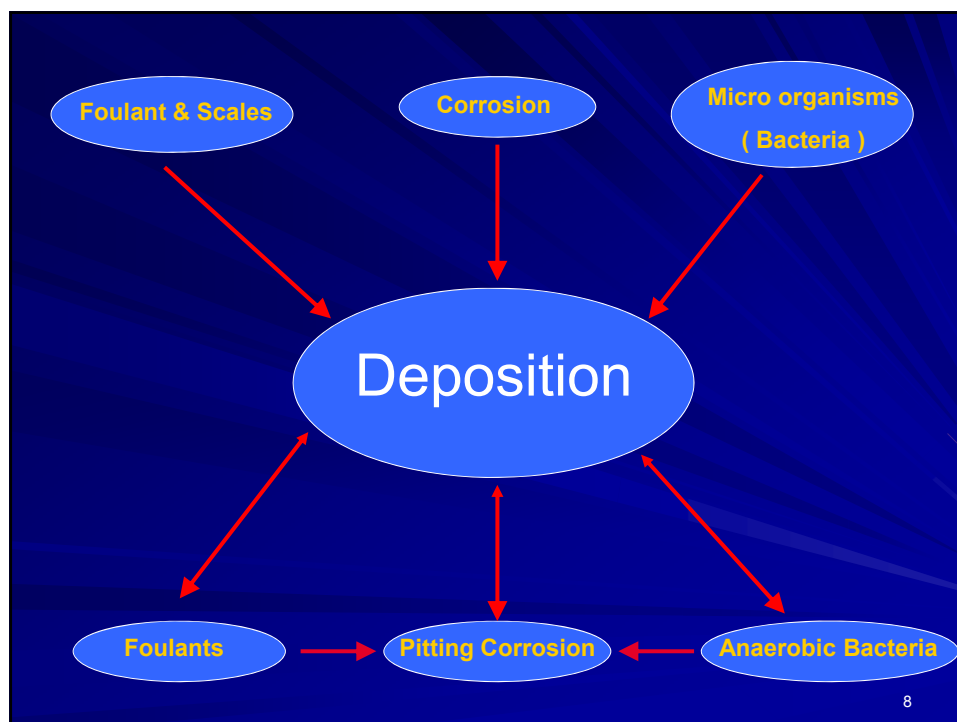
Ammonia condenser

Steam Surface condenser

Turnaround of Ammonia plant for mechanical cleaning of Ammonia Condenser and Steam Common Condenser

9

Inter stage cooler of CO_2 compressor

Oil cooler of compressor

Ammonia and Nitric Acid plants experienced sever scaling problems using Ortho-Phosphate/Zinc based treatment .

10

Plate cooler in Nitric Acid plant having heavy scales of Calcium Phosphate and Calcium carbonate

11

Open Tower Packing (Fill) :

- **Deposits of Solids and bio-fouling restrict air & water passages** .
- **Capacity diminishes rapidly with increased fouling .**
- **Extra weight can damage fill and construction supports .**

Typical fill clogging

12

7

Deposits Accelerate Corrosion

Corrosion Inhibitor film does not reach the metal surface

Pits
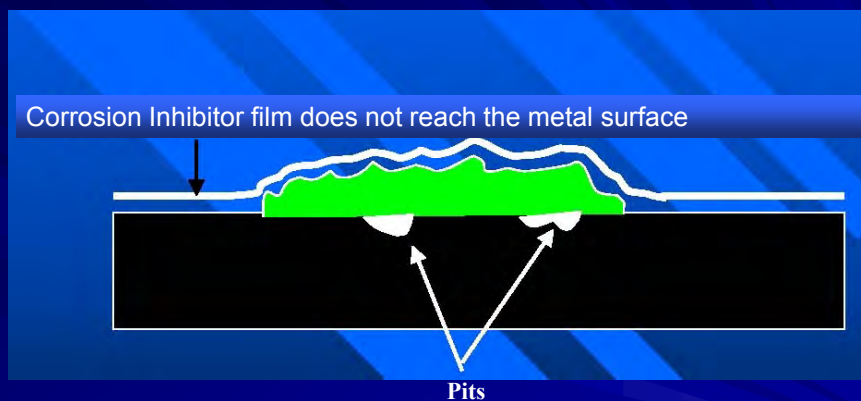
BACTERIA METABOLISM LOWERS PH LEADING TO UNDER DEPOSITS WHICH CORROSION

13

Under Deposit Corrosion

Deposit layer

Pits
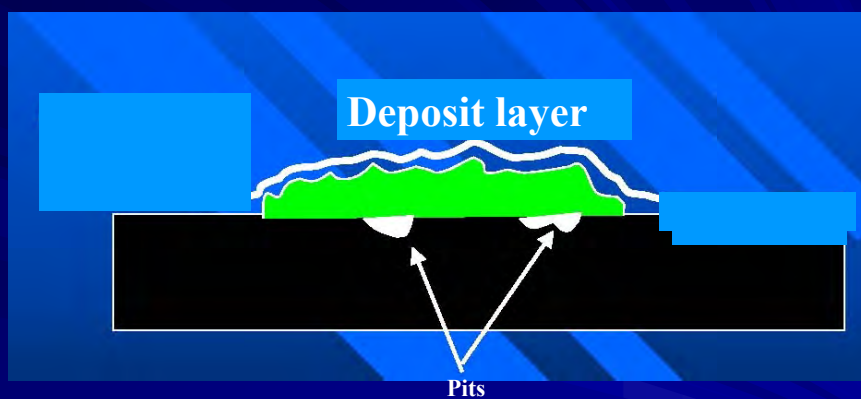
OXYGEN DIFFERENTIAL CELL LEADS TO PITTING WHICH PERFORATE METALS

14

Calcium carbonate scaling of an electric utility surface condenser due to poor treatment
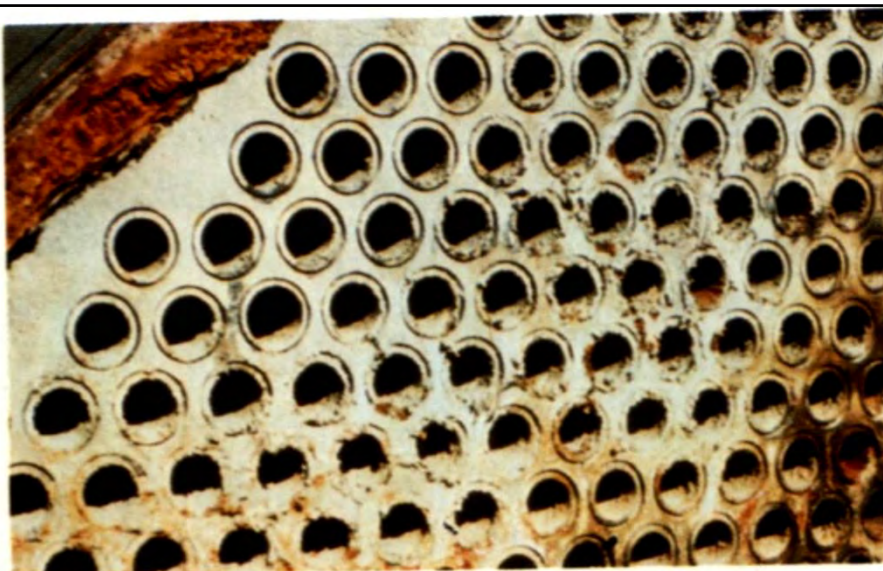
Calcium , Zinc and iron phosphate due to the formation of ortho phosphate by the action of High pH of cooling water of the ammonia cooling tower

Deposition of corrosion products and scales in

Cooling systems which restrict the water flow and also leading to tube failure .

Fouling reduces exchanger's heat transfer efficiency.
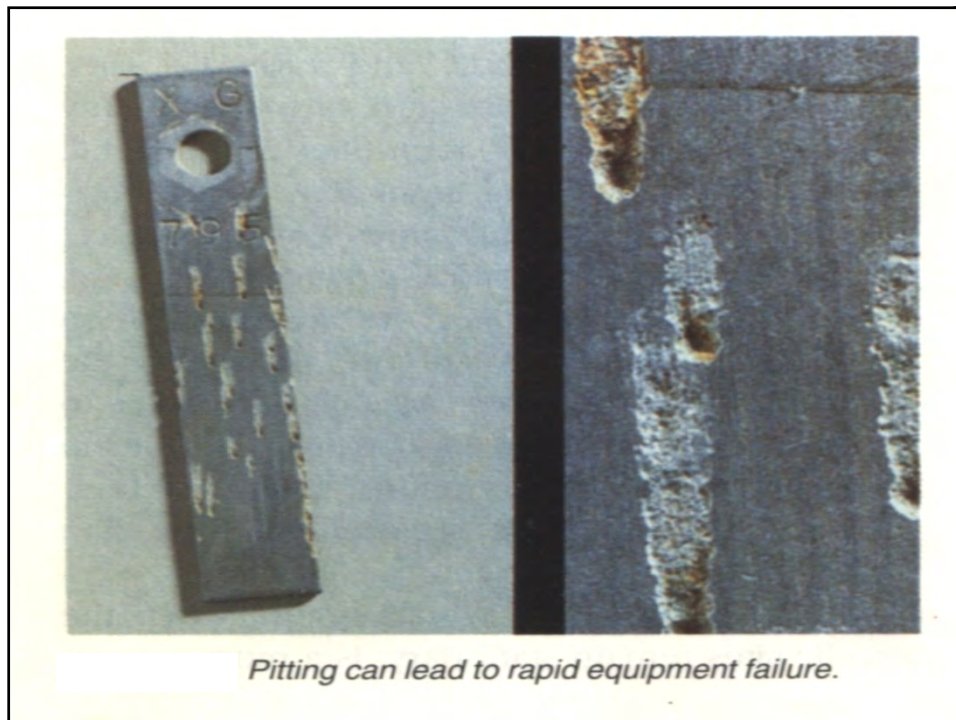
Pitting can lead to rapid equipment failure.

V . Results of water related problems

- **Lost heat transfer.**
- **Accelerated corrosion.**
- **System deterioration.**
- **Increased costs of repair and replacement.**
- **Wastage of product due to leaks.**
- **Lost of production capacity.**

20

11

VI . Applied Control Program

■ **Inhibitors:**   To protect Metals from Corrosion.
   - By BPTC and HEDP Phosphonate and low Zinc work at free pH

■ **Anti scalant:**   To prevent CALCIUM Hardness
                 Precipitation and scale formation.
   -By poly Acrylic and poly Malefic polymers.

■ **Anti foul ant:** To prevent mud ,clay, sand and oils... deposition.
   - By surfactant and nonionic glycol polymer.

■ **Biocide:**   To reduce Bacteria count and Bio film
                 growth. [corrosion and deposition effect]
   - By quats and organo sulfur compounds

■ **Chlorination:** By chlorine gas or hypo once per day
                 during hot weather
   -To maintain F.A.C at 0.2 to 0.5 ppm typical control range.   21

VII . Recommended cooling water treatment program

 1- Pre cleaning   2- Pre treatment   3- Maintenance Treatment

1- **Pre cleaning**   of old or new cooling system using all-organic chemicals
    (Penetrant – dispersant – anti foul ant – micro biocide) .
     To remove old scales and deposits or mill scale and oils

2- **Pre treatment**   (Passivation) of cooling system maintaining
    organic Po_4 at 4-6 ppm and Zn at 2-3 ppm for 7 days in the cooling water .

3- **Maintenance Treatment** as follow :
  * Organic PO4 maintained at 2.0 – 3.0 ppm in the cooling water .
  * Poly carboxylic polymers at 10 – 15 ppm .
  * Non-ionic surfactant and sulfonated polymers at 5 – 10 ppm .
  * Micro biocide based on isothiazoline and Quats alternatively at 10 – 15
   ppm once per week
  * chlorination every day in hot weather to maintain residual free Cl_2
    at 0.3 – 0.5 ppm in the hot return cooling water for 20 minute .   22

Before the recommended program

Clean heat exchanger after receiving the above mentioned program at Delta fertilizer – Talkha II – Ammonia plant
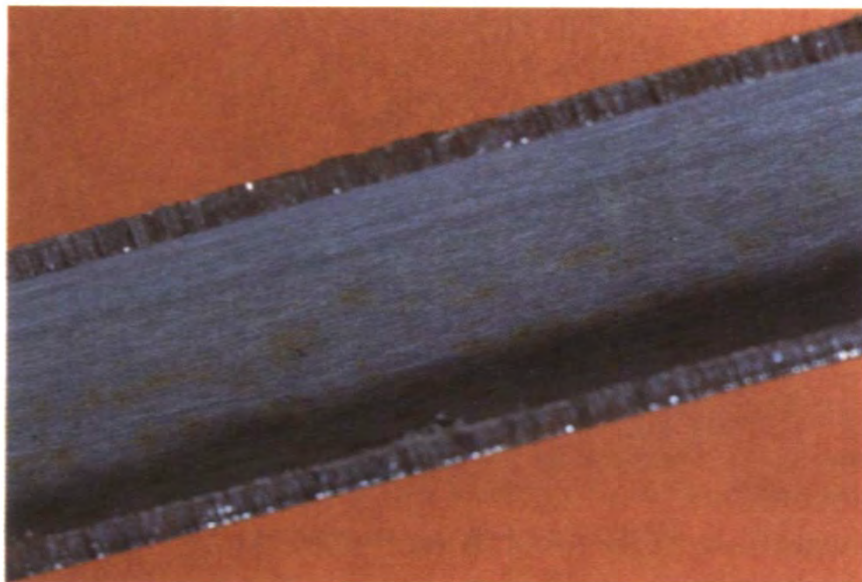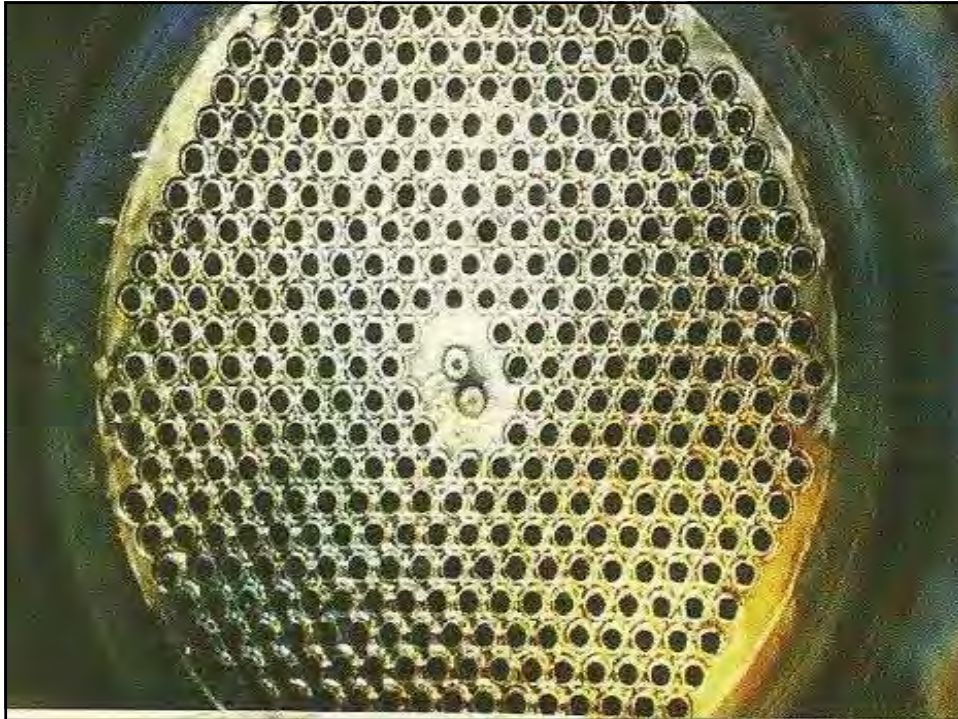
Mild steel corrosion protection provided by a passivating inhibitor.

Control and Monitoring of the treatment program Effect

1- Make-up and cooling water analysis to determine Dispersion level.

2- Measurement of corrosion rates by corrator and coupons .

3- Measurement of total Bacteria count TBC and inspection of cooling tower structure .

4- periodically inspection of test heat exchanger

27

Determination of Anti scalant and Dispersant action in cooling water by

DISPERSION LEVEL

D L

28

15

$$D L = \frac{Ca \text{ or } S.S \text{ IN COOLING WATER}}{Ca \text{ or } S.S \text{ IN M.u. water}} \times Cn$$

Cn = cycle of concentration based on TDS

$$= \frac{\text{measured TDS ppm} - \text{ppm of treatment}}{\text{TDS of M.u water}}$$

29

INTERPRETATION OF DL

■ D L = 1   i.e.   **No deposition**   - **good**

■ D L < 1   i.e.   **Deposition is taking place** - **Poor**

■ D L > 1   i.e.   **Deposit removal**   - **excellent**

Means cleaning of the Cooling System is taking place .

30

Determination of corrosion control by :

➢ **Instantaneous corrosion rate measurement by corrator .**

➢ **Coupon type corrosion rate measurement by weight lost of 30 days duration.**

➢ **Corrosion rate of mild steel should be below 4 mils per year.**

31
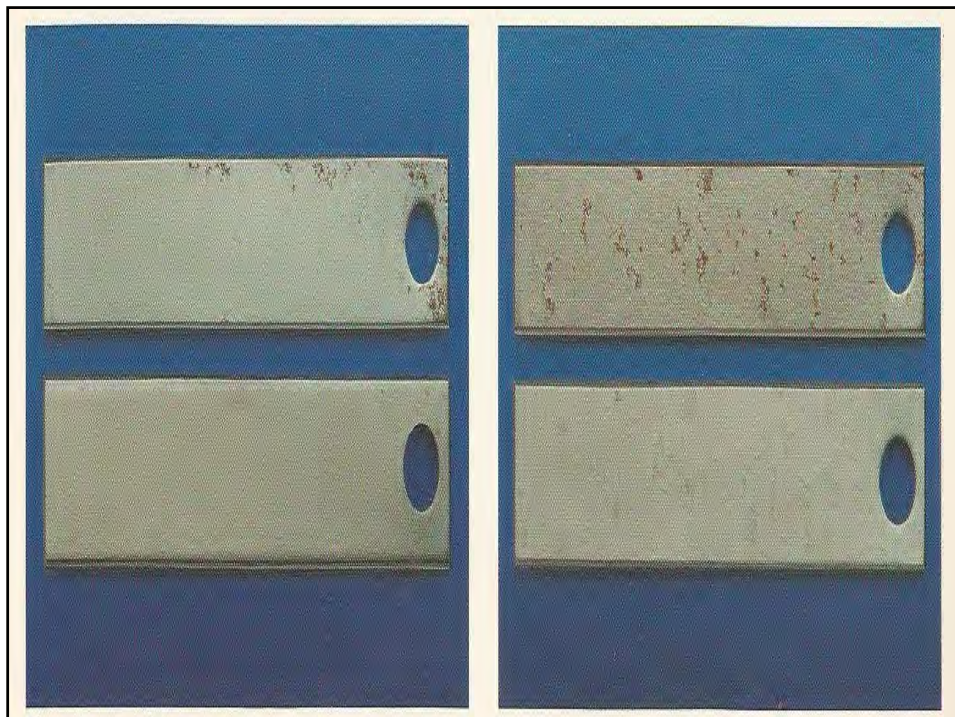
Microbiological Test

- **Chlorination once a day maintaining residual Cl2 at 0.3 - 0.5 ppm .**

- **Measurement the TBC should be below 10 thousand colony /ml of cooling water.**
  (check the biocide quantity and frequency of dosing)

- **Inspection of cooling tower structure**

- **The cooling tower should be clean free from algae and fungi and any fouling materials.**

33

Conclusion

Today's cooling water systems offer much more of a challenge to the water treatment expert. The environmental restrictions placed on industry have dramatically increased the application of non-metal corrosion inhibitors which by their nature must be carried in more alkaline PH ranges . Water conservation movements have also encouraged plants to increase cycles of concentration in recirculating waters , which further raises ion concentration and PH levels . All these trends have made the control of scale much more of a problem than in the past . For these reasons the role of antiscalants is more important now than ever before .

The Co polymer and Ter polymer line of scale control agents offers solutions to the many problems encountered.

Please find below Some information about zinc on Google:

1. Zinc deficiency – News max and also

2. The modern – day Zinc Deficiency Epidemic – knowledge of health

Zinc is very important element for human , soil and animals

- Accordingly we do not have discharge restrictions on zinc compounds
- Zinc sulfate is added to fertilizer blends and also added to potable water
- Daily requirement for men 10 mg of Zinc

35

Important information about zinc and HEDP and PBTC in concern of Environment and chlorine and oxidizing biocide stability .

36

Toxicity and Handling

DEQUEST phosphonates appear to possess no acute toxicological properties that would require special handling other than the good hygienic practices. Normal procedures for the safe handling of industrial chemicals should be employed with particular care being taken to avoid eye and/or skin contact with these materials as supplied.

Certain grades of DEQUEST products have various governmental approvals for production of potable water, sugar refining, cleaning of dairy and other food equipment and several other applications. Contact Solutia for more specific information regarding your particular governmental approval question, as new approvals are continually being granted.

Contact Solutia for the material safety data sheets on the DEQUEST products of interest for more complete information on toxicity, safe handling and first aid procedures.

It is recommended that D2016 is maintained above a temperature of + 5 °C at all times

Solutia European phosphonate catalog

Environmental

Phosphonates do not readily biodegrade in laboratory semi-continuous activated sludge tests; but in more realistic die away river tests they are rapidly degraded in sunlight in the presence of ferric ions. They are also degraded in soil, and certain pseudonomas species are known to feed on phosphonates. DEQUESTS do not bioaccumulate in aquatic species and are rapidly eliminated by fish. They can be eliminated from waters by classical water treatment with aluminium sulphate or lime; treatment of drinking water by chlorine or ozone also destroys phosphonates. Mobilization of heavy metals from sediments is extremely low and phosphonates partition rapidly to sediments from water.

Solutia European phosphonate catalog

A MORE STABLE PHOSPHONATE AGAINST OXIDIZING MICROBIOCIDES

Some scale inhibitors used in cooling water systems requiring the use of an oxidizing biocide have some stability limitations. Typical biocides include chlorine, bromine and, nowadays, ozone. In most of these cases **DEQUEST 7000** is the preferred choice of phosphonate. However, the inherent stability of phosphonates such as **DEQUEST 2000** and **DEQUEST 2010** have also been investigated in detail by Solutia, and several practical approaches to prevent phosphonate decomposition in programmes containing oxidizing biocides have been developed. We will be pleased to provide you with technical guidance on request.

Solutia European phosphonate catalog

Increasing order of phosphonate stabilisation is the following:

Chlorine: Dequest 7000 > Dequest 2010 >>>> Dequest 2000

Bromine: Dequest 7000 > Dequest 2000 >>> Dequest 2010

Ozone: Dequest 7000 = Dequest 2010 >> Dequest 2000

Chlorine dioxide: Dequest 7000 = Dequest 2010 >> Dequest 2000

Aqua Trust Mobile Lab

Aqua Trust has developed an on line computerized monitor and control system capable of making the determination of corrosion and fouling of cooling system on - site.

This approach has resulted in an improved understanding of the fouling phenomenon since it is able to encompass all parameters affecting an actual cooling system.

40

Those factors affecting fouling which relate to the control of chemical treatment program in use in the cooling systems are corrosion, conductivity and pH.

Three parameters which may have a significant effect on the fouling of heat exchangers.

Aqua Trust mobile lab will serve two cooling systems in parallel .

41

* **The monitor has been mounted in a specially modified van.**

* **The mobile lab was located at the client site and will be supplied with two cooling water streams from two different systems .**

* **Location close to the cooling towers.**

* **The mobile lab provides the proper operating air conditioned environment for computers and operators.**

* **The mobile lab has the ability to determine the corrosion rate by two channel corrator on line.**

42

* **Simultaneous monitoring of water temperature- online.**

* **Simultaneous monitoring of pHs of cooling water .**

* **Simultaneous monitoring of conductivity.**

* **Computerized full water analysis.**

* **Fully automated control for dosing of the recommended**

TREATMENT CHEMICAL PROGRAM

* **Data acquired from the field installation were transmitted directly to the main computer which provide a historical data base and an efficient summary of each field run.**

43

*The data is then available to a consulting and technical service staff for interpretation, graphical analysis and subsequent reporting to client.

*The mobile lab mounted with an internet camera to transfer the technical reports to the technical supervisor upon request.

*A full follow-up report is available every 4 hrs. The mobile lab will help the technical staff to troubleshoot any arises cooling water problem spontaneously by pressing a computer key.

44

*Aqua Trust mobile lab was designed and developed by Aqua Trust chairman and
Aqua Trust R&D engineers .

* The mobile lab is available for Aqua Trust clients to serve the cooling water treatment program.

45

2005/03/25

2005/05/09

Acknowledgement :

- **Thanks to Aqua Trust clients :**

- **Thyssen krupp UHDE Egyptian propylene & poly propylene co EPP-Port said**
- **Rolls – Royce peebles electric company – Eng Ignatius Tighe**
- **Moharem Press Company .**
- **Amyria Petroleum Company .**
- **Alexandria Petroleum Company.**
- **Delta fertilizer and chemicals company – Talkha.**
- **El Nasr fertilizer and chemicals company - Suez.**
- **Misr weaving and spinning Company – El-Mahalla El-Kobra**
  (Aqua Trust Treating cooling systems of two power station) .
- **El Nasr for intermediate chemicals co. - NICC.**
- **General fertilizer company – Homms – Syria .**
- **Kima – Egyptian Chemical Industries Aswan.**
- **El Nasr for coke and basic chemicals co. – Helwan.**
- **Alexandria mineral oils company – Amoc - Alex.**
- **Abu Qir fertilizers and chemicals co. – Alex.**

Many thanks for the opportunity given to Aqua Trust.

Faiza Abou Zeid

51

Thanks For Your Attention

Ready To

Answer Your Questions

52

Day 1: Monday: December 23rd, 2013

Session II

AFA
WORKSHOP
Water Treatment and Water Quality in
Fertilizer and Petrochemical Industries

Applying statistical techniques

in Decision Making

Dr. Abdel Hakim EL-MENHAWY

Aqua Trust For Water Treatment ~ Egypt

Applying statistical techniques in Decision Making

Part 1
Introduction

What is Statistics?

> No matter what line of work you select, you will find yourself faced with **decisions** where an **understanding** of **data analysis** is **helpful**.

> **Statistics is the science of** collecting, **organizing**, **presenting**, **analyzing**, and **interpreting numerical data** to **assist** in **making more effective decisions**.

Types of Statistics

➢ **Descriptive Statistics**: methods of **organizing**, **summarizing**, and **presenting** data in **an informative way.**

➢ **Inferential Statistics**: A **decision**, estimate, prediction, or generalization about a **population**, based on **a sample.**

Note: In statistics the word *population* and *sample* have a broader meaning. A population or sample may consist of *individuals* or *objects*

Population versus Sample

➢ A **population** is a collection of all possible individuals, objects, or measurements of interest.

➢ A **sample** is a portion, or part, of the population of interest

➢ **PARAMETER** A measurable characteristic of a population.

➢ **STATISTIC** A measurable characteristic of a sample.
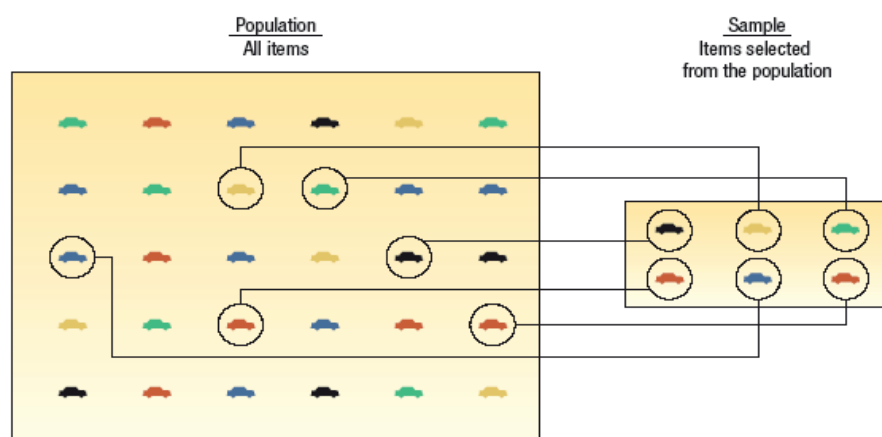
Why Sample the Population?

➢ To **contact** the **whole** population would be **time consuming**.

➢ The **cost** of studying all the items in a population **may be prohibitive**.

➢ The **physical impossibility** of checking all items in the population.

➢ The **destructive nature** of some tests.

➢ The **sample results** are **adequate**.

Using a sample to learn more about a population is done extensively in business, agriculture, politics, and government.

Types of Variables

➢ **Qualitative or Attribute variable: the characteristic being studied is nonnumeric**.

❖ **EXAMPLES:** Gender, religious affiliation, type of automobile owned, state of birth, eye color are examples.

➢ **Quantitative variable:** information is reported **numerically**.

❖ **EXAMPLES: balance in your checking account, minutes remaining in class, or number of children in a family.**

Quantitative Variables (Classifications)

Quantitative variables can be classified as either discrete or continuous.

➤ **Discrete variables:** can only assume certain values and there are usually "gaps" between values. (e.g. number of bedrooms in a house).

➤ **Continuous variable** can assume any value within a specified range. (e.g. pressure in a tire, height of students in a class).

Four Levels of Measurement

➤ **Nominal level:** data that is **classified** into categories and cannot be **arranged** in any particular order. (e.g. eye color, gender, religious affiliation.)

➤ **Ordinal level:** data **arranged** in some order, but the **differences** between data values cannot be determined or are **meaningless**. (e.g. During a taste test of 4 soft drinks, Mellow Yellow was ranked number 1, Sprite number 2, Seven-up number 3, and Orange Crush number 4).

Four Levels of Measurement

➢ **Interval level:** similar to the ordinal level, with the additional property that meaningful amounts of differences between data values can be determined. There is no natural zero point. **(e.g. Temperature on the Fahrenheit scale.)**

➢ **Ratio level:** the interval level with an inherent zero starting point. Differences and ratios are meaningful for this level of measurement. **(e.g. Monthly income of surgeons, or distance traveled by manufacturer's representatives per month.)**

Why Know Level of Measurement of a Data?

➢ **The level of measurement of the data dictates the calculations that can be done to summarize and present the data.**

➢ **To determine the statistical tests that should be performed on the data**

END of Part 1

Applying statistical techniques in Decision Making

Part 2
Descriptive Statistics

Organizing Qualitative Data
(FREQUENCY TABLE)

Qualitative data can be organized in FREQUENCY TABLE, and represented in Pie or Bar charts.

➤ **FREQUENCY TABLE:** A grouping of qualitative data into mutually exclusive classes showing the number of observations in each class.

TABLE 2–1 Frequency Table for Vehicles Sold at Whitner Autoplex Last Month

Car Type	Number of Cars
Domestic	50
Foreign	30

Organizing Qualitative Data
(Pie & Bar charts)
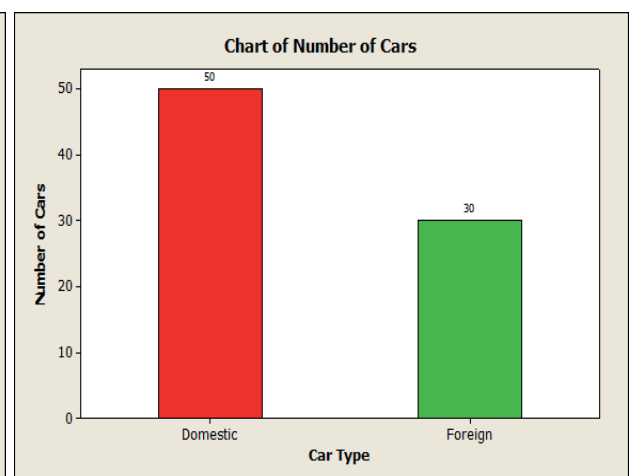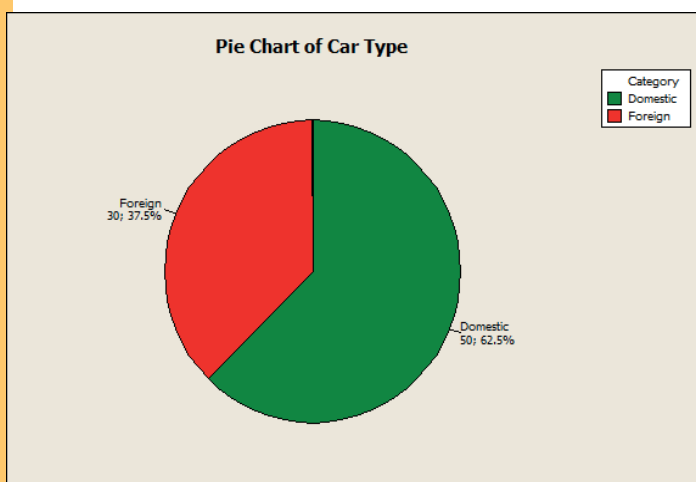
Vehicle Sold by Type Last Month At Whitner Autoples

(Example 1)

Organizing Quantitative Data

(FREQUENCY DISTRIBUTION)

Quantitative data can be organized in **FREQUENCY DISTRIBUTION**, and represented by **Histograms**, Frequency **polygons**, and **Cumulative** frequency distributions

FREQUENCY DISTRIBUTION: A grouping of data into mutually exclusive classes showing the number of observations in each class. **(Example 2)**

Selling Prices ($ thousands)	Frequency
15 up to 18	8
18 up to 21	23
21 up to 24	17
24 up to 27	18
27 up to 30	8
30 up to 33	4
33 up to 36	2
Total	80

Organizing Quantitative Data
(Graphic Presentation of a Frequency Distribution)

The three commonly used graphic forms are, **Histograms**, **Frequency polygons**, and **Cumulative frequency distributions:**
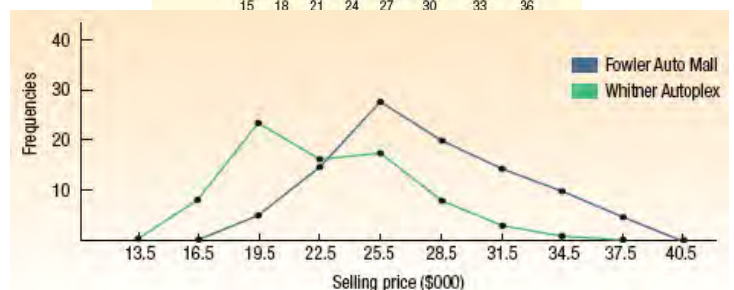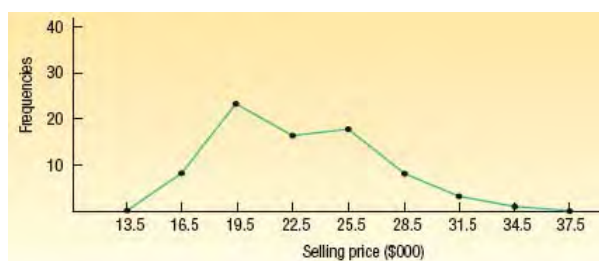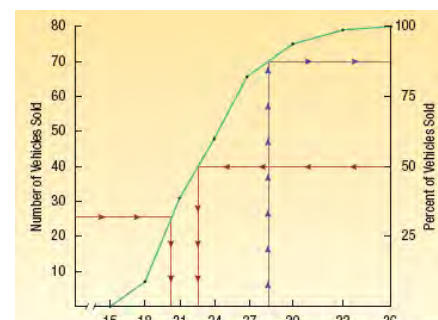
Summarizing Data
Measures of Central tendency

For **ungrouped data**, the **population mean** is the sum of all the population values divided by the total number of population values: **(Example 3)**

$$\text{Population Mean} \qquad \mu = \frac{\sum X}{N}$$

For **ungrouped** data, **sample mean** is the sum of all the sample values divided by the number of sample values: **(Example 4)**

$$\text{Sample Mean} \qquad \bar{X} = \frac{\sum X}{N}$$

The **weighted mean** of a set of numbers $X_1, X_2, ..., X_n$, with corresponding weights $w_1, w_2, ..., w_n$, is computed from the following formula: **(Example 5)**

$$\text{Weighted Mean} \qquad \bar{X}_w = \frac{w_1 X_1 + w_2 X_2 + ... + w_n X_n}{w_1 + w_2 + ... + w_n}$$

Summarizing Data
Measures of Central tendency

The Geometric Mean: The formula for the geometric mean is written

$$\text{Geometric Mean} \qquad GM = \sqrt[n]{(X_1)(X_2)...(X_n)}$$

It has a wide application in business and economics because we are often interested in finding the percentage changes in sales, salaries, or economic figures, such as the GDP, which compound or build on each other. **(Example 6)**

MEDIAN The midpoint of the values after they have been ordered from the smallest to the largest, or the largest to the smallest. **(Example 7)**

MODE The value of the observation that appears most frequently. **(Example 8)**

Summarizing Data
Measures of Dispersion (Population)

Range $= $ **Largest value** $-$ **Smallest value**

Mean Deviation $\quad \text{MD} = \dfrac{\sum |X - \bar{X}|}{n}$

Population Variance $\quad \sigma^2 = \dfrac{\sum(X - \mu)^2}{N}$

Population Standard Deviation $\quad \sigma = \sqrt{\dfrac{\sum(X - \mu)^2}{N}}$

Summarizing Data
Measures of Dispersion (Sample)

Sample Variance $\quad S^2 = \dfrac{\sum(X - \bar{X})^2}{n - 1}$

Sample Standard Deviation $\quad S = \sqrt{\dfrac{\sum(X - \bar{X})^2}{n - 1}}$

Summarizing Data
Sample Variance and Standard Deviation (grouped Data)

Arithmetic Mean of grouped Data $\quad \bar{X} = \dfrac{\sum fM}{n}$

Standard Deviation of grouped Data $\quad S = \sqrt{\dfrac{\sum f(M - \bar{X})^2}{n - 1}}$

Where:

S ... is sample standard deviation

M ... is the midpoint of the class

f ... is the class frequency

n ... is the number of observation in the sample

$\bar{X}$ ... is the sample mean

(Example 13)

1-21

Displaying Data

Measures of central location (the mean, median, and mode) for a set of observations and measures of data dispersion (e.g. range and the standard deviation) were introduced. Another characteristic of a set of data is the shape. There are four shapes commonly observed:

➢**symmetric,**

➢**positively skewed,**

➢**negatively skewed,**

➢**Bimodal.**

1-22

Displaying Data
Commonly Observed Shapes

Symmetric	Positively Skewed	Negatively Skewed	Bimodal
Ages	Monthly Salaries	Test Scores	Outside Diameter

Frequency — Ages — 45 $\overline{X}$ — Years

Frequency — Monthly Salaries — $3,000 $4,000 — Median Mean

Frequency — Test Scores — 75 80 Score — Mean Median

Frequency — Outside Diameter — .98 1.04 Inches — Mean
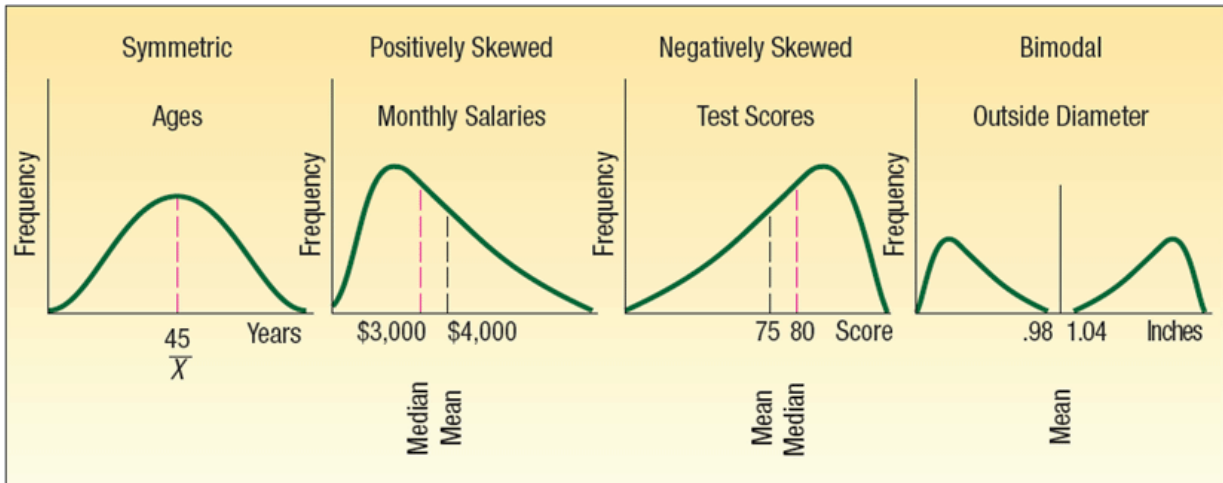
Displaying Data
The Empirical Rule

EMPIRICAL RULE For a symmetrical, bell-shaped frequency distribution, approximately 68 percent of the observations will lie within plus and minus one standard deviation of the mean; about 95 percent of the observations will lie within plus and minus two standard deviations of the mean; and practically all (99.7 percent) will lie within plus and minus three standard deviations of the mean.

70   80   90   100   110   120   130

68%
95%
99.7%
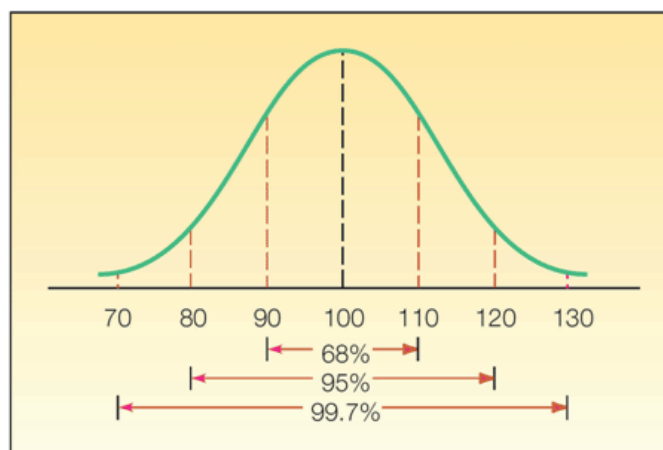
A Symmetrical, Bell-Shaped Curve Showing the Relationships between the Standard Deviation and the Observations

Displaying Data
Skewness - Formulas for Computing

The coefficient of skewness can range from -3 up to 3.

➤ **A value near -3, indicates considerable negative skewness.**

➤ **A value such as 1.63 indicates moderate positive skewness.**

➤ **A value of 0, which will occur when the mean and median are equal, indicates the distribution is symmetrical and that there is no skewness present.**

$$\text{Pearsn's coefficient of Skewness } sk = \frac{3(\bar{X} - \text{Median})}{s}$$

$$\text{Software coefficient of Skewness } sk = \frac{n}{(n-1)(n-2)} \sum \left(\frac{X - \bar{X}}{s}\right)^3$$

(Example 14)

Displaying Data
Dot Plots and Stem-and-leaf display

➤ **A dot plot groups the data as little as possible and the identity of an individual observation is not lost. (Example 15)**

➤ **Stem-and-leaf display is a statistical technique to present a set of data. Each numerical value is divided into two parts. The leading digit(s) becomes the stem and the trailing digit the leaf. The stems are located along the vertical axis, and the leaf values are stacked against each other along the horizontal axis. (Example 16)**

Stem	Leaf
8	8 9
9	6 3 5 6 4 4 7
10	8 7 3 4 6 3
11	7 3 2 7 2 1 9 8 3
12	7 5 7 0 5 5 0 4
13	9 5 2 9 4 6 8
14	8 2 3
15	6 5 5

Displaying Data
Quartiles, Deciles and Percentiles

The **standard deviation** is the most widely used measure of dispersion. Alternative ways of describing **spread** of data **include** determining the **location** of values that **divide** a set of observations into **equal** parts.

Location of Percentile $\quad L_p = (n + 1)\dfrac{P}{100}$

➢ These measures include **quartiles**, **deciles**, and **percentiles**.

(Example 17)

Displaying Data
Boxplot – Example 18

Alexander's Pizza offers free delivery of its pizza within 15 miles. Alex, the owner, wants some information on the time it takes for delivery. How long does a typical delivery take? Within what range of times will most deliveries be completed? For a sample of 20 deliveries, he determined the following information:

Minimum value = 13 minutes

Q_1 = 15 minutes

Median = 18 minutes

Q_3 = 22 minutes

Maximum value = 30 minutes

Develop a box plot for the delivery times. What conclusions can you make about the delivery times?

(Example 18)

END of Part 2

Applying statistical techniques in Decision Making

Part 3
Probability
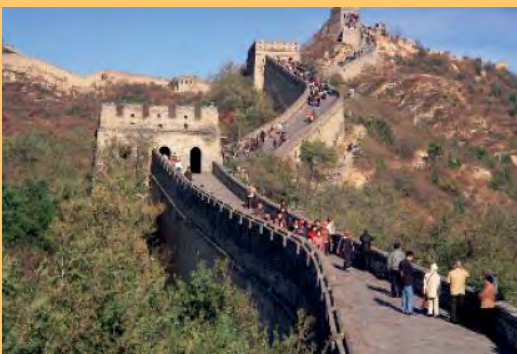
Probability

PROBABILITY **A value between zero and one, inclusive, describing the relative possibility (chance or likelihood) an event will occur.**
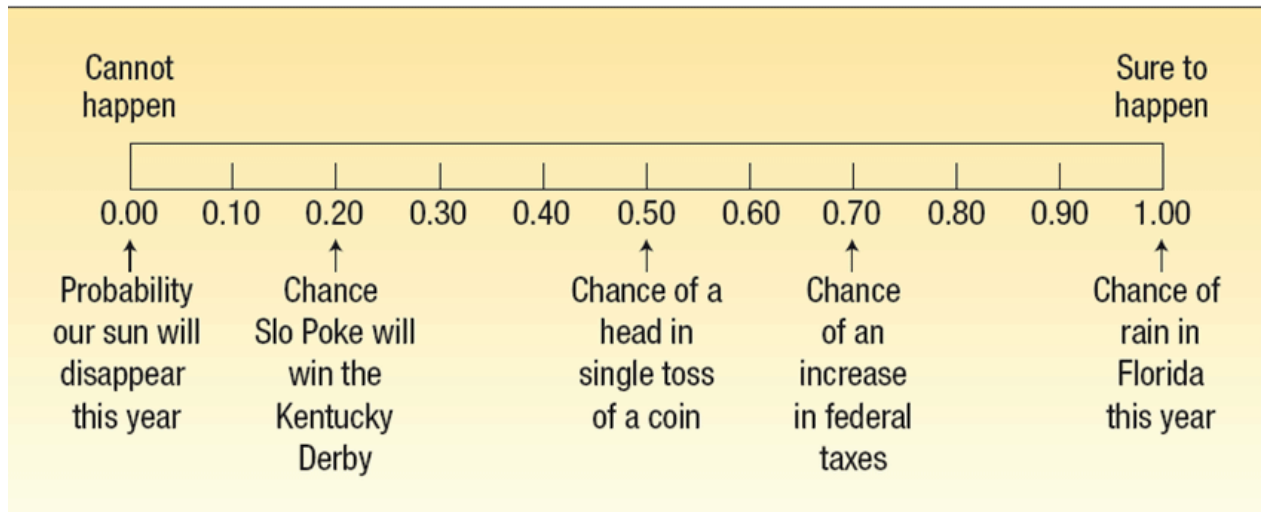
Experiment, Outcome and Event

- ➤ **An experiment is a process that leads to the occurrence of one and only one of several possible observations.**
- ➤ **An outcome is the particular result of an experiment.**
- ➤ **An event is the collection of one or more outcomes of an experiment**
  - ❑ **Events are mutually exclusive if the occurrence of any one event means that none of the others can occur at the same time.**
  - ❑ **Events are independent if the occurrence of one event does not affect the occurrence of another..**
  - ❑ **Events are collectively exhaustive if at least one of the events must occur when an experiment is conducted.**

Experiment, Outcome and Event

Experiment	Roll a die	Count the number of members of the board of directors for Fortune 500 companies who are over 60 years of age
All possible outcomes	Observe a 1 Observe a 2 Observe a 3 Observe a 4 Observe a 5 Observe a 6	None are over 60 One is over 60 Two are over 60 ... 29 are over 60 ... ... 48 are over 60 ...
Some possible events	Observe an even number Observe a number greater than 4 Observe a number 3 or less	More than 13 are over 60 Fewer than 20 are over 60

Ways of Assigning Probability

There are three ways of assigning probability:

➢ **CLASSICAL PROBABILITY**: Based on the assumption that the outcomes of an experiment are equally likely.

➢ **EMPIRICAL PROBABILITY**: The probability of an event happening is the fraction of the time similar events happened in the past.

➢ **SUBJECTIVE CONCEPT OF PROBABILITY:** The likelihood (probability) of a particular event happening that is assigned by an individual based on whatever information is available.

Rules for Computing Probabilities
Examples 1, 2, 3

Rules of Addition

➤ **Special Rule of Addition: If two events A and B are mutually exclusive**, the probability of one or the other event's occurring equals the sum of their probabilities.

$$P(A \text{ or } B) = P(A) + P(B)$$

Event A   Event B

➤ **The General Rule of Addition: If A and B are two events that are not mutually exclusive**, then P(A or B) is given by the following formula **(Example 1, 2, 3)**

$$P(A \text{ or } B) = P(A) + P(B) - P(A \text{ and } B)$$

$P(\text{Disney}) = .60$ $P(\text{Busch}) = .50$

$P(\text{Disney and Busch}) = .30$
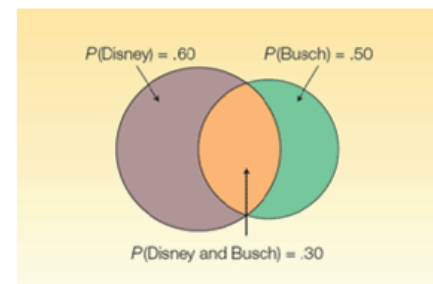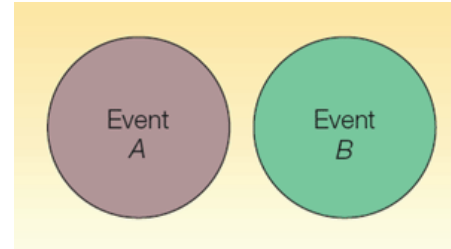
The Complement Rule
Example 4

The **complement rule** is used to determine the probability of an event occurring by subtracting the probability of the event not occurring from 1.

$$P(A) + P(\sim A) = 1$$

or

$$P(A) = 1 - P(\sim A).$$

Event A

$\sim A$
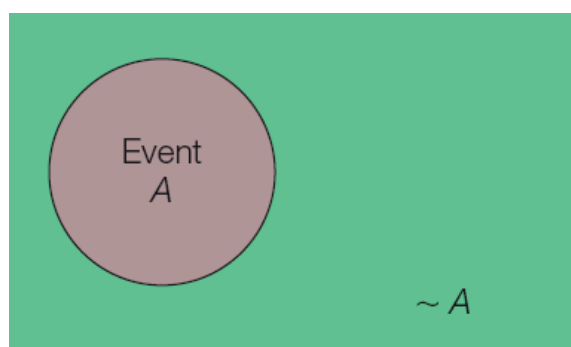
(Example 4)

Joint Probability – Venn Diagram

JOINT PROBABILITY: A probability that measures the likelihood two or more events will happen concurrently.
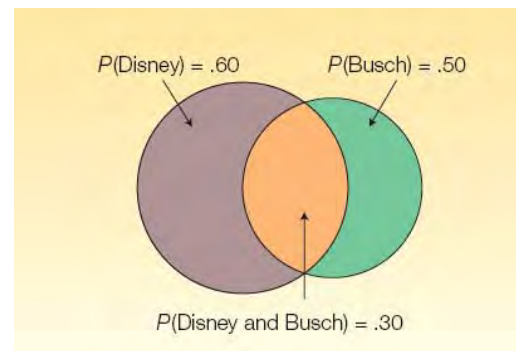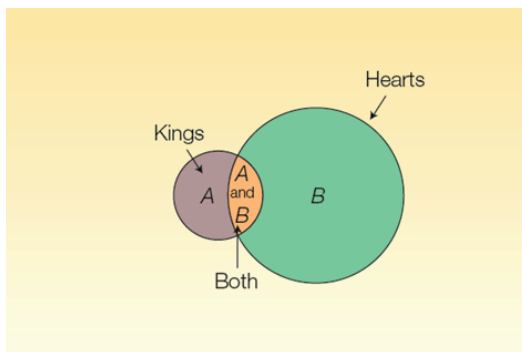
Special Rule of Multiplication (Example 5)

➤ The **special rule of multiplication** requires that two events A and B are **independent**.

➤ Two events A and B are independent if the occurrence of one has no effect on the probability of the occurrence of the other.

➤ This rule is written:

$$P(A \text{ and } B) = P(A)P(B) \quad \text{(Example 5)}$$

Conditional Probability

➢ **A conditional probability** is the probability of a particular event occurring, given that another event has occurred.

➢ The probability of the event A given that the event B has occurred is written **P(A|B)**.

General Multiplication Rule (Example 6)

➢ The **general rule of multiplication** is used to find the joint probability that two independent events will occur.

➢ It states that for two independent events, A and B, the joint probability that both events will happen is found by multiplying the probability that event A will happen by the conditional probability of event B occurring given that A has occurred.

GENERAL RULE OF MULTIPLICATION $\qquad P(A \text{ and } B) = P(A)P(B|A) \qquad$ **[5-6]**

(Example 6)

Contingency Tables (Example 7)

A CONTINGENCY TABLE: is a table used to classify sample observations according to two or more identifiable characteristics

E.g. A survey of 150 adults classified each as to gender and the number of movies attended last month. Each **respondent** is **classified** according to **two criteria**—the **number of movies attended and gender**.

Movies Attended	Gender Men	Women	Total
0	20	40	60
1	40	30	70
2 or more	10	10	20
Total	70	80	150

(Example 7)

Tree Diagrams (Example 7)

➢ **A tree diagram is useful for portraying conditional and joint probabilities. It is particularly useful for analyzing business decisions involving several stages.**

➢ **A tree diagram is a graph that is helpful in organizing calculations that involve several stages. Each segment in the tree is one stage of the problem. The branches of a tree diagram are weighted by probabilities.** (Example 7)

Bayes' Theorem (Example 8)

➢ **Bayes' Theorem is a method for revising a probability given additional information.**

➢ **It is computed using the following formula:**

BAYES' THEOREM	$P(A_i \mid B) = \dfrac{P(A_i)P(B \mid A_i)}{P(A_1)P(B \mid A_1) + P(A_2)P(B \mid A_2)}$	[5–7]

(Example 8)

Counting Rules (Examples 9, 10, 11)

➢ **The multiplication formula: indicates that if there are m ways of doing one thing and n ways of doing another thing, there are m x n ways** of doing both.

➢ A permutation is any arrangement of r objects selected from n possible objects. The order of arrangement is important in permutations.

PERMUTATION FORMULA	$_nP_r = \dfrac{n!}{(n-r)!}$	[5–9]

➢ **A combination is the number of ways to choose r objects from a group of n objects without regard to order. (Examples 9, 10 & 11).**

COMBINATION FORMULA	$_nC_r = \dfrac{n!}{r!(n-r)!}$	[5–10]

where:
   n is the total number of objects.
   r is the number of objects selected.

Applying statistical techniques in Decision Making

Part 3
Discrete Probability Distributions

What is a Probability Distribution?

PROBABILITY DISTRIBUTION: A listing of all the outcomes of an experiment and the probability associated with each outcome.

Experiment:

Toss a coin three times. Observe the number of heads. The possible results are: Zero heads, One head, Two heads, and Three heads. What is the probability distribution for the number of heads?

Possible Result	Coin Toss			Number of Heads
	First	Second	Third	
1	T	T	T	0
2	T	T	H	1
3	T	H	T	1
4	T	H	H	2
5	H	T	T	1
6	H	T	H	2
7	H	H	T	2
8	H	H	H	3

Characteristics of a Probability Distribution

➢ The probability of a particular outcome is between 0 and 1 inclusive.

➢ The outcomes are mutually exclusive events.

➢ The list is exhaustive. So the sum of the probabilities of the various events is equal to 1.

Example: Probability Distribution of Number of Heads Observed in 3 Tosses of a Coin

Number of Heads, x	Probability of Outcome, $P(x)$	
0	$\frac{1}{8} =$	.125
1	$\frac{3}{8} =$	.375
2	$\frac{3}{8} =$	.375
3	$\frac{1}{8} =$	.125
Total	$\frac{8}{8} =$	1.000
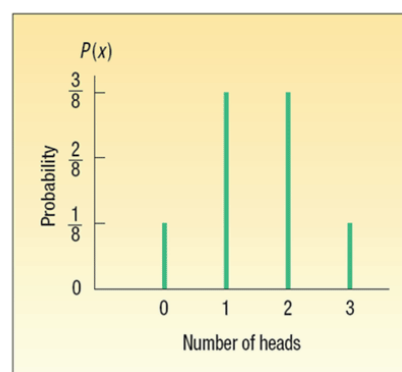
Random Variables

RANDOM VARIABLE: A quantity resulting from an experiment that, by chance, can assume different values.

Possible *outcomes* for three coin tosses
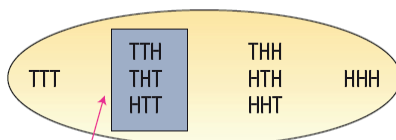
The *event* {one head} occurs and the *random variable x* = 1.

DISCRETE RANDOM VARIABLE: A random variable that can assume only certain clearly separated values. It is usually the result of counting something. (e.g. number of students in a class, number of children in a family …)

CONTINUOUS RANDOM VARIABLE can assume an infinite number of values within a given range. It is usually the result of some type of measurement (e.g. weight of each student in this class, temperature outside …)

The mean of a probability distribution: is a typical value used to represent the central location of a probability distribution. It is also referred to as its expected value.

| MEAN OF A PROBABILITY DISTRIBUTION | $\mu = \Sigma[xP(x)]$ | [6–1] |

Variance of a probability distribution: is measures the amount of spread in a distribution

| VARIANCE OF A PROBABILITY DISTRIBUTION | $\sigma^2 = \Sigma[(x - \mu)^2 P(x)]$ | [6–2] |

Binomial Probability Distribution

A Widely occurring discrete probability distribution, its characteristics are:

➢ There are only **two possible outcomes** on a particular trial of an experiment.

➢ The trials are **independent**, meaning that the outcome of one trial does not affect the outcome of any   other trial.

➢ An outcome on each trial of an experiment is classified into one of **two mutually exclusive** categories, **a success or a failure**.

➢ The probability of success and failure **stay the same for each trial**.

➢ The random variable counts the number of **successes** in a fixed number of trials.

Binomial Probability Formulae (Examples 13, 14, 15)

Binomial Probability Formula

BINOMIAL PROBABILITY FORMULA	$P(x) = {}_nC_x \, \pi^x(1 - \pi)^{n-x}$	[6–3]

where:

    C denotes a combination.
    n is the number of trials.
    x is the random variable defined as the number of successes.
    π is the probability of a success on each trial.

Binomial Dist. – Mean and Variance

MEAN OF A BINOMIAL DISTRIBUTION	$\mu = n\pi$	[6–4]

VARIANCE OF A BINOMIAL DISTRIBUTION	$\sigma^2 = n\pi(1 - \pi)$	[6–5]

Binomial Distribution – Table (Examples 13, 14, 15)

Binomial – Shapes for Varying π (n constant)

CHART 6–2 Graphing the Binomial Probability Distribution for a π of .05, .10, .20, .50, and .70 and an n of 10
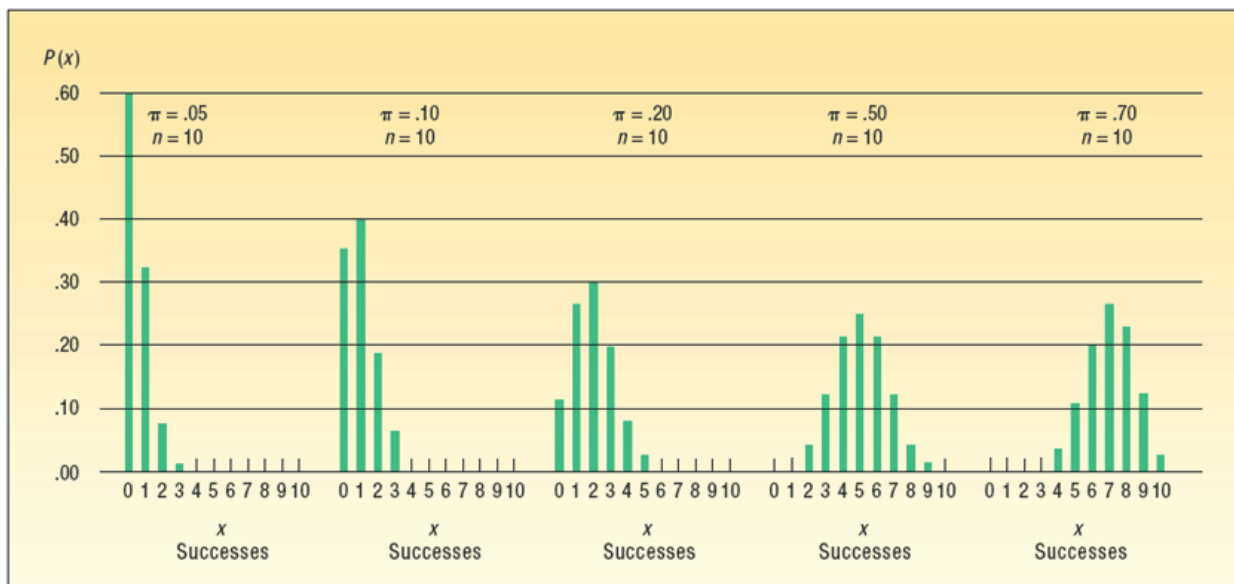
Binomial – Shapes for Varying n
(π constant)
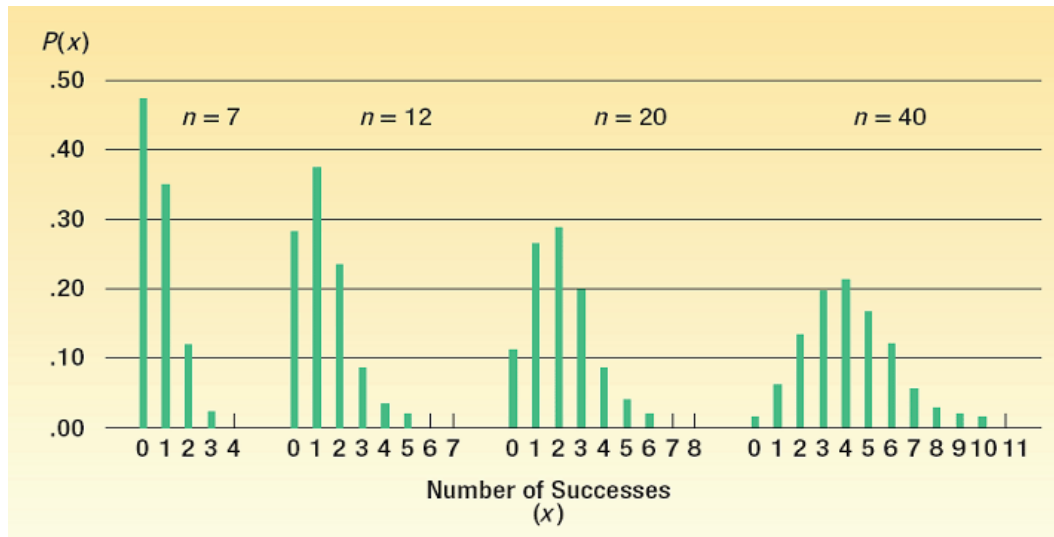
Hypergeometric Probability Distribution (Example 18)

- ➢ **An outcome on each trial of an experiment is classified into one of two mutually exclusive categories—a success or a failure.**
- ➢ **The probability of success and failure changes from trial to trial.**
- ➢ **The trials are not independent, meaning that the outcome of one trial affects the outcome of any other trial.**
- ➢ **Note: Use hypergeometric distribution if experiment is binomial, but sampling is without replacement from a finite population where n/N is more than 0.05**
- ➢ **Hypergeometric Probability Distribution - Formula**

HYPERGEOMETRIC DISTRIBUTION $P(x) = \dfrac{(_SC_x)(_{N-S}C_{n-x})}{_NC_n}$ **[6–6]**

where:

N is the size of the population.
S is the number of successes in the population.
x is the number of successes in the sample. It may be 0, 1, 2, 3, ...
n is the size of the sample or the number of trials.
C is the symbol for a combination.

Poisson Probability Distribution

The **Poisson probability distribution** describes the number of times some **event occurs** during **a specified interval.** The interval may be time, distance, area, or volume.

Assumptions of the Poisson Distribution

➤ The probability is proportional to the length of the interval.

➤ The intervals are independent.

The Poisson probability distribution is characterized by the number of times an event happens during some interval or continuum.

Examples include:

➤ The number of misspelled words per page in a newspaper.

➤ The number of calls per hour received by Company.

➤ The number of vehicles sold per day at GMC in North Carolina.

➤ The number of goals scored in a college soccer game.

1-55

Poisson Probability Formulae (Example 19)

Poisson Probability Formula

POISSON DISTRIBUTION	$P(x) = \dfrac{\mu^x e^{-\mu}}{x!}$	[6–7]

where:

μ (mu) is the mean number of occurrences (successes) in a particular interval.
e is the constant 2.71828 (base of the Napierian logarithmic system).
x is the number of occurrences (successes).
$P(x)$ is the probability for a specified value of x.

Poisson Dist. – Mean and Variance

MEAN OF A POISSON DISTRIBUTION	$\mu = n\pi$	[6–8]

The variance of the Poisson distribution is also equal to n π.
Poisson Distribution – Table (Example 19)

1-56

More About the Poisson Probability Distribution

•The Poisson probability distribution is always positively skewed and the random variable has no specific upper limit.

•The Poisson distribution for the lost bags illustration, where μ=0.3, is highly skewed. As μ becomes larger, the Poisson distribution becomes more symmetrical.
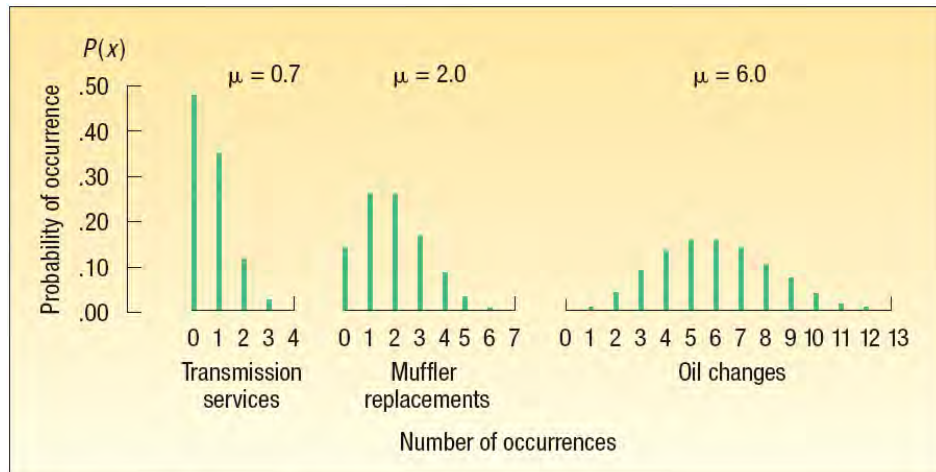
Applying statistical techniques in Decision Making

Part 3
Continuous Probability Distributions

The Uniform Distribution(Example 20)

The uniform probability distribution is perhaps the **simplest distribution** for **a continuous random variable.** This distribution is **rectangular in shape** and is defined by minimum and maximum values.
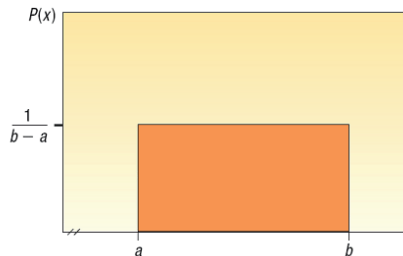
CHART 7–1 A Continuous Uniform Distribution

MEAN OF THE UNIFORM DISTRIBUTION	$\mu = \dfrac{a+b}{2}$	[7–1]
STANDARD DEVIATION OF THE UNIFORM DISTRIBUTION	$\sigma = \sqrt{\dfrac{(b-a)^2}{12}}$	[7–2]
UNIFORM DISTRIBUTION	$P(x) = \dfrac{1}{b-a}$ if $a \le x \le b$ and 0 elsewhere	[7–3]

Characteristics of a Normal Probability Distribution

> It is **bell-shaped** and has a single peak at the center of the distribution.

> It is **symmetrical** about the mean

> It is **asymptotic**: The curve gets closer and closer to the X-axis but never actually touches it. To put it another way, the tails of the curve extend indefinitely in both directions.

> The location of a normal distribution is determined by the mean, μ, the dispersion or spread of the distribution is determined by the standard deviation, σ.

> The arithmetic **mean, median,** and **mode are equal**

> The total **area under the curve is 1.00**; half the area under the normal curve is to the right of this center point and the other half to the left of it

The Normal Distribution - Graphically

Normal curve is symmetrical
Two halves identical

Tail

Tail

Theoretically, curve extends to − ∞

Mean, median, and mode are equal

Theoretically, curve extends to + ∞
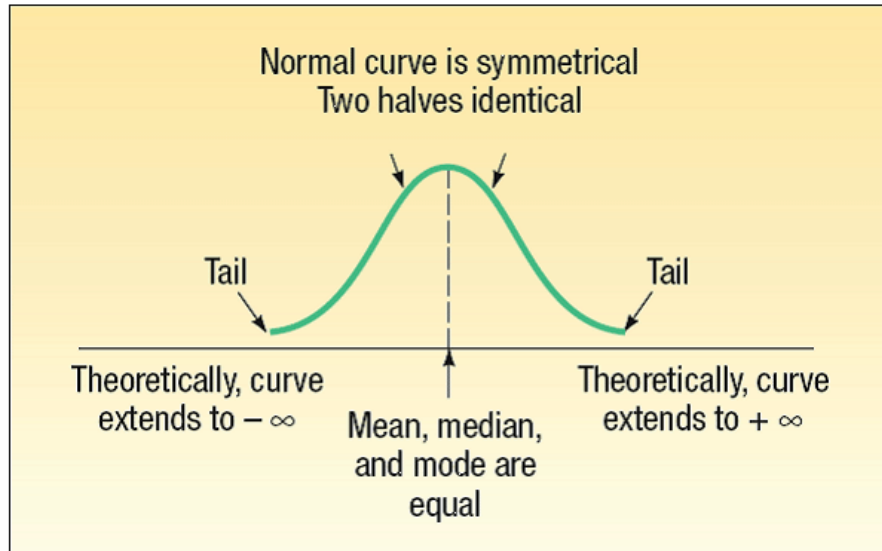
The Family of Normal Distribution

σ = 3.1 years, Camden plant
σ = 3.9 years, Dunkirk plant
σ = 5.0 years, Elmira plant

0 4 7 10 13 16 19 22 25 28 31 34 37 40
μ = 20 years of service
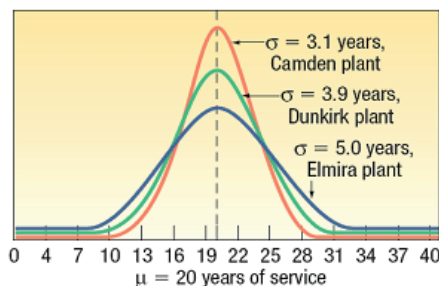
Equal Means and Different Standard Deviations

σ = 26 psi
σ = 41 psi
σ = 52 psi

μ
2,000
psi

μ
2,107
psi

μ
2,186
psi
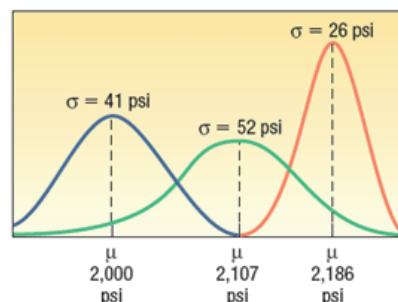
Different Means and Standard Deviations

Sugar Yummies
σ = 1.6 grams

Alphabet Gems
σ = 1.6 grams

Weight Droppers
σ = 1.6 grams

μ
283
grams

μ
301
grams

μ
321
grams
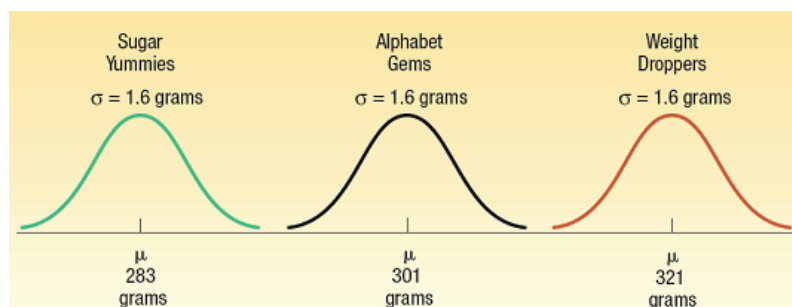
Different Means and Equal Standard Deviations

The Standard Normal Probability Distribution

➢ The standard normal distribution is a normal distribution with a **mean of 0** and a **standard deviation of 1.**

➢ It is also called the **z distribution**.

➢ A **z-value** is the signed distance between a selected value, designated X, and the population mean μ, divided by the population standard deviation, σ.

➢ The formula is:

$$z = \frac{X - \mu}{\sigma}$$

Areas Under the Normal Curve (Example 21)

z	0.00	0.01	0.02	0.03	0.04	0.05	...
1.3	0.4032	0.4049	0.4066	0.4082	0.4099	0.4115	
1.4	0.4192	0.4207	0.4222	0.4236	0.4251	0.4265	
1.5	0.4332	0.4345	0.4357	0.4370	0.4382	0.4394	
1.6	0.4452	0.4463	0.4474	0.4484	0.4495	0.4505	
1.7	0.4554	0.4564	0.4573	0.4582	0.4591	0.4599	
1.8	0.4641	0.4649	0.4656	0.4664	0.4671	0.4678	
1.9	0.4713	0.4719	0.4726	0.4732	0.4738	0.4744	

.4332

μ = 283   285.4   Grams
0   1.50   z Values
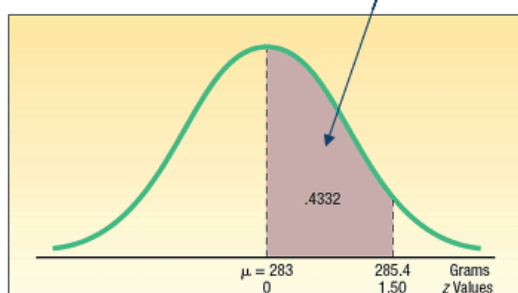
(Example 21)

The Empirical Rule

- About 68 percent of the area under the normal curve is within one standard deviation of the mean.
- About 95 percent is within two standard deviations of the mean.
- Practically all is within three standard deviations of the mean.
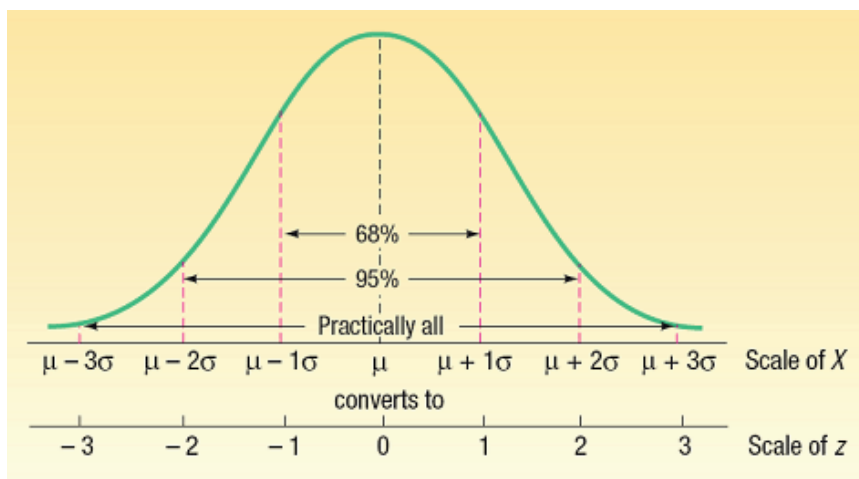
(Example 22)

Normal Distribution (Examples 23, 24, 25, 26, 27, 28)

➤ **Finding Probabilities Example 23**
➤ **Finding Probabilities Example 24**
➤ **Finding Probabilities Example 25**
➤ **Finding Probabilities Example 26**
➤ **Finding Probabilities Example 27**
➤ **Using Z in Finding X Given Area Example 28**

Normal Approximation to the Binomial

- The normal distribution (a continuous distribution) yields a good approximation of the binomial distribution (a discrete distribution) for large values of *n.*

- The normal probability distribution is generally a good approximation to the binomial probability distribution when $n\pi$ and $n(1-\pi)$ are both greater than 5.

Normal Approximation to the Binomial

Using the normal distribution (a continuous distribution) as a substitute for a binomial distribution (a discrete distribution) for large values of *n* seems reasonable because, as *n* increases, a binomial distribution gets closer and closer to a normal distribution.
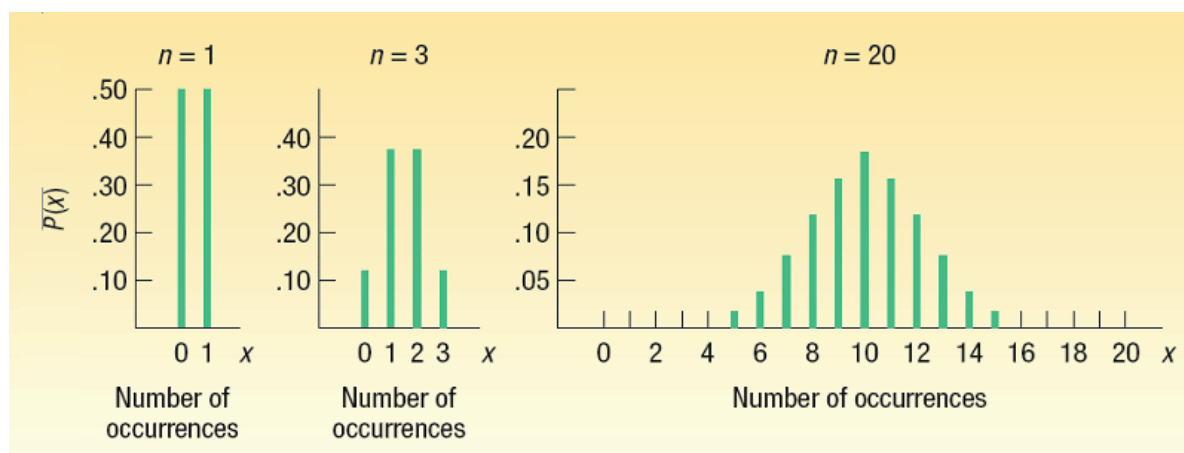
CHART 7–7 Binomial Distributions for an *n* of 1, 3, and 20, Where $\pi = .50$

Continuity Correction Factor

The value .5 subtracted or added, depending on the problem, to a selected value when a binomial probability distribution (a discrete probability distribution) is being approximated by a continuous probability distribution (the normal distribution).
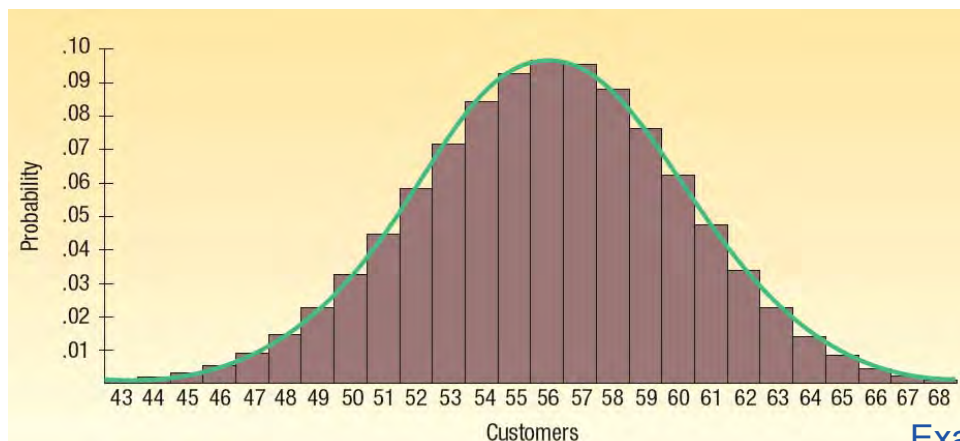
How to Apply the Correction Factor

Only one of four cases may arise:

1. For the probability *at least X* occurs, use the area *above* (*X* -.5).

2. For the probability that *more than X* occurs, use the area *above* (*X+*.5).

3. For the probability that *X or fewer* occurs, use the area *below* (*X* -.5).

4. For the probability that *fewer than X* occurs, use the area *below* (*X+*.5).

End of Part 3

Applying statistical techniques in Decision Making

Part 4

Sampling Methods and Hypothesis tests

Reasons for Sampling

➤ **To contact the entire population is too time consuming.**

➤ **The cost of studying all the items in the population is often too expensive.**

➤ **The sample results are usually adequate.**

➤ **Certain tests are destructive.**

➤ **Checking all the items is physically impossible.**

Classification of Sampling Methods
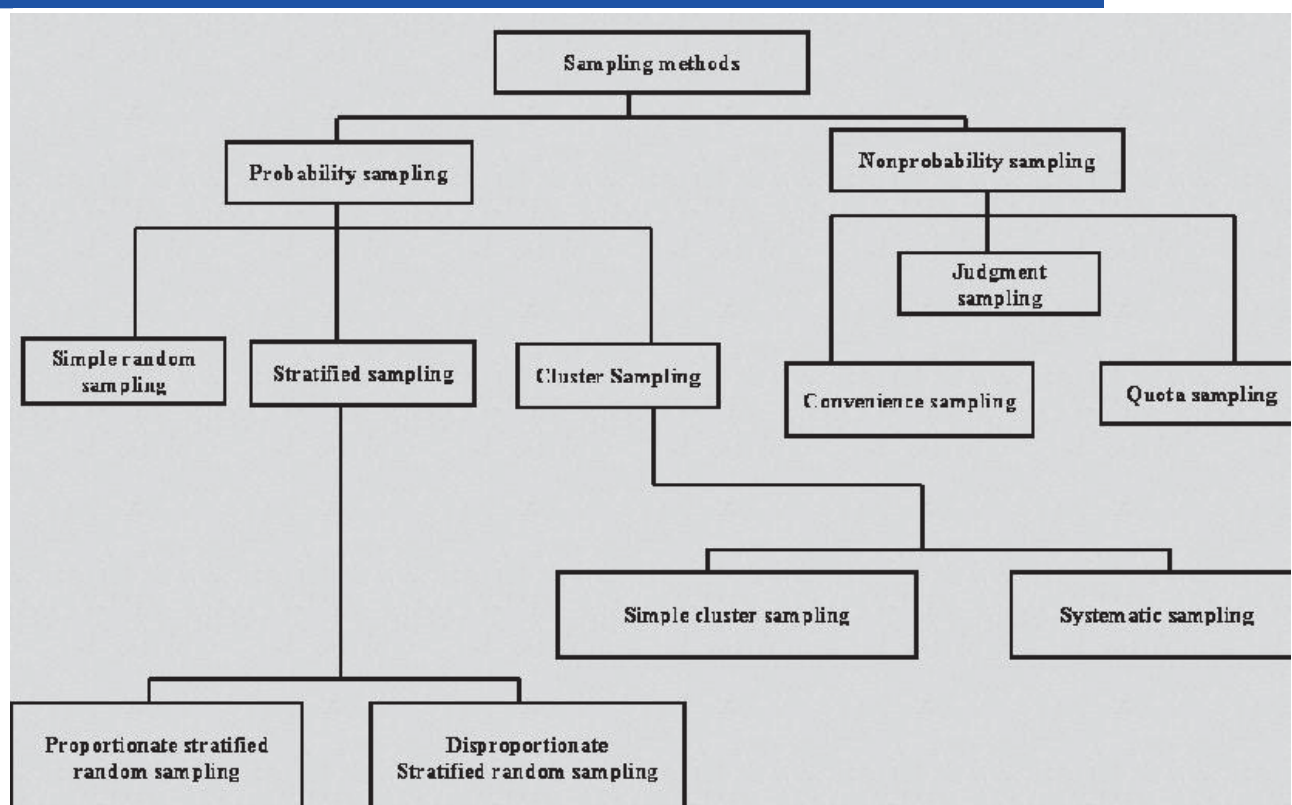
Classification of Sampling Methods

➢ In **nonprobability** sample inclusion in the sample is based on the judgment of the person selecting the sample.

➢ A **probability sample** is a sample selected such that each item or person in the population being studied has a known **likelihood** of being included in the sample.

➢ The **sampling error** is the difference between a **sample statistic** and its corresponding **population parameter**

Probability Sampling

Most Commonly Used Probability <u>Sampling Methods</u>:

➢**Simple** Random Sample

➢**Systematic** Random Sampling

➢**Stratified** Random Sampling

➢**Cluster** Sampling

The **sampling distribution of the sample mean** is a probability distribution consisting of all possible sample means of a given sample size selected from a population <u>Example (1)</u>

Central Limit Theorem

CENTRAL LIMIT THEOREM If **all** samples of a particular size are selected from **any** population, the **sampling distribution of the sample mean** is approximately a **normal distribution**. This approximation improves with **larger** samples.

➤ If the population follows a normal probability distribution, then for any sample size the sampling distribution of the sample mean will also be normal.

➤ If the population distribution is symmetrical (but not normal), the normal shape of the distribution of the sample mean emerge with samples as small as 10.

➤ If a distribution that is skewed or has thick tails, it may require samples of 30 or more to observe the normality feature.

➤ The mean of the sampling distribution equal to μ and the variance equal to σ2/n.

Sampling Methods and the Central Limit Theorem 275
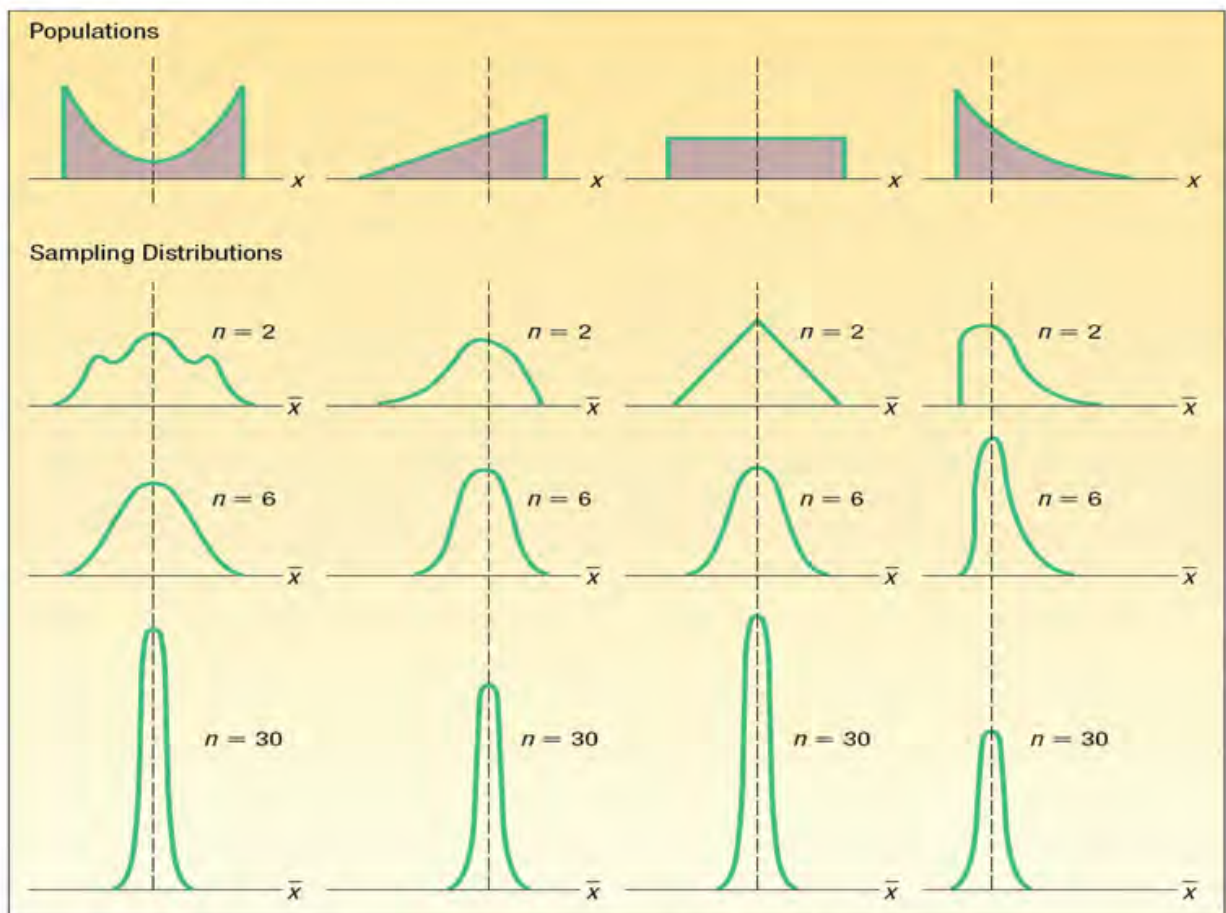
CHART 8–2 Results of the Central Limit Theorem for Several Populations

Using the Sampling Distribution of the Sample Mean (Sigma Known) Example (2)

➢ If a population follows the normal distribution, the sampling distribution of the sample mean will also follow the normal distribution.

➢ If the shape is known to be nonnormal, but the sample contains at least 30 observations, the central limit theorem guarantees the sampling distribution of the mean follows a normal distribution.

➢ To determine the probability a sample mean falls within a particular region, use:

$$z = \frac{\overline{X} - \mu}{\sigma / \sqrt{n}}$$

Using the Sampling Distribution of the Sample Mean (Sigma Unknown)

➢ If the population does not follow the normal distribution, but the sample is of at least 30 observations, the sample means will follow the normal distribution.

➢ To determine the probability a sample mean falls within a particular region, use:

$$t = \frac{\overline{X} - \mu}{s / \sqrt{n}}$$

Applying statistical techniques in Decision Making

Point and Interval Estimates

➢ **A point estimate is a single value (point) derived from a sample and used to estimate a population value.**

➢ **A confidence interval estimate is a range of values constructed from sample data so that the population parameter is likely to occur within that range at a specified probability. The specified probability is called the level of confidence.**

Factors Affecting Confidence Interval Estimates

The factors that determine the width of a confidence interval are:
➢ **Sample size, n.**
➢ **Variability in the population**, usually σ estimated by s.
➢ Desired **level of confidence.**

For a **95% confidence interval:**
➢ about 95% of the similarly constructed intervals will contain the parameter being estimated.
➢ Also 95% of the sample means for a specified sample size will lie within 1.96 standard deviations of the hypothesized population

Interval Estimates - Interpretation
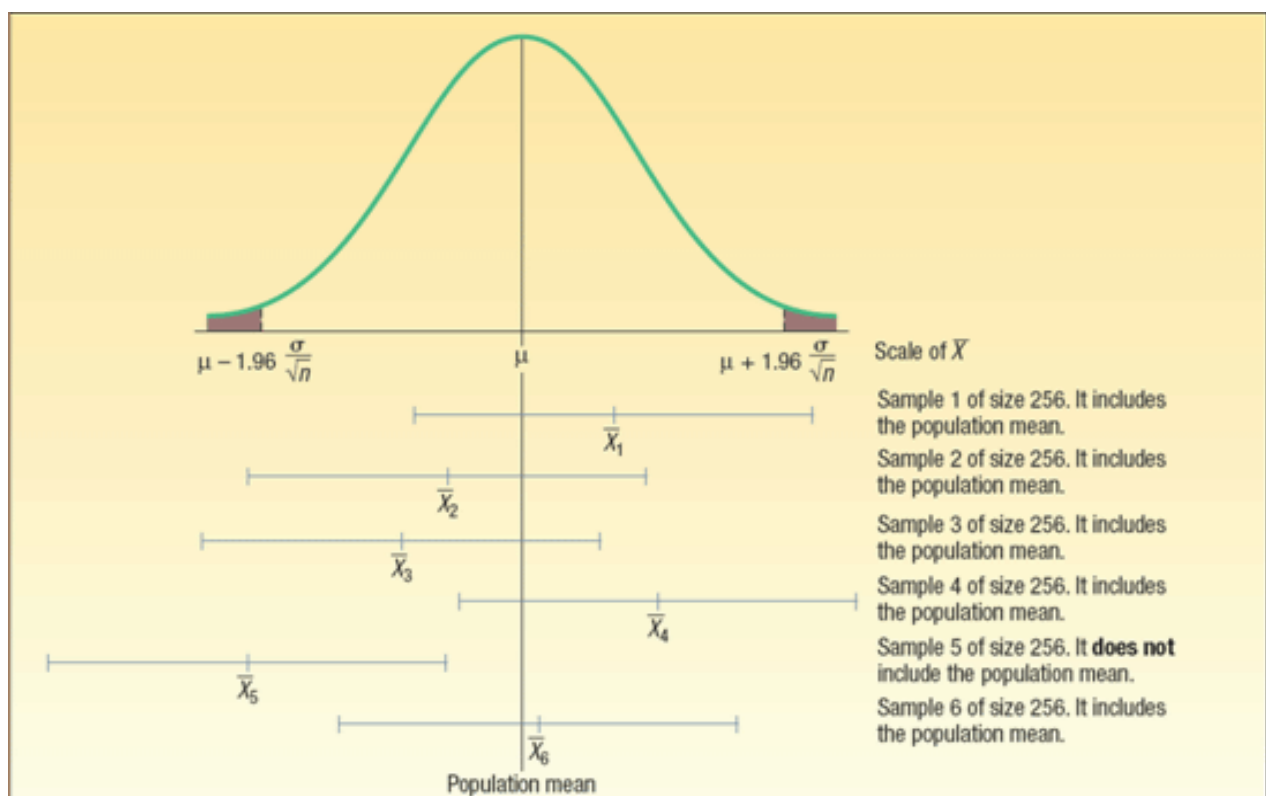
How to Obtain z value for a Given Confidence Level

The *95 percent confidence* refers to **the middle 95 percent of the observations.** Therefore, the remaining 5 percent are equally divided between the two tails.
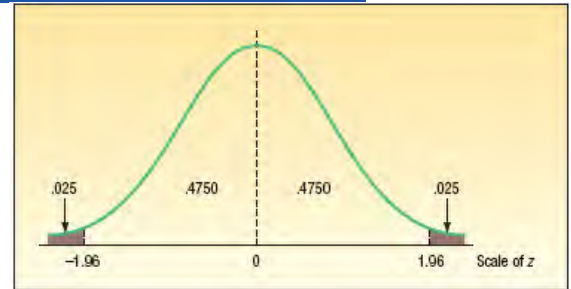
Following is a portion of Appendix B.1.

z	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
1.5	0.4332	0.4345	0.4357	0.4370	0.4382	0.4394	0.4406	0.4418	0.4429	0.4441
1.6	0.4452	0.4463	0.4474	0.4484	0.4495	0.4505	0.4515	0.4525	0.4535	0.4545
1.7	0.4554	0.4564	0.4573	0.4582	0.4591	0.4599	0.4608	0.4616	0.4625	0.4633
1.8	0.4641	0.4649	0.4656	0.4664	0.4671	0.4678	0.4686	0.4693	0.4699	0.4706
1.9	0.4713	0.4719	0.4726	0.4732	0.4738	0.4744	0.4750	0.4756	0.4761	0.4767
2.0	0.4772	0.4778	0.4783	0.4788	0.4793	0.4798	0.4803	0.4808	0.4812	0.4817
2.1	0.4821	0.4826	0.4830	0.4834	0.4838	0.4842	0.4846	0.4850	0.4854	0.4857
2.2	0.4861	0.4864	0.4868	0.4871	0.4875	0.4878	0.4881	0.4884	0.4887	0.4890
2.3	0.4893	0.4896	0.4898	0.4901	0.4904	0.4906	0.4909	0.4911	0.4913	0.4916
2.4	0.4918	0.4920	0.4922	0.4925	0.4927	0.4929	0.4931	0.4932	0.4934	0.4936

Point Estimates and Confidence Intervals for a Mean σ Known Example (3)

CONFIDENCE INTERVAL FOR POPULATION MEAN WITH σ KNOWN	$\bar{X} \pm z \dfrac{\sigma}{\sqrt{n}}$	[9–1]

$\bar{x}$ – sample mean

z – z-value for a particular confidence level

σ – the population standard deviation

n – the number of observations in the sample

The width of the interval is determined by the level of confidence and the size of the standard error of the mean.
The standard error is affected by two values:
➢ **Standard deviation**
➢ **Number of observations in the sample**

Population Standard Deviation (σ) Unknown

In most sampling situations the population standard deviation (σ) is not known. Below are some examples where it is unlikely the population standard deviations would be known.

1. The Dean of the Business College wants to estimate the mean number of hours full-time students work at paying jobs each week. He selects a sample of 30 students, contacts each student and asks them how many hours they worked last week.

2. The Dean of Students wants to estimate the distance the typical commuter student travels to class. She selects a sample of 40 commuter students, contacts each, and determines the one-way distance from each student's home to the center of campus.

3. The Director of Student Loans wants to know the mean amount owed on student loans at the time of his/her graduation. The director selects a sample of 20 graduating students and contacts each to find the information.

Characteristics of the t-distribution
Example (4 & 5)

1. It is, like the z distribution, a continuous distribution.
2. It is, like the z distribution, bell-shaped and symmetrical.
3. There is not one t distribution, but rather a family of t distributions. All t distributions have a mean of 0, but their standard deviations differ according to the sample size, n.
4. The t distribution is more spread out and flatter at the center than the standard normal distribution As the sample size increases, however, the t distribution approaches the standard normal distribution
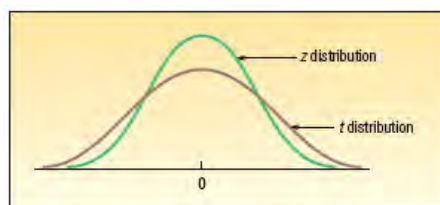
Comparing the z and t Distributions when n is small, 95% Confidence Level
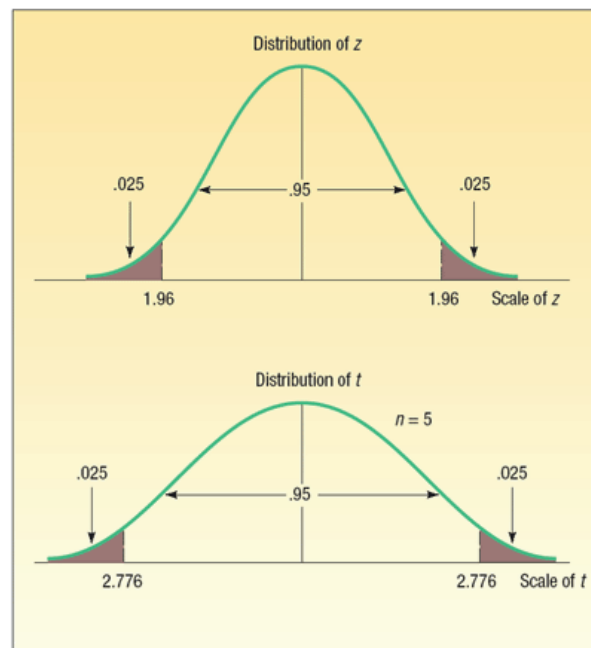
CHART 9–2 Values of *z* and *t* for the 95 Percent Level of Confidence

Confidence Interval Estimates for the Mean

Use *Z*-distribution

If the population standard deviation is known or the sample is greater than 30.

$$\overline{X} \pm z \frac{\sigma}{\sqrt{n}}$$

Use *t*-distribution

If the population standard deviation is unknown and the sample is less than 30.

$$\overline{X} \pm t \frac{s}{\sqrt{n}}$$

When to Use the z or t Distribution for Confidence Interval Computation

Estimation and Confidence Intervals
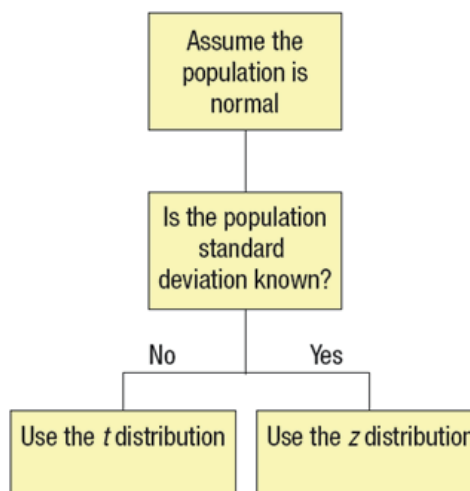
CHART 9–3 Determining When to Use the z Distribution or the t Distribution

A Confidence Interval for a Proportion (π)

The examples below illustrate the nominal scale of measurement.

1. The career services director at Southern Technical Institute reports that 80 percent of its graduates enter the job market in a position related to their field of study.

2. A company representative claims that 45 percent of Burger King sales are made at the drive-through window.

3. A survey of homes in the Chicago area indicated that 85 percent of the new construction had central air conditioning.

4. A recent survey of married men between the ages of 35 and 50 found that 63 percent felt that both partners should earn a living.

Using the Normal Distribution to Approximate the Binomial Distribution

To develop a confidence interval for a proportion, we need to meet the following assumptions.

1. The binomial conditions, discussed in Chapter 6, have been met. Briefly, these conditions are:

   a. The sample data is the result of counts.

   b. There are only two possible outcomes.

   c. The probability of a success remains the same from one trial to the next.

   d. The trials are independent. This means the outcome on one trial does not affect the outcome on another.

2. The values $n\pi$ and $n(1-\pi)$ should both be greater than or equal to 5. This condition allows us to invoke the central limit theorem and employ the standard normal distribution, that is, z, to complete a confidence interval.

Confidence Interval for a Population Proportion – Formula Example (6)

SAMPLE PROPORTION	$p = \dfrac{X}{n}$	[9–3]

CONFIDENCE INTERVAL FOR A POPULATION PROPORTION	$p \pm z\sqrt{\dfrac{p(1-p)}{n}}$	[9–4]

Finite-Population Correction Factor

- A population that has a fixed upper bound is said to be finite.
- For a finite population, where the total number of objects is N and the size of the sample is n, the following adjustment is made to the standard errors of the sample means and the proportion:
- However, if $n/N < .05$, the finite-population correction factor may be ignored.

Standard Error of the Mean   Standard Error of the Proportion

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \sqrt{\frac{N-n}{N-1}} \qquad\qquad \sigma_p = \sqrt{\frac{p(1-p)}{n}} \sqrt{\frac{N-n}{N-1}}$$

Effects on FPC when n/N Changes

Finite-Population Correction Factor for Selected Samples When the Population Is 1,000

Sample Size	Fraction of Population	Correction Factor
10	.010	.9955
25	.025	.9879
50	.050	.9752
100	.100	.9492
200	.200	.8949
500	.500	.7075

Observe that FPC approaches 1 when n/N becomes smaller

Confidence Interval Formulas for Estimating Means and Proportions with Finite Population Correction
Example (7)

C.I. for the Mean (μ)

$$\bar{X} \pm z \frac{\sigma}{\sqrt{n}} \sqrt{\frac{N-n}{N-1}}$$

C.I. for the Mean (μ)

$$\bar{X} \pm t \frac{s}{\sqrt{n}} \sqrt{\frac{N-n}{N-1}}$$

C.I. for the Proportion (π)

$$p \pm z \sqrt{\frac{p(1-p)}{n}} \sqrt{\frac{N-n}{N-1}}$$

Selecting an Appropriate Sample Size

There are 3 factors that determine the size of a sample, none of which has any direct relationship to the size of the population.

The **level of confidence** desired; The **margin of error** the researcher will tolerate. The **variation in the population** being Studied.

Sample Size for Estimating the Population Mean
Examples 8, 9

$$n = \left(\frac{z \cdot \sigma}{E} \right)^2$$

Sample Size for Estimating a Population Proportion
Examples10 & 11

$$n = p(1-p)\left(\frac{Z}{E} \right)^2$$

n is the size of the sample
z is the standard normal value corresponding to the desired level of confidence
E is the maximum allowable error
σ is the population standard deviation.
P is the population proportion

Applying statistical techniques in Decision Making

Part 4

One-Sample Tests of Hypothesis

Hypothesis, Hypothesis and Testing

HYPOTHESIS: A statement about the value of a population parameter developed for the purpose of testing

HYPOTHESIS TESTING A procedure based on sample evidence and probability theory to determine whether the hypothesis is a reasonable statement.

Step 1	Step 2	Step 3	Step 4	Step 5	
State null and alternate hypotheses	Select a level of significance	Identify the test statistic	Formulate a decision rule	Take a sample, arrive at decision	Do not reject H_0 or reject H_0 and accept H_1
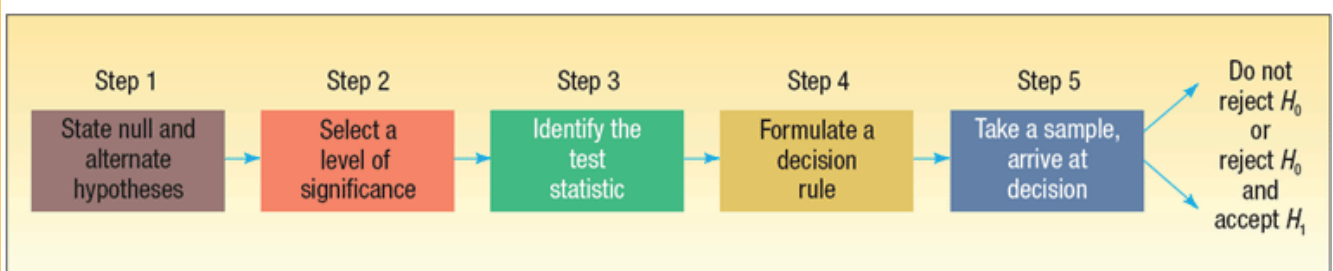
Null and Alternate Hypothesis and Test Statistic versus Critical Value

NULL HYPOTHESIS: A statement about the value of a population parameter developed for the purpose of testing numerical evidence.

ALTERNATE HYPOTHESIS: A statement that is accepted if the sample data provide sufficient evidence that the null hypothesis is false.

TEST STATISTIC: A value, determined from sample information, used to determine whether to reject the null hypothesis.

Example: z, t, F, χ^2

CRITICAL VALUE: The dividing point between the region where the null hypothesis is rejected and the region where it is not rejected.

Important Things to Remember about H0 and H1

- ➤ H_0: **null hypothesis and** H_1: **alternate hypothesis**
- ➤ H_0 **and** H_1 **are mutually exclusive and collectively exhaustive**
- ➤ H_0 **is always presumed to be true**
- ➤ H_1 **has the burden of proof**
- ➤ **A random sample (n) is used to** "*reject H_0*"
- ➤ **If we conclude** 'do not reject H_0', **this does not necessarily mean that the null hypothesis is true, it only suggests that there is not sufficient evidence to reject** H_0; **rejecting the null hypothesis then, suggests that the alternative hypothesis may be true.**
- ➤ **Equality is always part of** H_0 (e.g. "=" , "≥", "≤").
- ➤ "≠" "<" **and** ">" **always part of** H_1

How to Set Up a Claim as Hypothesis

- ➢ **In actual practice, the status quo is set up as H_0**
- ● **If the claim is "boastful" the claim is set up as H_1 (we apply the Missouri rule – "show me"). Remember, H_1 has the burden of proof**
- ● **In problem solving, look for key words and convert them into symbols. Some key words include: "improved, better than, as effective as, different from, has changed, etc."**

1-32

How to Set Up a Claim as Hypothesis

Keywords	Inequality Symbol	Part of:
Larger (or more) than	>	H_1
Smaller (or less)	<	H_1
No more than	$\leq$	H_0
At least	$\geq$	H_0
Has increased	>	H_1
Is there difference?	$\neq$	H_1
Has not changed	=	H_0
Has "improved", "is better than". "is more effective"	See left text	H_1

1-33

Decisions and Consequences in Hypothesis Testing

Null Hypothesis	Researcher	
	Does Not Reject H_0	Rejects H_0
H_0 is true	Correct decision	Type I error
H_0 is false	Type II error	Correct decision

One-tail vs. Two-tail Test

One-tail, Left Tail Test

Two-tail or Non-directional Test
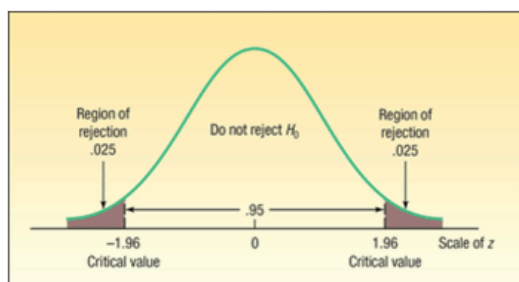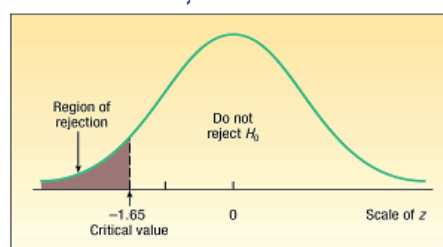
One-tail, Right Tail Test
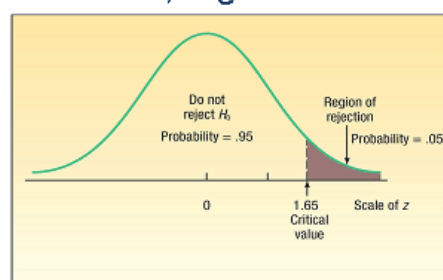
(1) Hypothesis Setups for Testing a Mean (μ) Examples (12 & 13)

$H_0: \mu = \text{value}$
$H_1: \mu \neq \text{value}$
Reject H_0 if:
$|Z| > Z_{\alpha/2}$
$|t| > t_{\alpha/2,\, n-1}$

$H_0: \mu \geq \text{value}$
$H_1: \mu < \text{value}$
Reject H_0 if:
$Z < -Z_{\alpha}$
$t < -t_{\alpha,\, n-1}$

$H_0: \mu \leq \text{value}$
$H_1: \mu > \text{value}$
Reject H_0 if:
$Z > Z_{\alpha}$
$t > t_{\alpha,\, n-1}$

$$t = \frac{\bar{x} - \mu}{s/\sqrt{n}}$$

$$z = \frac{\bar{x} - \mu}{\sigma/\sqrt{n}}$$

(2) Hypothesis Setups for Testing a Proportion (π)

$H_0: \pi = \text{value}$
$H_1: \pi \neq \text{value}$
Reject H_0 if:
$|Z| > Z_{\alpha/2}$

$H_0: \pi \geq \text{value}$
$H_1: \pi < \text{value}$
Reject H_0 if:
$Z < -Z_{\alpha}$

$H_0: \pi \leq \text{value}$
$H_1: \pi > \text{value}$
Reject H_0 if:
$Z > Z_{\alpha}$

$$z = \frac{p - \pi}{\sqrt{\dfrac{\pi(1-\pi)}{n}}}$$

Type of Errors in Hypothesis Testing

- Type I Error
  - Defined as the probability of rejecting the null hypothesis when it is actually true.
  - This is denoted by the Greek letter "α"
  - Also known as the *significance level* of a test

- Type II Error
  - Defined as the probability of "accepting" the null hypothesis when it is actually false.
  - This is denoted by the Greek letter "β"

(3) p-Value in Hypothesis Testing Example (14)

- *p*-VALUE is the probability of observing a sample value as extreme as, or more extreme than, the value observed, given that the null hypothesis is true.

- In testing a hypothesis, we can also compare the *p*-value to the significance level (α).

- Decision rule using the p-value:

  > Reject H_0 if *p*-value < significance level

What does it mean when p-value < α?

(a) .10, we have **some evidence** that H_0 is not true.

(b) .05, we have **strong evidence** that H_0 is not true.

(c) .01, we have **very strong evidence** that H_0 is not true.

(d) .001, we have **extremely strong evidence** that H_0 is not true.

(4) Testing for the Population Mean: Population Standard Deviation Unknown Example (15 & 16)

- When the population standard deviation (σ) is unknown, the sample standard deviation (s) is used in its place
- The t-distribution is used as test statistic, which is computed using the formula:

TESTING A MEAN, σ UNKNOWN	$t = \dfrac{\overline{X} - \mu}{s/\sqrt{n}}$	[10–2]

with $n - 1$ degrees of freedom, where:
    $\overline{X}$ is the sample mean.
    μ is the hypothesized population mean.
    s is the sample standard deviation.
    n is the number of observations in the sample.

(5) Tests Concerning Proportion
Example (17)

- A Proportion is the fraction or percentage that indicates the part of the population or sample having a particular trait of interest.
- The sample proportion is denoted by *p* and is found by *x/n*
- The test statistic is computed as follows:

| TEST OF HYPOTHESIS, ONE PROPORTION | $z = \dfrac{p - \pi}{\sqrt{\dfrac{\pi(1 - \pi)}{n}}}$ | [10–3] |

where:

π is the population proportion.
p is the sample proportion.
n is the sample size.

Assumptions in Testing a Population Proportion using the z-Distribution

- A random sample is chosen from the population.
- It is assumed that the binomial assumptions discussed in Chapter 6 are met:

  (1) the sample data collected are the result of counts;

  (2) the outcome of an experiment is classified into one of two mutually exclusive categories—a "success" or a "failure";

  (3) the probability of a success is the same for each trial; and
  (4) the trials are independent

- The test we will conduct shortly is appropriate when both $n\pi$ and $n(1- \pi)$ are at least 5.
- When the above conditions are met, the normal distribution can be used as an approximation to the binomial distribution

Test Statistic for Testing a Single Population Proportion

Sample proportion

Hypothesized population proportion

$$z = \frac{p - \pi}{\sqrt{\dfrac{\pi(1-\pi)}{n}}}$$

Sample size

Type II Error Example (18)

- Recall Type I Error, the level of significance, denoted by the Greek letter "α", is defined as the probability of rejecting the null hypothesis when it is actually true.

- Type II Error, denoted by the Greek letter "β", is defined as the probability of "accepting" the null hypothesis when it is actually false.

Applying statistical techniques in Decision Making

Part 4

Two-Sample Tests of Hypothesis

Comparing two populations
Some Examples

> Is there **a difference in the mean number of defects** produced on the **day** and the **afternoon shifts** at Kimble Products?

> Is there **a difference in the mean number of days absent** between **young workers** (under 21 years of age) and **older workers** (more than 60 years of age) in the fast-food industry?

> Is there is **a difference in the proportion of Ohio State University graduates** and University of Cincinnati graduates who pass the state Certified Public Accountant Examination on their first attempt?

> Is there a **difference in the mean** value of residential real estate sold by **male agents** and **female agents** in south Florida?

> Is there **an increase in the production rate** if **music** is piped into the production area?

(1) Comparing Two Population Means Example (19)

- **No assumptions about the shape of the populations are required.**
- **The samples are from independent populations.**
- **The formula for computing the value of z is:**

Use if sample sizes > 30
or if σ_1 and σ_2 are known

$$z = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\dfrac{\sigma_1^2}{n_1} + \dfrac{\sigma_2^2}{n_2}}}$$

Use if sample sizes > 30
and if σ_1 and σ_2 are unknown

$$z = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\dfrac{s_1^2}{n_1} + \dfrac{s_2^2}{n_2}}}$$

Two-Sample Tests about Proportions EXAMPLES

- **The vice president of human resources wishes to know whether there is a difference in the proportion of hourly employees who miss more than 5 days of work per year at the Atlanta and the Houston plants.**

- **General Motors is considering a new design for the Pontiac Grand Am. The design is shown to a group of potential buyers under 30 years of age and another group over 60 years of age. Pontiac wishes to know whether there is a difference in the proportion of the two groups who like the new design.**

- **A consultant to the airline industry is investigating the fear of flying among adults. Specifically, the company wishes to know whether there is a difference in the proportion of men versus women who are fearful of flying.**

(2)Two Sample Tests of Proportions Example (20)

> ➤ **We investigate whether two samples came from populations with an equal proportion of successes.**
> ➤ **The two samples are pooled using the following formula.**

POOLED PROPORTION
$$p_c = \frac{X_1 + X_2}{n_1 + n_2}$$
[11–3]

where:
X_1 is the number possessing the trait in the first sample.
X_2 is the number possessing the trait in the second sample.
n_1 is the number of observations in the first sample.
n_2 is the number of observations in the second sample.

(2) Two Sample Tests of Proportions continued

The value of the test statistic is computed from the following formula.

TWO-SAMPLE TEST OF PROPORTIONS
$$z = \frac{p_1 - p_2}{\sqrt{\dfrac{p_c(1 - p_c)}{n_1} + \dfrac{p_c(1 - p_c)}{n_2}}}$$

POOLED PROPORTION
$$p_c = \frac{X_1 + X_2}{n_1 + n_2}$$

(3) Comparing Population Means with Unknown Population Standard Deviations (the Pooled t-test)
Example (21)

The t distribution is used as the test statistic if one or more of the samples have less than 30 observations. The required assumptions are:

➢ **Both populations must follow the normal distribution.**
➢ **The populations must have equal standard deviations.**
➢ **The samples are from independent populations.**

(3) Small sample test of means continued

Finding the value of the test statistic requires two steps.

➢ **Pool the sample standard deviations.**

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$

➢ **Use the pooled standard deviation in the formula.**

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{s_p^2 \left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}$$

(4) Comparing Population Means with Unequal Population Standard Deviations Example (22)

Compute the following t-statistic if it is not reasonable to assume the population standard deviations are equal. The sample standard deviations s1 and s2 are used in place of the respective population standard deviations.

$$t = \frac{\overline{X}_1 - \overline{X}_2}{\sqrt{\dfrac{s_1^2}{n_1} + \dfrac{s_2^2}{n_2}}}$$

In addition, the degrees of freedom are adjusted downward by a rather complex approximation formula. The effect is to reduce the number of degrees of freedom in the test, which will require a larger value of the test statistic to reject the null hypothesis.

$$df = \frac{[(s_1^2/n_1) + (s_2^2/n_2)]^2}{\dfrac{(s_1^2/n_1)^2}{n_1 - 1} + \dfrac{(s_2^2/n_2)^2}{n_2 - 1}}$$

(5) Two-Sample Tests of Hypothesis Dependent Samples Example (23)

Dependent samples: are samples that are paired or related in some fashion.
For example:
➢ If you wished to buy a car you would look at the same car at two (or more) different dealerships and compare the prices.
➢ If you wished to measure the effectiveness of a new diet you would weigh the dieters at the start and at the finish of the program.
Use the following test when the samples are **dependent**:

$$t = \frac{\overline{d}}{s_d / \sqrt{n}}$$

Where
$\overline{d}$ is the mean of the differences
s_d is the standard deviation of the differences
n is the number of pairs (differences)

Dependent versus Independent Samples

How do we tell between dependent and independent samples?

➢ **Dependent sample is characterized by a measurement followed by an intervention of some kind and then another measurement. This could be called a "before" and "after" study.**

➢ **Dependent sample is characterized by matching or pairing observation.**

Why do we prefer dependent samples to independent samples? By using dependent samples, we are able to reduce the variation in the sampling distribution.

End of Part 4

Applying statistical techniques in Decision Making

Part 5
Analysis of Variance

The F Distribution

- It was named to honor Sir Ronald Fisher, one of the founders of modern-day statistics.

- It is
  - used to test whether two samples are from populations having equal variances
  - applied when we want to compare several population means simultaneously. The simultaneous comparison of several population means is called analysis of variance(ANOVA).
  - In both of these situations, the populations must follow a normal distribution, and the data must be at least interval-scale.

Characteristics of F-Distribution

1. There is a "family" of F Distributions. A particular member of the family is determined by two parameters: the degrees of freedom in the numerator and the degrees of freedom in the denominator.
2. The F distribution is continuous
3. F cannot be negative.
4. The F distribution is positively skewed.
5. It is asymptotic. As $F \to \infty$ the curve approaches the X-axis but never touches it.
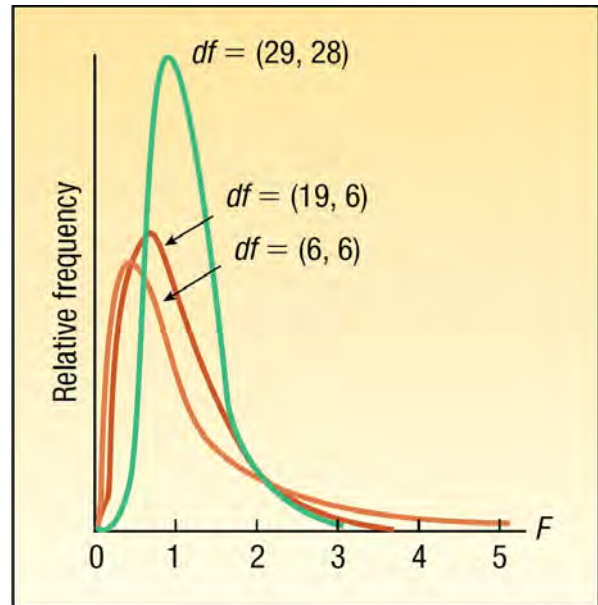
Comparing Two Population Variances

The F distribution is used to test the hypothesis that the variance of one normal population equals the variance of another normal population.

Examples:

- Two Barth shearing machines are set to produce steel bars of the same length. The bars, therefore, should have the same mean length. We want to ensure that in addition to having the same mean length they also have similar variation.

- The mean rate of return on two types of common stock may be the same, but there may be more variation in the rate of return in one than the other. A sample of 10 technology and 10 utility stocks shows the same mean rate of return, but there is likely more variation in the Internet stocks.

- A study by the marketing department for a large newspaper found that men and women spent about the same amount of time per day reading the paper. However, the same report indicated there was nearly twice as much variation in time spent per day among the men than the women.

Test for Equal Variances

$$H_0: \sigma_1^2 = \sigma_2^2$$
$$H_1: \sigma_1^2 \neq \sigma_2^2$$

To conduct the test, we select a random sample of n_1 observations from one population, and a random sample of n_2 observations from the second population. The test statistic is defined as follows.

TEST STATISTIC FOR COMPARING TWO VARIANCES	$F = \dfrac{s_1^2}{s_2^2}$	[12–1]

Test for Equal Variances - Example
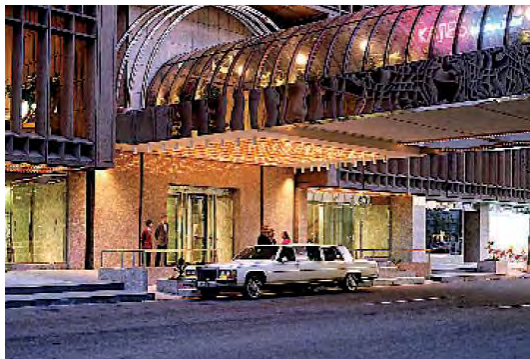
Lammers Limos offers limousine service from the city hall in Toledo, Ohio, to Metro Airport in Detroit. Sean Lammers, president of the company, is considering two routes. One is via U.S. 25 and the other via I-75. He wants to study the time it takes to drive to the airport using each route and then compare the results. He collected the following sample data, which is reported in minutes.

Using the .10 significance level, **is there a difference in the variation** in the driving times for the two routes?

U.S. Route 25	Interstate 75
52	59
67	60
56	61
45	51
70	56
54	63
64	57
	65

(Ex5_1)

Test for Equal Variances - Example

Step 1: The hypotheses are:

$$H_0: \sigma_1^2 = \sigma_2^2$$
$$H_1: \sigma_1^2 \neq \sigma_2^2$$

Step 2: The significance level is .05.

Step 3: The test statistic is the F distribution.

Test for Equal Variances - Example

Step 4: State the decision rule.

Reject H_0 if
$$F > F_{\alpha/2, v1, v2}$$
$$F > F_{.10/2, 7-1, 8-1}$$
$$F > F_{.05, 6, 7}$$

TABLE 12–1 Critical Values of the F Distribution, $\alpha = .05$

Degrees of Freedom for Denominator	Degrees of Freedom for Numerator			
	5	6	7	8
1	230	234	237	239
2	19.3	19.3	19.4	19.4
3	9.01	8.94	8.89	8.85
4	6.26	6.16	6.09	6.04
5	5.05	4.95	4.88	4.82
6	4.39	4.28	4.21	4.15
7	3.97	3.87	3.79	3.73
8	3.69	3.58	3.50	3.44
9	3.48	3.37	3.29	3.23
10	3.33	3.22	3.14	3.07

Test for Equal Variances - Example

Step 5: Compute the value of F and make a decision

U.S. Route 25

$$\bar{X} = \frac{\Sigma X}{n} = \frac{408}{7} = 58.29 \qquad s = \sqrt{\frac{\Sigma(X - \bar{X})^2}{n-1}} = \sqrt{\frac{485.43}{7-1}} = 8.9947$$

Interstate 75

$$\bar{X} = \frac{\Sigma X}{n} = \frac{472}{8} = 59.00 \qquad s = \sqrt{\frac{\Sigma(X - \bar{X})^2}{n-1}} = \sqrt{\frac{134}{8-1}} = 4.3753$$

$$F = \frac{s_1^2}{s_2^2} = \frac{(8.9947)^2}{(4.3753)^2} = 4.23$$

The decision is to reject the null hypothesis, because the computed F value (4.23) is larger than the critical value (3.87).

We conclude that there is a difference in the variation of the travel times along the two routes.

Test for Equal Variances – Excel Example

Data Analysis

Analysis Tools

Anova: Two-Factor Without Replication
Correlation
Covariance
Descriptive Statistics
Exponential Smoothing
F-Test Two-Sample for Variances
Fourier Analysis
Histogram
Moving Average
Random Number Generation

OK
Cancel
Help

num 1 variance test

	A	B	C	D	E	F	G
1	U. S. 25	Interstate 75		F-Test Two-Sample for Variances			
2	52	59			U. S. 25	Interstate 75	
3	67	60		Mean	58.29	59.00	
4	56	61		Variance	80.90	19.14	
5	45	51		Observations	7.00	8.00	
6	70	56		df	6.00	7.00	
7	54	63		F	4.23		
8	64	57		P(F<=f) one-tail	0.04		
9		65		F Critical one-tail	3.87		
10							
11							

Comparing Means of Two or More Populations

The *F* distribution is also used for testing whether two or more sample means came from the same or equal populations.

Assumptions:
- The sampled populations follow the normal distribution.
- The populations have equal standard deviations.
- The samples are randomly selected and are independent.

Comparing Means of Two or More Populations

- The Null Hypothesis is that the population means are the same. The Alternative Hypothesis is that at least one of the means is different.
- The Test Statistic is the *F* distribution.
- The Decision rule is to reject the null hypothesis if *F* (computed) is greater than *F* (table) with numerator and denominator degrees of freedom.
- Hypothesis Setup and Decision Rule:

$$H_0: \mu_1 = \mu_2 = \ldots = \mu_k$$
$$H_1: \text{The means are not all equal}$$
$$\text{Reject } H_0 \text{ if } F > F_{\alpha, k-1, n-k}$$

Analysis of Variance – F statistic

- If there are *k* populations being sampled, the numerator degrees of freedom is *k* − 1.

- If there are a total of *n* observations the denominator degrees of freedom is *n* − *k*.

- The test statistic is computed by:

$$F = \frac{SST/(k-1)}{SSE/(n-k)}$$

Comparing Means of Two or More Populations – Illustrative Example

Joyce Kuhlman manages a regional financial center. She wishes to compare the productivity, as measured by the number of customers served, among three employees. Four days are randomly selected and the number of customers served by each employee is recorded. The results are:

Wolfe	White	Korosa
55	66	47
54	76	51
59	67	46
56	71	48
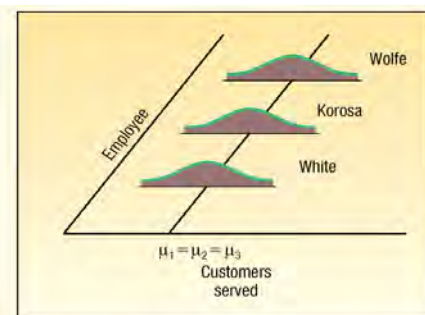
Case Where Treatment Means Are the Same
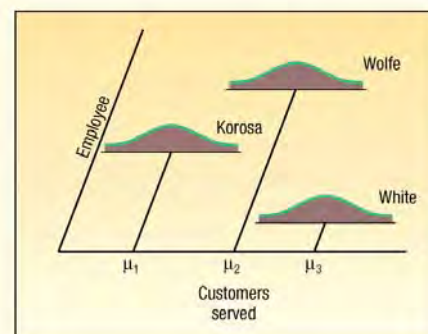
Case Where Treatment Means Are Different

Comparing Means of Two or More Populations – Example

Recently a group of four major carriers joined in hiring Brunner Marketing Research, Inc., to survey recent passengers regarding their level of satisfaction with a recent flight. The survey included questions on ticketing, boarding, in-flight service, baggage handling, pilot communication, and so forth.

Twenty-five questions offered a range of possible answers: excellent, good, fair, or poor. A response of excellent was given a score of 4, good a 3, fair a 2, and poor a 1. These responses were then totaled, so the total score was an indication of the satisfaction with the flight. Brunner Marketing Research, Inc., randomly selected and surveyed passengers from the four airlines.

Eastern	TWA	Allegheny	Ozark
94	75	70	68
90	68	73	70
85	77	76	72
80	83	78	65
	88	80	74
		68	65
		65	

Is there a difference in the mean satisfaction level among the four airlines? Use the .01 significance level.

(Ex5_2)

Comparing Means of Two or More Populations – Example

Step 1: State the null and alternate hypotheses.

H_0: $\mu_E = \mu_A = \mu_T = \mu_O$
H_1: The means are not all equal
Reject H_0 if $F > F_{\alpha,k-1,n-k}$

Step 2: State the level of significance.
The .01 significance level is stated in the problem.

Step 3: Find the appropriate test statistic.
Because we are comparing means of more than two groups, use the F statistic

Comparing Means of Two or More Populations – Example

Step 4: State the decision rule.

Reject H_0 if $F > F_{\alpha, k-1, n-k}$

$F > F_{.01, 4-1, 22-4}$

$F > F_{.01, 3, 18}$

$F > 5.09$

Comparing Means of Two or More Populations – Example

Step 5: Compute the value of F and make a decision

ANOVA Table

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F
Treatments	SST	$k-1$	$SST/(k-1) = MST$	MST/MSE
Error	SSE	$n-k$	$SSE/(n-k) = MSE$	
Total	SS total	$n-1$		

$$SS\ total = \Sigma(X - \bar{X}_G)^2$$

where:
    X is each sample observation.
    $\bar{X}_G$ is the overall or grand mean.

$$SSE = \Sigma(X - \bar{X}_c)^2$$

where:
    $\bar{X}_c$ is the sample mean for treatment c.

Comparing Means of Two or More Populations – Example

$$\overline{X}_G = \frac{1,664}{22} = 75.64$$

	Eastern	TWA	Allegheny	Ozark	Total
	94	75	70	68	
	90	68	73	70	
	85	77	76	72	
	80	83	78	65	
		88	80	74	
			68	65	
			65		
Column total	349	391	510	414	1,664
n	4	5	7	6	22
Mean	87.25	78.20	72.86	69.00	75.64

Computing SS Total and SSE

$(X - \overline{X}_G)^2$

Eastern	TWA	Allegheny	Ozark
18.36	−0.64	−5.64	−7.64
14.36	−7.64	−2.64	−5.64
9.36	1.36	0.36	−3.64
4.36	7.36	2.36	−10.64
	12.36	4.36	−1.64
		−7.64	−10.64
		−10.64	

$(X - \overline{X}_G)^2$

	Eastern	TWA	Allegheny	Ozark	Total
	337.09	0.41	31.81	58.37	
	206.21	58.37	6.97	31.81	
	87.61	1.85	0.13	13.25	
	19.0	54.17	5.57	113.21	
		152.77	19.01	2.69	
			58.37	113.21	
			113.21		
Total	649.91	267.57	235.07	332.54	1,485.09

SS total $= \Sigma(X - \overline{X}_G)^2$

$(X - \overline{X}_c)$

Eastern	TWA	Allegheny	Ozark
6.75	−3.2	−2.86	−1
2.75	−10.2	0.14	1
−2.25	−1.2	3.14	3
−7.25	4.8	5.14	−4
	9.8	7.14	5
		−4.86	−4
		−7.86	

$(X - \overline{X}_c)^2$

	Eastern	TWA	Allegheny	Ozark	Total
	45.5625	10.24	8.18	1	
	7.5625	104.04	0.02	1	
	5.0625	1.44	9.86	9	
	52.5625	23.04	26.42	16	
		96.04	50.98	25	
			23.62	16	
			61.78		
Total	110.7500	234.80	180.86	68	594.41

SSE $= \Sigma(X - \overline{X}_c)^2$

Computing SST

$$SST = SS \ total - SSE = 1{,}485.09 - 594.41 = 890.68.$$

ANOVA Table

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F
Treatments	SST	$k-1$	$SST/(k-1) = MST$	MST/MSE
Error	SSE	$n-k$	$SSE/(n-k) = MSE$	
Total	SS total	$n-1$		

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F
Treatments	890.68	3	296.89	8.99
Error	594.41	18	33.02	
Total	1,485.09	21		

The computed value of F is 8.99, which is greater than the critical value of 5.09, so the null hypothesis is rejected.

Conclusion: The population means are not all equal. The mean scores are not the same for the four airlines; at this point we can only conclude there is a difference in the treatment means. We cannot determine which treatment groups differ or how many treatment groups differ.

Confidence Interval for the Difference Between Two Means

When we reject the null hypothesis that the means are equal, we may want to know which treatment means differ. One of the simplest procedures is through the use of confidence intervals.

$$(\overline{X}_1 - \overline{X}_2) \pm t \sqrt{MSE\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}$$

where

$\overline{X}_1$ is the mean of the first sample.

$\overline{X}_2$ is the mean of the second sample.

t is obtained from Appendix B.2. The degrees of freedom is equal to $n - k$.

MSE is the mean square error term obtained from the ANOVA table $[SSE/(n - k)]$.

n_1 is the number of observations in the first sample.

n_2 is the number of observations in the second sample.

Confidence Interval for the Difference Between Two Means - Example

From the previous example, develop a 95% confidence interval for the difference in the mean rating for Eastern and Ozark. Can we conclude that there is a difference between the two airlines' ratings?

$$(\bar{X}_E - \bar{X}_O) \pm t\sqrt{MSE\left(\frac{1}{n_E} + \frac{1}{n_O}\right)} = (87.25 - 69.00) \pm 2.101\sqrt{33.0\left(\frac{1}{4} + \frac{1}{6}\right)}$$
$$= 18.25 \pm 7.79$$

The 95 percent confidence interval ranges from 10.46 up to 26.04. Both endpoints are positive; hence, we can conclude these treatment means differ significantly. That is, passengers on Eastern rated service significantly different from those on Ozark.

Excel

Two-Way Analysis of Variance

- For the two-factor ANOVA we test whether there is a significant difference between the *treatment effect* and whether there is a difference in the *blocking effect*. Let B_r be the block totals (r for rows)

- Let SSB represent the sum of squares for the blocks where:

$$SSB = k\Sigma(\bar{x}_b - \bar{x}_G)^2$$

k is the number of treatments.
b is the number of blocks.
$\overline{X}_b$ is the sample mean of block b.
$\overline{X}_G$ is the overall or grand mean.

Two-Way Analysis of Variance - Example

WARTA, the Warren Area Regional Transit Authority, is expanding bus service from the suburb of Starbrick into the central business district of Warren. There are four routes being considered from Starbrick to downtown Warren: (1) via U.S. 6, (2) via the West End, (3) via the Hickory Street Bridge, and (4) via Route 59.

WARTA conducted several tests to determine whether there was a difference in the mean travel times along the four routes. Because there will be many different drivers, the test was set up so each driver drove along each of the four routes. Next slide shows the travel time, in minutes, for each driver-route combination. At the .05 significance level, is there a difference in the mean travel time along the four routes? If we remove the effect of the drivers, is there a difference in the mean travel time? **(Ex5_3)**

Two-Way Analysis of Variance - Example

Sample Data

Driver	Travel Time From Starbrick to Warren (minutes)			
	U.S. 6	West End	Hickory St.	Rte. 59
Deans	18	17	21	22
Snaverly	16	23	23	22
Ormson	21	21	26	22
Zollaco	23	22	29	25
Filbeck	25	24	28	28

Two-Way Analysis of Variance - Example

Step 1: State the null and alternate hypotheses.

H_0: $\mu_u = \mu_w = \mu_h = \mu_r$
H_1: Not all treatment means are the same
Reject H_0 if $F > F_{\alpha, k-1, n-k}$

Step 2: State the level of significance.
The .05 significance level is stated in the problem.

Step 3: Find the appropriate test statistic.
Because we are comparing means of more than two groups, use the F statistic

Step 4: State the decision rule.

Reject H_0 if $F > F_{\alpha, v1, v2}$
$F > F_{.05, k-1, n-k}$
$F > F_{.05, 4-1, 20-4}$
$F > F_{.05, 3, 16}$
$F > 3.24$

Two-Way Analysis of Variance - Example

Travel Time From Starbrick to Warren (minutes)						
Driver	U.S. 6	West End	Hickory St.	Rte. 59	Driver Sums	Driver Means
Deans	18	17	21	22	78	19.5
Snaverly	16	23	23	22	84	21
Omson	21	21	26	22	90	22.5
Zollaco	23	22	29	25	99	24.75
Filbeck	25	24	28	28	105	26.25

$$SSB = k\Sigma(\overline{x}_b - \overline{x}_G)^2$$

$$\begin{aligned}
SSB &= k\Sigma(\overline{X}_b - \overline{X}_G)^2 \\
&= 4(19.5 - 22.8)^2 + 4(21.0 - 22.8)^2 + 4(22.5 - 22.8)^2 \\
&\quad + 4(24.75 - 22.8)^2 + 4(26.25 - 22.8)^2 \\
&= 119.7
\end{aligned}$$

Two-Way Analysis of Variance - Example

SUM OF SQUARES ERROR, TWO-WAY $SSE = SS\ total - SST - SSB$

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F
Treatments	SST	$k - 1$	$SST/(k - 1) = MST$	MST/MSE
Blocks	SSB	$b - 1$	$SSB/(b - 1) = MSB$	MSB/MSE
Error	SSE	$(k - 1)(b - 1)$	$SSE/(k - 1)(b - 1) = MSE$	
Total	SS total	$n - 1$		

$SSE = SS\ total - SST - SSB = 229.2 - 72.8 - 119.7 = 36.7$

Source of Variation	(1) Sum of Squares	(2) Degrees of Freedom	(3) Mean Square (1)/(2)
Treatments	72.8	3	24.27
Blocks	119.7	4	29.93
Error	36.7	12	3.06
Total	229.2	19	

Two-Way Analysis of Variance – Excel Example

	A	B	C	D	E	F	G	H	I	J	K	L	M
2	Driver	US6	WestEnd	HickorySt	Rte 59		Anova: Two-Factor Without Replication						
3	Deans	18	17	21	22								
4	Snaverly	16	23	23	22		SUMMARY	Count	Sum	Average	Variance		
5	Ormson	21	21	26	22								
6	Zollaco	23	22	29	25		US6	5	103	20.6	13.3		
7	Filbeck	25	24	28	28		WestEnd	5	107	21.4	7.3		
8							HickorySt	5	127	25.4	11.3		
9							Rte 59	5	119	23.8	7.2		
10													
11					Block (Driver)								
12							ANOVA						
13							Source of Variation	SS	df	MS	F	P-value	F crit
14							Rows	119.7	4	29.925	9.785	0.001	3.259
15					Treatment (Route)		Columns	72.8	3	24.267	7.935	0.004	3.490
16							Error	36.7	12	3.058			
17													
18							Total	229.2	19				

Using Excel to perform the calculations, we conclude:
(1) The mean time is not the same for all drivers
(2) The mean times for the routes are not all the same

Two-way ANOVA with Interaction

INTERACTION The effect of one factor on a response variable differs depending on the value of another factor.

- In the previous section, we studied the separate or independent effects of two variables, routes into the city and drivers, on mean travel time.

- There is another effect that may influence travel time. This is called an interaction effect between route and driver on travel time. For example, is it possible that one of the drivers is especially good driving one or more of the routes?

- The **combined effect** of driver and route may also explain differences in mean travel time.

- To measure interaction effects it is necessary to have at least two observations in each cell.

Interaction Effect

- When we use a two-way ANOVA to study interaction, we now call the two variables as **factors** instead of blocks

- Interaction occurs if the combination of two factors has some effect on the variable under study, in addition to each factor alone.

- The variable being studied is referred to as the **response variable.**

- One way to study interaction is by plotting factor means in a graph called an **interaction plot**.

Graphical Observation of Mean Times

Our graphical observations show us that interaction effects are possible. The next step is to conduct statistical tests of hypothesis to further investigate the possible interaction effects. In summary, our study of travel times has several questions:

- Is there really an interaction between routes and drivers?

- Are the travel times for the drivers the same?

- Are the travel times for the routes the same?

Of the three questions, we are most interested in the test for interactions. To put it another way, does a particular route/driver combination result in significantly faster (or slower) driving times? Also, the results of the hypothesis test for interaction affect the way we analyze the route and driver questions.

Interaction Plot (data means) for Travel time
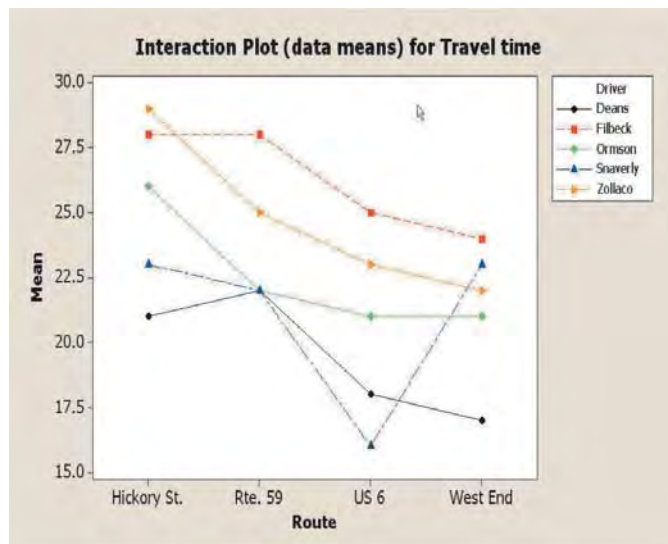
Example – ANOVA with Replication

Suppose the WARTA blocking experiment discussed earlier is repeated by measuring two more travel times for each driver and route combination with the data shown in the Excel worksheet.

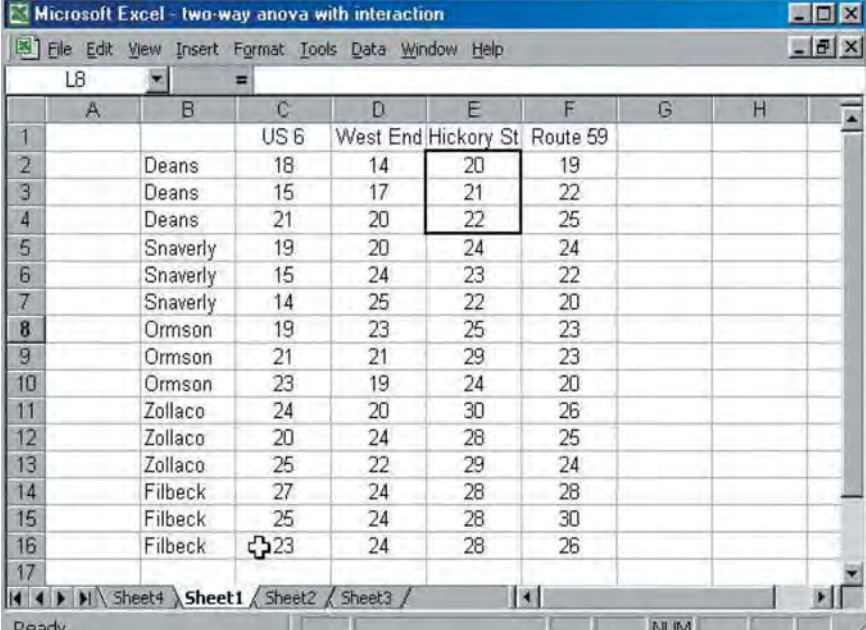|	A	B	C	D	E	F	G	H
1			US 6	West End	Hickory St	Route 59		
2		Deans	18	14	20	19		
3		Deans	15	17	21	22		
4		Deans	21	20	22	25		
5		Snaverly	19	20	24	24		
6		Snaverly	15	24	23	22		
7		Snaverly	14	25	22	20		
8		Ormson	19	23	25	23		
9		Ormson	21	21	29	23		
10		Ormson	23	19	24	20		
11		Zollaco	24	20	30	26		
12		Zollaco	20	24	28	25		
13		Zollaco	25	22	29	24		
14		Filbeck	27	24	28	28		
15		Filbeck	25	24	28	30		
16		Filbeck	23	24	28	26		
17								

Microsoft Excel - two-way anova with interaction

File Edit View Insert Format Tools Data Window Help

L8

Sheet4 \ Sheet1 / Sheet2 / Sheet3

Ready   NUM

(Ex5_4)

1-92

Three Tests in ANOVA with Replication

The ANOVA now has three sets of hypotheses to test:

1. H_0: There is no interaction between drivers and routes.
    H_1: There is interaction between drivers and routes.

2. H_0: The driver means are the same.
    H_1: The driver means are *not* the same.

3. H_0: The route means are the same.
    H_1: The route means are *not* the same.

1-93

ANOVA Table

Source	Sum of Squares	df	Mean Square	F
Route	Factor A	$k - 1$	$SSA/(k - 1) = MSA$	MSA/MSE
Driver	Factor B	$b - 1$	$SSB/(b - 1) = MSB$	MSB/MSE
Interaction	SSI	$(k - 1)(b - 1)$	$SSI/(k - 1)(b - 1) = MSI$	MSI/MSE
Error	SSE	$n - kb$	$SSE/(n - kb) = MSE$	
Total	SS total	$n - 1$		

Excel Output

One-way ANOVA for Each Driver

H_0: Route travel times are equal.

Deans: H_0: Route travel times are equal.

Source	DF	SS	MS	F	P
Dean RTE	3	51.00	17.00	2.43	0.140
Error	8	56.00	7.00		
Total	11	107.00			

Snaverly: H_0: Route travel times are equal.

Source	DF	SS	MS	F	P
SN RTE	3	102.00	34.00	7.16	0.012
Error	8	38.00	4.75		
Total	11	140.00			

Ormson: H_0: Route travel times are equal.

Source	DF	SS	MS	F	P
Ormson RTE	3	51.00	17.00	3.78	0.059
Error	8	36.00	4.50		
Total	11	87.00			

Zollaco: H_0: Route travel times are equal.

Source	DF	SS	MS	F	P
Z-RTE	3	86.25	28.75	8.85	0.006
Error	8	26.00	3.25		
Total	11	112.25			

Filbeck: H_0: Route travel times are equal.

Source	DF	SS	MS	F	P
Filbeck RTE	3	38.25	12.75	6.38	0.016
Error	8	16.00	2.00		
Total	11	54.25			

1-96

END of Part 5

Applying statistical techniques in Decision Making

Part 6
Correlation

Relationship between Two Variables

➤ When we study the **relationship** between **two variables** we refer to the data as **bivariate.**

➤ **One graphical technique** we use to show the **relationship** between variables is called a **scatter diagram**.

EXAMPLES

➤ Is there a **relationship** between the number of **hours that students studied** for an exam and the **score earned**

➤ Is there a **relationship** between the **miles per gallon** achieved by large pickup trucks and the **size of the engine**?

➤ Can we base an estimate of the **cost to heat** a home in January on the **number of square feet** in the home?

Correlation Analysis

➢ **Correlation Analysis** is the study of the **relationship between variables**. It is also defined as **group of techniques** to **measure** the **association between two variables**.

➢ **Scatter** Diagram is a chart that **portrays** the **relationship** between the **two variables**. It is the usual **first step** in **correlations analysis**

➢ The **Dependent Variable** is the variable being predicted or estimated, and the **Independent** Variable provides the basis for estimation. It is the predictor variable.

Minitab Scatter Plots
(1) Scatter Diagram (Example 1)
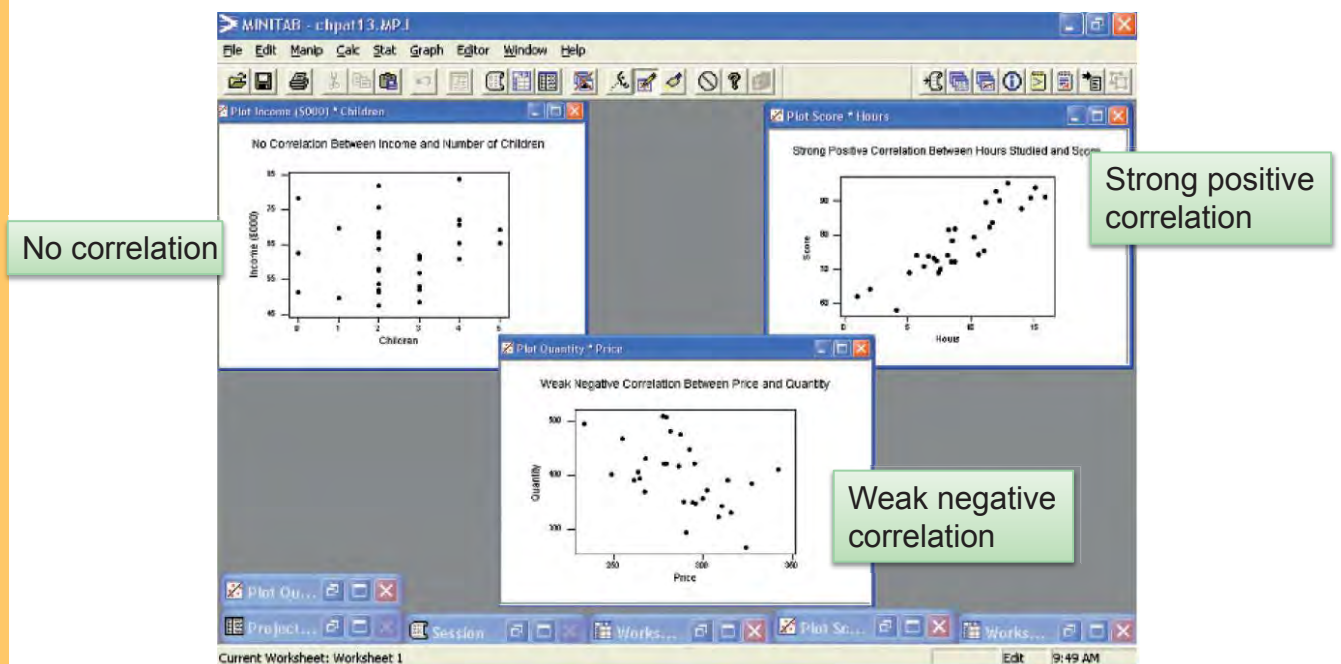
(2) The Coefficient of Correlation, r

The Coefficient of Correlation (r) is a measure of the strength of the relationship between two variables

- ➤ It shows the **direction** and **strength** of the linear relationship between two interval or ratio-scale variables
- ➤ It can range from **-1.00 to +1.00.**
- ➤ Values of -1.00 or +1.00 indicate **perfect** and strong correlation.
- ➤ Values close to 0.0 indicate **weak** correlation.
- ➤ **Negative** values indicate an **inverse** relationship and **positive** values indicate a **direct** relationship.

(2) The Coefficient of Correlation, r
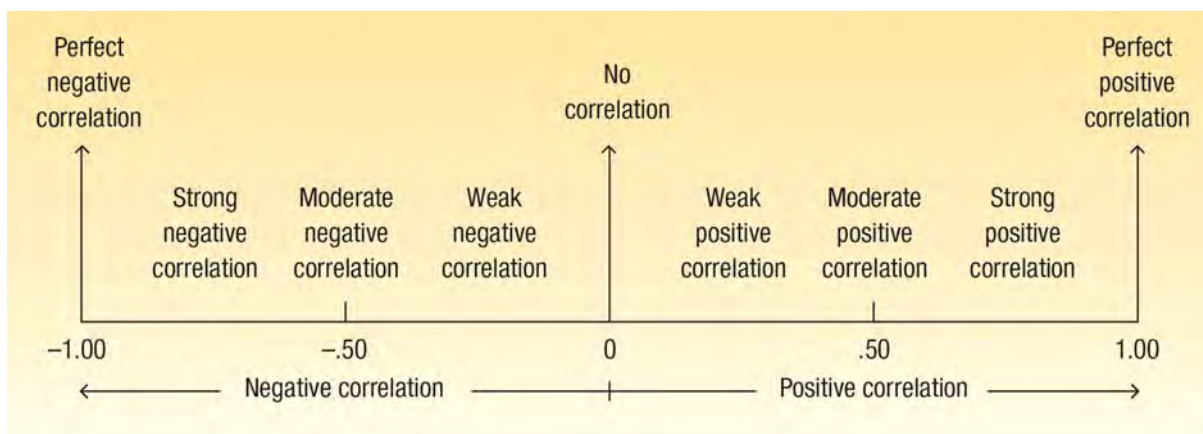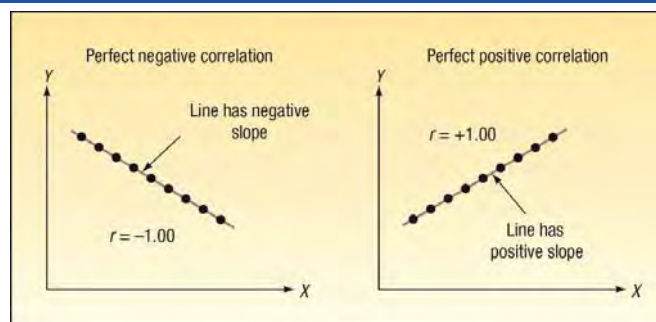
(3) Coefficient of Determination (Example 2)

The coefficient of determination (r2) is the proportion of the total variation in the dependent variable (Y) that is explained or accounted for by the variation in the independent variable (X). It is the square of the coefficient of correlation:

➢ It ranges from 0 to 1.

➢ It does not give any information on the direction of the relationship between the variables.

(4) Significance of Correlation Coefficient (Example 3)

H_0: $\rho = 0$ (the correlation in the population is 0)
H_1: $\rho \neq 0$ (the correlation in the population is not 0)

Reject H_0 if:
$$t > t_{\alpha/2,n-2} \text{ or } t < -t_{\alpha/2,n-2}$$

where

$$t = r\sqrt{\frac{n-2}{1-r^2}}$$

Rank-Order Correlation (Example 4)

Spearman's coefficient of rank correlation reports the association between two sets of **ranked** observations. The features are:

➤ It can range from **–1.00 up to 1.00.**

➤ It is similar to **Pearson's** coefficient of correlation, but is based on **ranked** data.

➤ It computed using the formula:

$$r_s = 1 - \frac{6 \sum d^2}{n(n^2 - 1)}$$

Testing the Significance of rs (Example 5)

➤State the Null and Alternate Hypothesis:

H_0: Rank correlation in population is 0.

H_1 There is a positive association among the ranks.

➤Determine the Significance Level and Test Statistic

For a sample of 10 or more, the significance r_s of is determined by computing t using the following formula. The sampling distribution of follows the t distribution with n - 2 degrees of freedom.

$$t = r_s \sqrt{\frac{n - 2}{1 - r_s^2}}$$

Contingency Tables (Example 6)

➢ **A scatter diagram requires that both of the variables be at least interval scale.**

➢ **What if we wish to study the relationship between two variables when one or both are nominal or ordinal scale? In this case we tally the results in a contingency table.**

➢ **A contingency table is a cross-tabulation that simultaneously summarizes two variables of interest**

Contingency Table Analysis

A contingency table is used to investigate whether two traits or characteristics are related. Each observation is classified according to two criteria. We use the usual hypothesis testing procedure.

➢ **The degrees of freedom is equal to:**

(number of rows-1)(number of columns-1).

➢ **The expected frequency is computed as:**

EXPECTED FREQUENCY $f_e = \dfrac{(\text{Row total})(\text{Column total})}{\text{Grand total}}$

Chi-Square Distribution
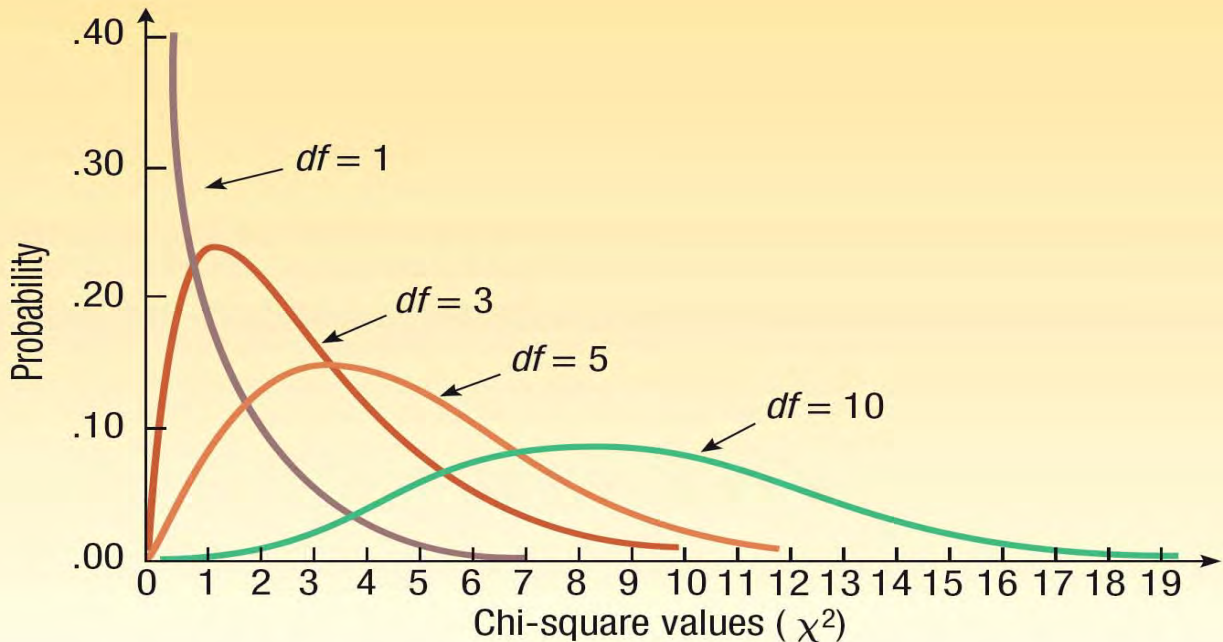
Chi-Square Distribution

The major characteristics of the **chi-square** distribution

➢ **It is positively skewed.**

➢ **It is non-negative.**

➢ **It is based on degrees of freedom.**

➢ **When degrees of freedom change a new distribution is created.**

Contingency Analysis

We can use the **chi-square statistic** to formally test for a relationship between two nominal-scaled variables. To put it another way, Is one variable independent of the other?

➢ Ford Motor Company operates an assembly plant in Dearborn, Michigan. The plant operates three shifts per day, 5 days a week. The quality control manager wishes to compare the quality level on the three shifts. Vehicles are classified by quality level (acceptable, unacceptable) and shift (day, afternoon, night). Is there a difference in the quality level on the three shifts? That is, is the quality of the product related to the shift when it was manufactured? Or is the quality of the product independent of the shift on which it was manufactured?

Contingency Analysis (Example 7)

➢ A sample of 100 drivers who were stopped for speeding violations was classified by gender and whether or not they were wearing a seat belt. For this sample, is wearing a seatbelt related to gender?

➢ Does a male released from federal prison make a different adjustment to civilian life if he returns to his hometown or if he goes elsewhere to live? The two variables are adjustment to civilian life and place of residence. Note that both variables are measured on the nominal scale.

END of Part 6

Applying statistical techniques in Decision Making

Part 7
Simple Regressions

Regression Analysis - Introduction

- Recall in Chapter 4 the idea of showing the relationship between *two* variables with a scatter diagram was introduced.
- In that case we showed that, as the age of the buyer increased, the amount spent for the vehicle also increased.
- In this chapter we carry this idea further. Numerical measures to express the strength of relationship between two variables are developed.
- In addition, an equation is used to express the relationship between variables, allowing us to estimate one variable on the basis of another.

EXAMPLES
1. Is there a relationship between the amount Healthtex spends per month on advertising and its sales in the month?
2. Can we base an estimate of the cost to heat a home in January on the number of square feet in the home?
3. Is there a relationship between the miles per gallon achieved by large pickup trucks and the size of the engine?
4. Is there a relationship between the number of hours that students studied for an exam and the score earned?

Correlation Analysis

Correlation Analysis is the study of the relationship between variables. It is also defined as group of techniques to measure the association between two variables.

Scatter Diagram is a chart that portrays the relationship between the two variables. It is the usual first step in correlations analysis

The Dependent Variable is the variable being predicted or estimated.
The Independent Variable provides the basis for estimation. It is the predictor variable.

Scatter Diagram Example

The sales manager of Copier Sales of America, which has a large sales force throughout the United States and Canada, wants to determine whether there is a relationship between the number of sales calls made in a month and the number of copiers sold that month. The manager selects a random sample of 10 representatives and determines the number of sales calls each representative made last month and the number of copiers sold.

Sales Representative	Number of Sales Calls	Number of Copiers Sold
Tom Keller	20	30
Jeff Hall	40	60
Brian Virost	20	40
Greg Fish	30	60
Susan Welch	10	30
Carlos Ramirez	10	40
Rich Niles	20	40
Mike Kiel	20	50
Mark Reynolds	20	30
Soni Jones	30	70

(Ex6_1_1)

1-21

The Coefficient of Correlation, *r*

The Coefficient of Correlation (*r*) is a measure of the strength of the relationship between two variables.

- It shows the direction and strength of the linear relationship between two interval or ratio-scale variables
- It can range from -1.00 to +1.00.
- Values of -1.00 or +1.00 indicate perfect and strong correlation.
- Values close to 0.0 indicate weak correlation.
- Negative values indicate an inverse relationship and positive values indicate a direct relationship.
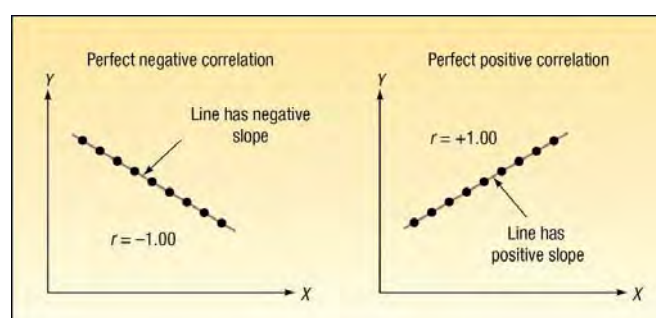
1-22

Correlation Coefficient - Interpretation
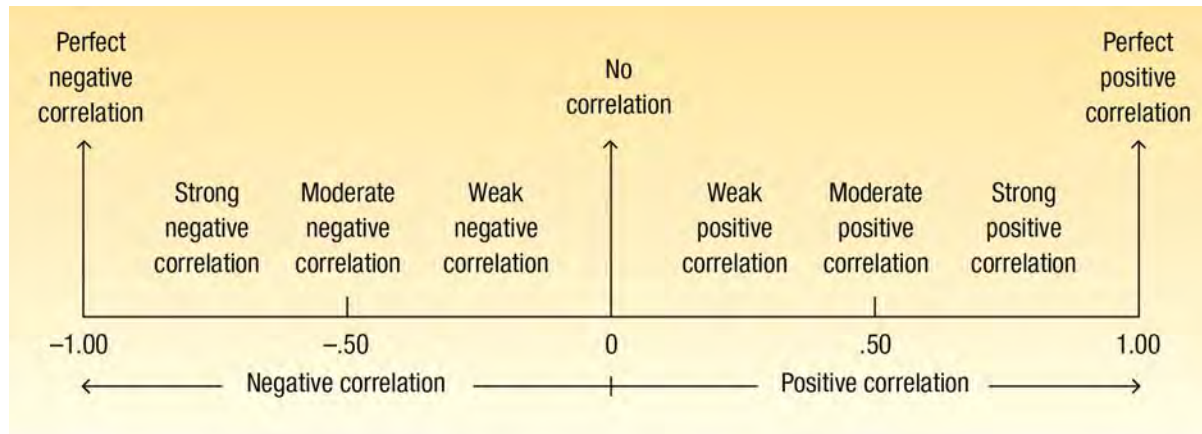
Minitab Scatter Plots
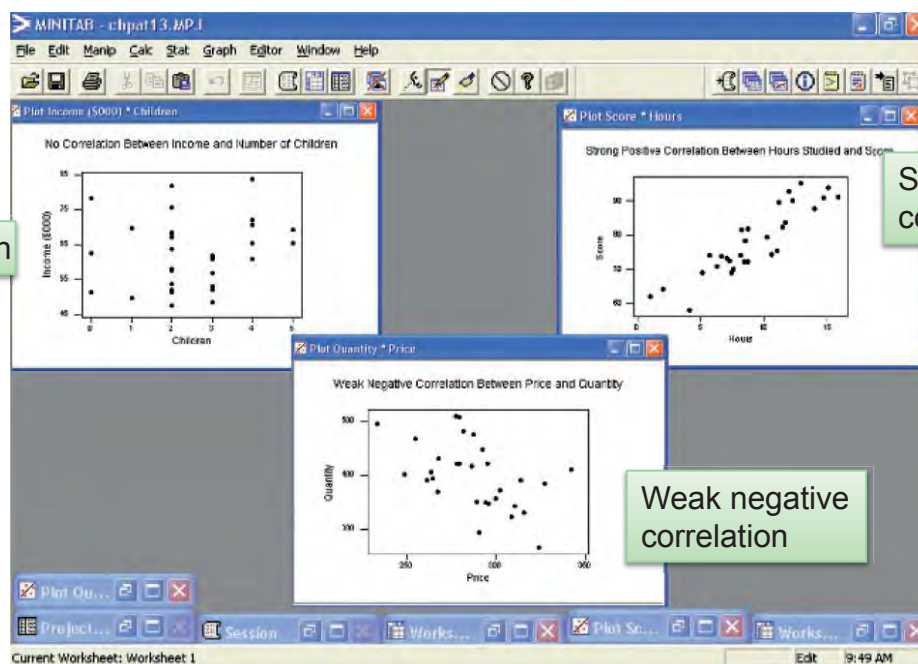
Coefficient of Determination

The coefficient of determination (r^2) is the proportion of the total variation in the dependent variable (Y) that is explained or accounted for by the variation in the independent variable (X). It is the square of the coefficient of correlation.

- It ranges from 0 to 1.
- It does not give any information on the direction of the relationship between the variables.

Correlation Coefficient - Example

Using the Copier Sales of America data which a scatterplot is shown below, compute the correlation coefficient and coefficient of determination.

Sales Representative	Number of Sales Calls	Number of Copiers Sold
Tom Keller	20	30
Jeff Hall	40	60
Brian Virost	20	40
Greg Fish	30	60
Susan Welch	10	30
Carlos Ramirez	10	40
Rich Niles	20	40
Mike Kiel	20	50
Mark Reynolds	20	30
Soni Jones	30	70

Using the formula:
CORRELATION COEFFICIENT

$$r = \frac{\Sigma(X - \bar{X})(Y - \bar{Y})}{(n - 1)s_x s_y}$$
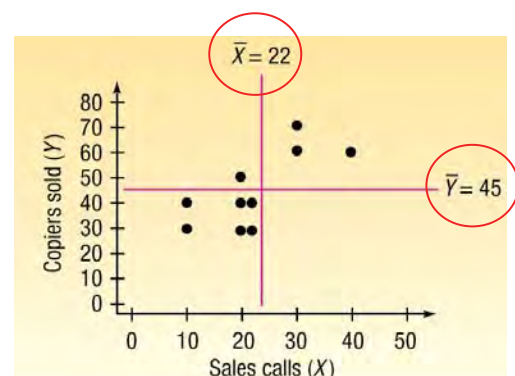
Correlation Coefficient - Example

Sales Representative	Calls, Y	Sales, X	$X - \bar{X}$	$Y - \bar{Y}$	$(X - \bar{X})(Y - \bar{Y})$
Tom Keller	20	30	−2	−15	30
Jeff Hall	40	60	18	15	270
Brian Virost	20	40	−2	−5	10
Greg Fish	30	60	8	15	120
Susan Welch	10	30	−12	−15	180
Carlos Ramirez	10	40	−12	−5	60
Rich Niles	20	40	−2	−5	10
Mike Kiel	20	50	−2	5	−10
Mark Reynolds	20	30	−2	−15	30
Soni Jones	30	70	8	25	200
					$\overline{900}$

$$r = \frac{\Sigma(X - \bar{X})(Y - \bar{Y})}{(n - 1)s_x s_y} = \frac{900}{(10 - 1)(9.189)(14.337)} = 0.759$$

How do we interpret a correlation of 0.759?
First, it is positive, so we see there is a direct relationship between the number of sales calls and the number of copiers sold. The value of 0.759 is fairly close to 1.00, so we conclude that the association is strong.

However, does this mean that more sales calls *cause* more sales?
No, we have not demonstrated cause and effect here, only that the two variables—sales calls and copiers sold—are related.

Coefficient of Determination (r^2) – Copier Sales Example

- The coefficient of determination, r^2 ,is 0.576, found by $(0.759)^2$

- This is a proportion or a percent; we can say that 57.6 percent of the variation in the number of copiers sold is explained, or accounted for, by the variation in the number of sales calls.

Testing the Significance of the Correlation Coefficient

H_0: ρ = 0 (the correlation in the population is 0)
H_1: $\rho \neq 0$ (the correlation in the population is not 0)

Reject H_0 if:

$t > t_{\alpha/2,n-2}$ or $t < -t_{\alpha/2,n-2}$

$$t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}}$$ with $n-2$ degrees of freedom

Testing the Significance of the Correlation Coefficient – Copier Sales Example

H_0: ρ = 0 (the correlation in the population is 0)
H_1: $\rho \neq 0$ (the correlation in the population is not 0)

Reject H_0 if:

$t > t_{\alpha/2,n-2}$ or $t < -t_{\alpha/2,n-2}$

$t > t_{0.025,8}$ or $t < -t_{0.025,8}$

$t > 2.306$ or $t < -2.306$

Region of rejection (there is correlation) .025 H_0 not rejected (no correlation in population)   Region of rejection (there is correlation) .025

−2.306   0   2.306   Scale of t
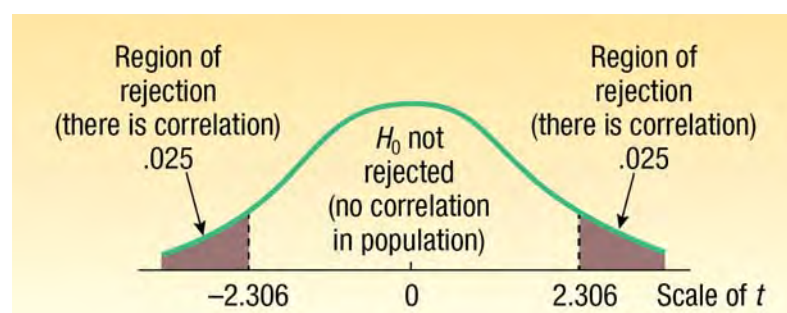
Testing the Significance of the Correlation Coefficient – Copier Sales Example
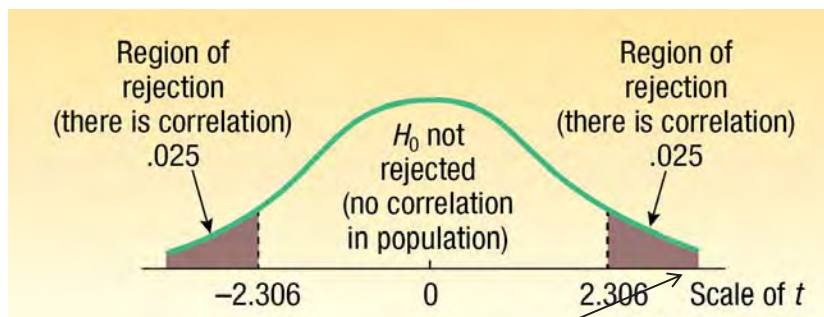
Computing t, we get

$$t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}} = \frac{.759\sqrt{10-2}}{\sqrt{1-.759^2}} = 3.297$$

The computed t (3.297) is within the rejection region, therefore, we will reject H_0. This means the correlation in the population is not zero. From a practical standpoint, it indicates to the sales manager that there is correlation with respect to the number of sales calls made and the number of copiers sold in the population of salespeople.

Linear Regression Model

GENERAL FORM OF LINEAR REGRESSION EQUATION $\hat{Y} = a + bX$

where

$\hat{Y}$ read Y hat, is the estimated value of the Y variable for a selected X value.

a is the Y-intercept. It is the estimated value of Y when $X = 0$. Another way to put it is: a is the estimated value of Y where the regression line crosses the Y-axis when X is zero.

b is the slope of the line, or the average change in $\hat{Y}$ for each change of one unit (either increase or decrease) in the independent variable X.

X is any value of the independent variable that is selected.

Computing the Slope of the Line and the Y-intercept

SLOPE OF THE REGRESSION LINE

$$b = r\frac{s_y}{s_x}$$

where

r is the correlation coefficient.

s_y is the standard deviation of Y (the dependent variable).

s_x is the standard deviation of X (the independent variable).

Y-INTERCEPT

$$a = \overline{Y} - b\overline{X}$$

where

$\overline{Y}$ is the mean of Y (the dependent variable).

$\overline{X}$ is the mean of X (the independent variable).

Regression Analysis

In regression analysis we use the independent variable (X) to estimate the dependent variable (Y).

- The relationship between the variables is linear.
- Both variables must be at least interval scale.
- The least squares criterion is used to determine the equation.

REGRESSION EQUATION An equation that expresses the linear relationship between two variables.

LEAST SQUARES PRINCIPLE Determining a regression equation by minimizing the sum of the squares of the vertical distances between the actual *Y values and* the predicted values of *Y.*

Regression Analysis – Least Squares Principle

- The least squares principle is used to obtain *a* and *b.*
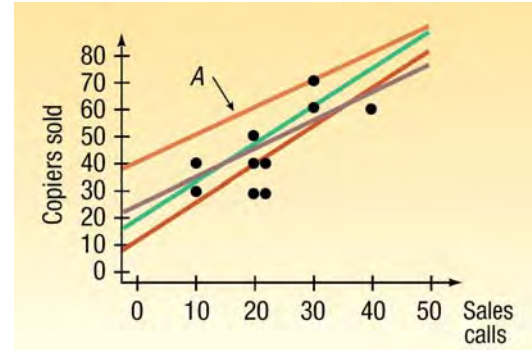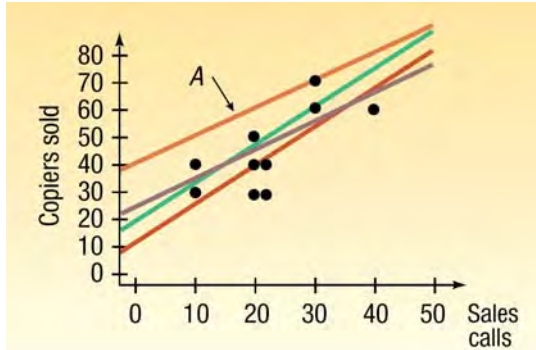
- The equations to determine *a* and *b* are:

$$b = \frac{n(\Sigma XY) - (\Sigma X)(\Sigma Y)}{n(\Sigma X^2) - (\Sigma X)^2}$$

$$a = \frac{\Sigma Y}{n} - b\frac{\Sigma X}{n}$$

Regression Equation - Example

Recall the example involving Copier Sales of America. The sales manager gathered information on the number of sales calls made and the number of copiers sold for a random sample of 10 sales representatives. Use the least squares method to determine a linear equation to express the relationship between the two variables.

What is the expected number of copiers sold by a representative who made 20 calls?

Sales Representative	Number of Sales Calls	Number of Copiers Sold
Tom Keller	20	30
Jeff Hall	40	60
Brian Virost	20	40
Greg Fish	30	60
Susan Welch	10	30
Carlos Ramirez	10	40
Rich Niles	20	40
Mike Kiel	20	50
Mark Reynolds	20	30
Soni Jones	30	70

Finding the Regression Equation - Example

Step 1 – Find the slope (*b*) of the line

$$b = r\left(\frac{s_y}{s_x}\right) = .759\left(\frac{14.337}{9.189}\right) = 1.1842$$

Step 2 – Find the *y*-intercept (*a*)

$$a = \overline{Y} - b\overline{X} = 45 - 1.1842(22) = 18.9476$$

The regression equation is :

$$\hat{Y} = a + bX$$

$$\hat{Y} = 18.9476 + 1.1842X$$

$$\hat{Y} = 18.9476 + 1.1842(20)$$

$$\hat{Y} = 42.6316$$

Computing the Estimates of Y

Step 1 – Using the regression equation, substitute the value of each X to solve for the estimated sales

Sales Representative	Sales Calls (X)	Estimated Sales ($\hat{Y}$)	Sales Representative	Sales Calls (X)	Estimated Sales ($\hat{Y}$)
Tom Keller	20	42.6316	Carlos Ramirez	10	30.7896
Jeff Hall	40	66.3156	Rich Niles	20	42.6316
Brian Virost	20	42.6316	Mike Kiel	20	42.6316
Greg Fish	30	54.4736	Mark Reynolds	20	42.6316
Susan Welch	10	30.7896	Soni Jones	30	54.4736

Tom Keller

$$\hat{Y} = 18.9476 + 1.1842X$$

$$\hat{Y} = 18.9476 + 1.1842(20)$$

$$\hat{Y} = 42.6316$$

Soni Jones

$$\hat{Y} = 18.9476 + 1.1842X$$

$$\hat{Y} = 18.9476 + 1.1842(30)$$

$$\hat{Y} = 54.4736$$

Plotting the Estimated and the Actual Y's

$(X = 40, \hat{Y} = 66.3156)$

$(X = 20, \hat{Y} = 42.6316)$

Copiers sold

Sales calls
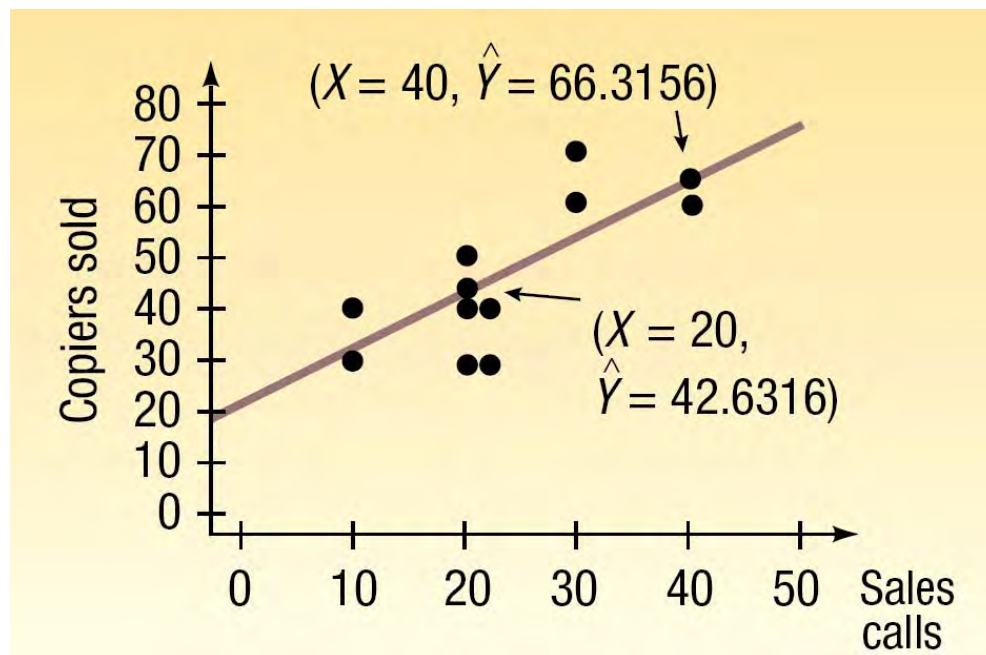
1-3

The Standard Error of Estimate

- The standard error of estimate measures the scatter, or dispersion, of the observed values around the line of regression
- Formulas used to compute the standard error

$$= \sqrt{\frac{(Y - \hat{Y})^2}{2}}$$

$$= \sqrt{\frac{Y^2 - a\ Y - b\ XY}{2}}$$

1-

Standard Error of the Estimate - Example

Recall the example involving Copier Sales of America. The sales manager determined the least squares regression equation is given below.

Determine the standard error of estimate as a measure of how well the values fit the regression line.

Sales Representative	Actual Sales, (Y)	Estimated Sales, (Ŷ)	Deviation, (Y − Ŷ)	Deviation Squared, (Y − Ŷ)²
Tom Keller	30	42.6316	−12.6316	159.557
Jeff Hall	60	66.3156	−6.3156	39.887
Brian Virost	40	42.6316	−2.6316	6.925
Greg Fish	60	54.4736	5.5264	30.541
Susan Welch	30	30.7896	−0.7896	0.623
Carlos Ramirez	40	30.7896	9.2104	84.831
Rich Niles	40	42.6316	−2.6316	6.925
Mike Kiel	50	42.6316	7.3684	54.293
Mark Reynolds	30	42.6316	−12.6316	159.557
Soni Jones	70	54.4736	15.5264	241.069
			0.0000	784.211

$$\hat{Y} = 18.9476 + 1.1842X$$

$$= \sqrt{\frac{(Y - \hat{Y})^2}{2}}$$

$$= \sqrt{\frac{784.211}{10 - 2}} = 9.901$$

Standard Error of the Estimate - Excel

Assumptions Underlying Linear Regression

For each value of X, there is a group of Y values, and these

- Y values are *normally distributed*. The *means* of these normal distributions of Y values all lie on the straight line of regression.
- The *standard deviations* of these normal distributions are equal.
- The Y values are statistically independent. This means that in the selection of a sample, the Y values chosen for a particular X value do not depend on the Y values for any other X values.
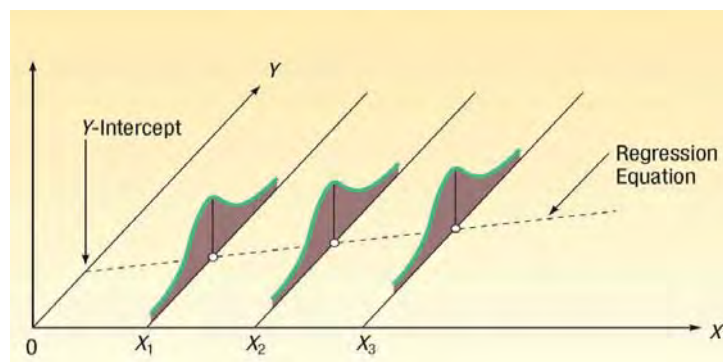
Confidence Interval and Prediction Interval Estimates of Y

A **confidence interval** reports the *mean* value of Y for a given X.
A **prediction interval** reports the *range of values* of Y for a *particular* value of X.

CONFIDENCE INTERVAL FOR THE MEAN OF Y, GIVEN X	$\hat{Y} \pm t(s_{y \cdot x})\sqrt{\dfrac{1}{n} + \dfrac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$	[13–7]

PREDICTION INTERVAL FOR Y, GIVEN X	$\hat{Y} \pm ts_{y \cdot x}\sqrt{1 + \dfrac{1}{n} + \dfrac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$	[13–8]

Confidence Interval Estimate (Example)

☐e return to the ☐opier Sales of ☐merica illustration☐☐etermine a ☐☐percent confidence interval for all sales representatives ☐ho ma☐e 2☐ calls☐

CONFIDENCE INTERVAL FOR THE MEAN OF Y, GIVEN X

$$\hat{Y} \pm t(s_{y \cdot x})\sqrt{\frac{1}{n} + \frac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$$ [13–7]

where

$\hat{Y}$ is the predicted value for any selected X value.
X is any selected value of X.
$\bar{X}$ is the mean of the Xs, found by $\Sigma X / n$.
n is the number of observations.
$s_{y \cdot x}$ is the standard error of estimate.
t is the value of t from Appendix B.2 with $n - 2$ degrees of freedom.

Confidence Interval Estimate (Example)

CONFIDENCE INTERVAL FOR THE MEAN OF Y, GIVEN X

$$\hat{Y} \pm t(s_{y \cdot x})\sqrt{\frac{1}{n} + \frac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$$ [13–7]

Step 1 – ☐ompute the point estimate of ☐

☐n other ☐ords, determine the number of copiers ☐e e☐pect a sales representative to sell if he or she ma☐es 2☐ calls☐

T☐e re☐ression e☐☐☐☐ion is ☐

$$\hat{Y} = 18.9476 + 1.1842X$$

$$\hat{Y} = 18.9476 + 1.1842(25)$$

$$\hat{Y} = 48.5526$$

| CONFIDENCE INTERVAL FOR THE MEAN OF Y, GIVEN X | $\hat{Y} \pm t(s_{y \cdot x})\sqrt{\dfrac{1}{n} + \dfrac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$ | [13–7] |

Step 2 – Find the value of t

- To find the t value, we need to first know the number of degrees of freedom. In this case the degrees of freedom is $n - 2 = 10 - 2 = 8$.

- We set the confidence level at 95 percent. To find the value of t, move down the left-hand column of Appendix B.2 to 8 degrees of freedom, then move across to the column with the 95 percent level of confidence.

- The value of t is 2.306.

| CONFIDENCE INTERVAL FOR THE MEAN OF Y, GIVEN X | $\hat{Y} \pm t(s_{y \cdot x})\sqrt{\dfrac{1}{n} + \dfrac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$ | [13–7] |

Step 3 – Compute $X - \bar{X}^2$ and $X - \bar{X}^2$

Sales Representative	Sales Calls, (X)	Copier Sales, (Y)	(X − X̄)	(X − X̄)²
Tom Keller	20	30	−2	4
Jeff Hall	40	60	18	324
Brian Virost	20	40	−2	4
Greg Fish	30	60	8	64
Susan Welch	10	30	−12	144
Carlos Ramirez	10	40	−12	144
Rich Niles	20	40	−2	4
Mike Kiel	20	50	−2	4
Mark Reynolds	20	30	−2	4
Soni Jones	30	70	8	64
			0	760

Confidence Interval Estimate – Example

CONFIDENCE INTERVAL
FOR THE MEAN OF Y,
GIVEN X

$$\hat{Y} \pm t(s_{y \cdot x})\sqrt{\frac{1}{n} + \frac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$$ [13–7]

Step □ – Use the formula above by substituting the numbers computed in previous slides

$$\text{Confidence Interval} = \hat{Y} \pm ts_{y \cdot x}\sqrt{\frac{1}{n} + \frac{(X - \bar{X})^2}{\Sigma(X - \bar{X})^2}}$$

$$= 48.5526 \pm 2.306(9.901)\sqrt{\frac{1}{10} + \frac{(25 - 22)^2}{760}}$$

$$= 48.5526 \pm 7.6356$$

□hus, the □□ percent confidence interval for the average sales of all sales representatives □ho ma□e 2□ calls is from □□□□1□□□ up to □□□1882 copiers□

1-□□

□e□i□tion □nte□□a□ Estimate □E□amp□e

□e return to the □opier Sales of □merica illustration□□etermine a □□ percent prediction interval for Sheila □a□er, a □est □oast sales representative □ho made 2□ calls□

1-□□

Prediction Interval Estimate (Example)

PREDICTION INTERVAL FOR Y, GIVEN X	$\hat{Y} \pm ts_{y \cdot x} \sqrt{1 + \dfrac{1}{n} + \dfrac{(X - \overline{X})^2}{\Sigma(X - \overline{X})^2}}$	[13–8]

Step 1 – Compute the point estimate of Y

In other words, determine the number of copiers we expect a sales representative to sell if he or she makes 25 calls.

The regression equation is :

$$\hat{Y} = 18.9476 + 1.1842X$$

$$\hat{Y} = 18.9476 + 1.1842(25)$$

$$\hat{Y} = 48.5526$$

1-41

Prediction Interval Estimate (Example)

PREDICTION INTERVAL FOR Y, GIVEN X	$\hat{Y} \pm ts_{y \cdot x} \sqrt{1 + \dfrac{1}{n} + \dfrac{(X - \overline{X})^2}{\Sigma(X - \overline{X})^2}}$	[13–8]

Step 2 – Using the information computed earlier in the confidence interval estimation example, use the formula above.

$$\text{Prediction Interval} = \hat{Y} \pm ts_{y \cdot x} \sqrt{1 + \frac{1}{n} + \frac{(X - \overline{X})^2}{\Sigma(X - \overline{X})^2}}$$

$$= 48.5526 \pm 2.306(9.901) \sqrt{1 + \frac{1}{10} + \frac{(25 - 22)^2}{760}}$$

$$= 48.5526 \pm 24.0746$$

If Sheila Baker makes 25 sales calls, the number of copiers she will sell will be between about 25 and 73 copiers.

1-42

Confidence and Prediction Intervals – Minitab Illustration
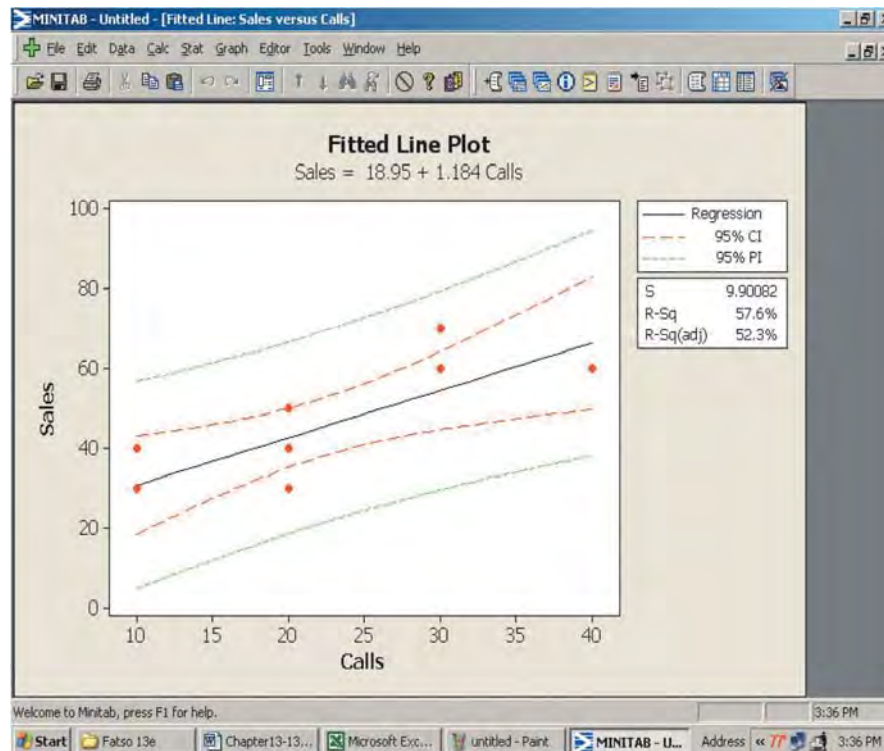
Applying statistical techniques in decision making

Part 4
Multiple Regressions

Multiple Regression Analysis

The general multiple regression with k independent variables is given by:

$$\hat{Y} = a + b_1X_1 + b_2X_2 + b_3X_3 + \cdots + b_kX_k$$

$X_1 \ldots X_k$ are the independent variables

a is the Y-intercept

b_1 is the net change in Y for each unit change in X_1 holding $X_2 \ldots X_k$ constant. It is called a partial regression coefficient or just a regression coefficient.

The least squares criterion is used to develop this equation.

Determining b_1, b_2, etc. is very tedious, a software package such as Excel or MINITAB is recommended.

1-2
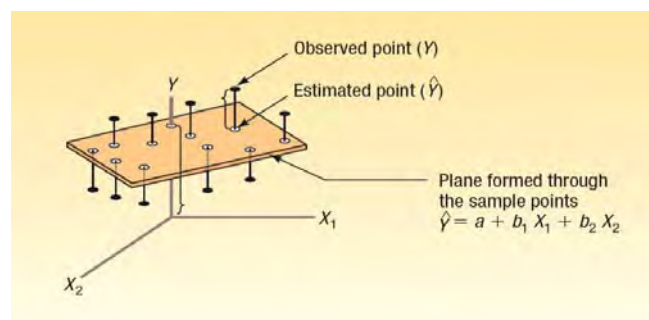
Multiple Linear Regression – Example

Salsberry Realty sells homes along the east coast of the United States. One of the questions most frequently asked by prospective buyers is: If we purchase this home, how much can we expect to pay to heat it during the winter? The research department at Salsberry has been asked to develop some guidelines regarding heating costs for single-family homes.

Three variables are thought to relate to the heating costs: (1) the mean daily outside temperature, (2) the number of inches of insulation in the attic, and (3) the age in years of the furnace.

selected a random sample of 20 recently sold homes. It determined the cost to heat each home last January, as well

Home	$\hat{Y}$ Heating Cost ($)	X_1 Mean Outside Temperature (°F)	X_2 Attic Insulation (inches)	X_3 Age of Furnace (years)
1	$250	35	3	6
2	360	29	4	10
3	165	36	7	3
4	43	60	6	9
5	92	65	5	6
6	200	30	5	5
7	355	10	6	7
8	290	7	10	10
9	230	21	9	11
10	120	55	2	5
11	73	54	12	4
12	205	48	5	1
13	400	20	5	15
14	320	39	4	7
15	72	60	8	6
16	272	20	5	8
17	94	58	7	3
18	190	40	8	11
19	235	27	9	8
20	139	30	7	5

Multiple Linear Regression – Minitab Example

Regression outputs produced by Minitab and Excel

a

b_1

b_2

b_3
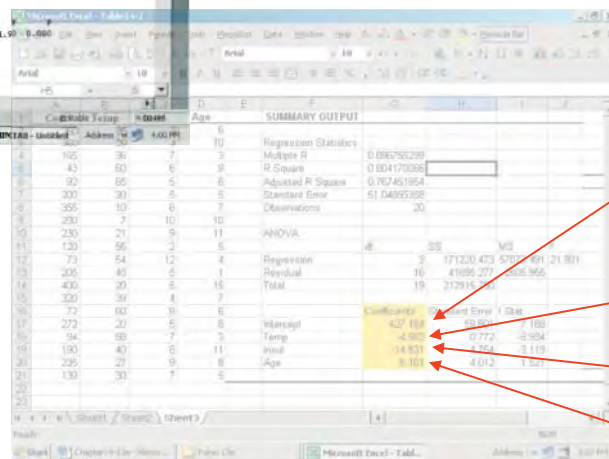
The Multiple Regression Equation – Interpreting the Regression Coefficients and Applying the Model for Estimation

$$\hat{Y} = 427.194 - 4.583X_1 - 14.831X_2 + 6.101X_3$$

Interpreting the Regression Coefficients

The regression coefficient for mean outside temperature, X_1, is 4.583. The coefficient is negative – as the outside temperature increases, the cost to heat the home decreases. For every unit increase in temperature, holding the other two independent variables constant, monthly heating cost is expected to decrease by $4.583.

The attic insulation variable, X_2, also shows an inverse relationship (negative coefficient). The more insulation in the attic, the less the cost to heat the home. For each additional inch of insulation, the cost to heat the home is expected to decline by $14.83 per month.

The age of the furnace variable shows a direct relationship. With an older furnace, the cost to heat the home increases. For each additional year older the furnace is, the cost is expected to increase by $6.101 per month.

Applying the Model for Estimation

What is the estimated heating cost for a home if the mean outside temperature is 30 degrees, there are 5 inches of insulation in the attic, and the furnace is 10 years old?

$$\hat{Y} = 427.194 - 4.583(30) - 14.831(5) + 6.101(10) = 276.56$$

Multiple Standard Error of Estimate

The multiple standard error of estimate is a measure of the effectiveness of the regression equation.

- It is measured in the same units as the dependent variable.

- It is difficult to determine what is a large value and what is a small value of the standard error.

Multiple Regression and Correlation Assumptions

- The independent variables and the dependent variable have a linear relationship. The dependent variable must be continuous and at least interval-scale.

- The residual must be the same for all values of . When this is the case, we say the difference exhibits homoscedasticity.

- The residuals should follow the normal distributed with mean 0.

- Successive values of the dependent variable must be uncorrelated.

Coefficient of Multiple Determination (R^2)

COEFFICIENT OF MULTIPLE DETERMINATION The percent of variation in the dependent variable, $\hat{Y}$, explained by the set of independent variables, $X_1, X_2, X_3, \ldots X_k$.

Coefficient of Multiple Determination:
1. Symbolized by R^2.
2. Ranges from 0 to 1.
3. Cannot assume negative values.
4. Easy to interpret.

The Adjusted R^2
1. The number of independent variables in a multiple regression equation makes the coefficient of determination larger.
2. If the number of variables, k, and the sample size, n, are equal, the coefficient of determination is 1.0.
3. To balance the effect that the number of independent variables has on the coefficient of multiple determination, adjusted R^2 is used instead.
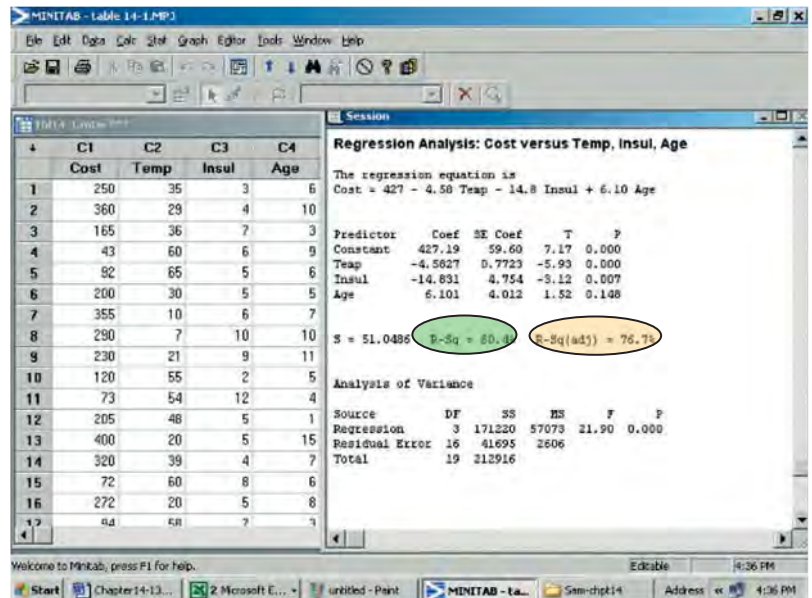
Global Test: Testing the Multiple Regression Model

The global test is used to investigate whether any of the independent variables have significant coefficients.

The hypotheses are:

$$H_0 : \beta_1 = \beta_2 = \ldots = \beta_k = 0$$
$$H_1 : \text{Not all } \beta \text{ s equal } 0$$

Decision Rule:

Reject H_0 if $F > F_{\alpha, k, n-k-1}$

Finding the Computed and Critical F
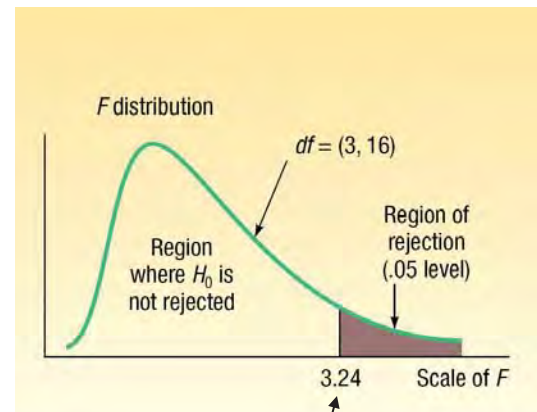
$F_{\alpha,k,n-k-1}$

$F_{.05,3,16}$
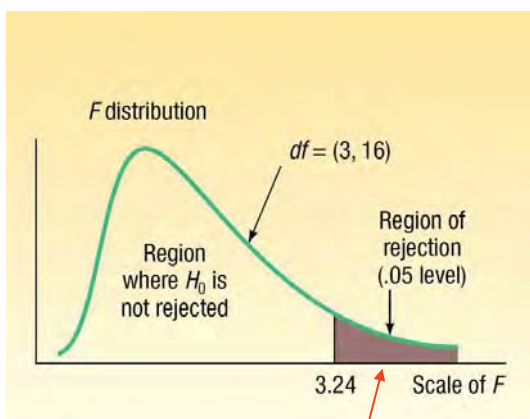
Interpretation

- The computed value of F is 21.90, which is in the rejection region.
- The null hypothesis that all the multiple regression coefficients are zero is therefore rejected.
- Interpretation: some of the independent variables (amount of insulation, etc.) do have the ability to explain the variation in the dependent variable (heating cost).
- Logical question – which ones?

Evaluating Individual Regression Coefficients ($\beta_i = 0$)

- This test is used to determine which independent variables have nonzero regression coefficients.
- The variables that have zero regression coefficients are usually dropped from the analysis.
- The test statistic is the t distribution with $n-k-1$ degrees of freedom.
- The hypothesis test is as follows:

$$H_0: \beta_i = 0$$
$$H_1: \beta_i \neq 0$$
$$\text{Reject } H_0 \text{ if } t > t_{\alpha/2,n-k-1} \ or \ t < -t_{\alpha/2,n-k-1}$$

$$t = \frac{b_i - 0}{s_{b_i}}$$

Critical t for the Slopes

For temperature:	For insulation:	For furnace age:
$H_0: \beta_1 = 0$	$H_0: \beta_2 = 0$	$H_0: \beta_3 = 0$
$H_1: \beta_1 \neq 0$	$H_1: \beta_2 \neq 0$	$H_1: \beta_3 \neq 0$

□□□□□□$_0$ □□:

$$\frac{\alpha/2, \ k \ 1}{0}$$
$$\frac{\alpha/2, \ k \ 1}{0}$$

$$\frac{\alpha/2, \ k \ 1}{0}$$
$$\frac{\alpha/2, \ k \ 1}{0}$$

$$\frac{0}{.0\square2\square20 \ \square1}$$
$$\frac{0}{.0\square2\square20 \ \square1}$$

$$\frac{0}{.02\square\square\square}$$
$$\frac{0}{.02\square\square\square}$$

$$\frac{0}{2.120}$$
$$\frac{0}{2.120}$$

Region of rejection .025   Do not reject H_0 Region of rejection .025

.95

0   Scale of t

Critical value   Critical value

-2.120   **2.120**

Computed t for the Slopes

For temperature:

$H_0: \beta_1 = 0$

$H_1: \beta_1 \neq 0$

For insulation:

$H_0: \beta_2 = 0$

$H_1: \beta_2 \neq 0$

For furnace age:

$H_0: \beta_3 = 0$

$H_1: \beta_3 \neq 0$

$$t = \frac{b_i - 0}{s_{b_i}}$$

Conclusion on Significance of Slopes
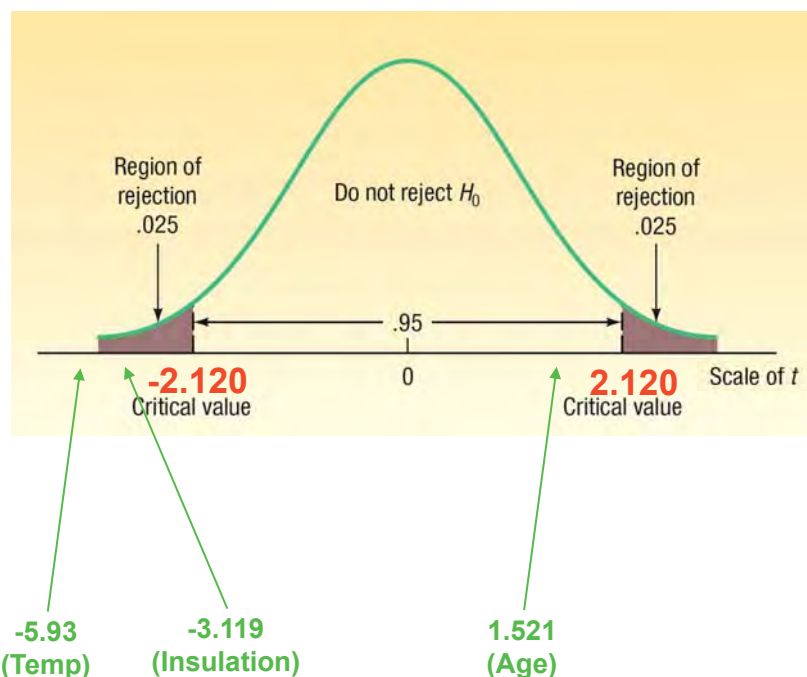
Region of rejection .025

Do not reject H_0

Region of rejection .025

.95

-2.120
Critical value

0

2.120
Critical value

Scale of t

-5.93
(Temp)

-3.119
(Insulation)

1.521
(Age)

New Regression Model without Variable "Age" – Minitab
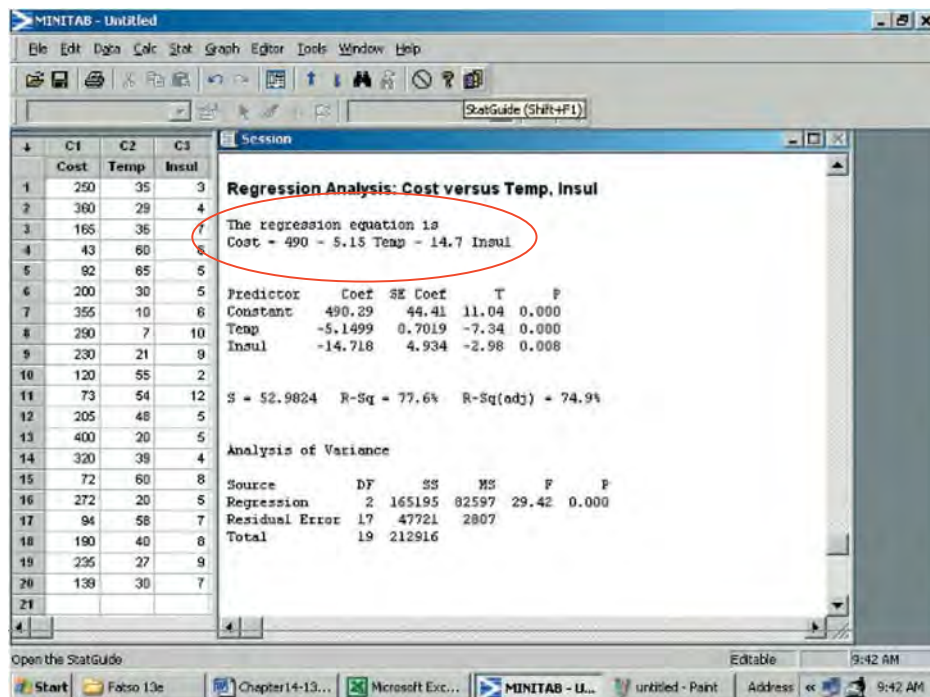
New Regression Model without Variable "Age" – Minitab

The new regression equation is:

$$\hat{Y} = 490.29 - 5.1499X_1 - 14.718X_2$$

The details of the global test are as follows:

H_0: $\beta_1 = \beta_2 = 0$
H_1: Not all of the β_j's $= 0$

The F distribution is the test statistic and there are $k = 2$ degrees of freedom in the numerator and $n - (k + 1) = 20 - (2 + 1) = 17$ degrees of freedom in the denominator. Using the .05 significance level and Appendix B.4, the decision rule is to reject H_0 if F is greater than 3.59. We compute the value of F as follows:

$$F = \frac{SSR/k}{SSE/(n - (k + 1))} = \frac{165,195/2}{47,721/(20 - (2 + 1))} = 29.42$$

Testing the New Model for Significance

F distribution

d.f. (2,17)

Region
where H_0 is
not rejected

Region of
rejection
(.05 level)

Scale of F

**3.5
9**

Computed F = 29.42
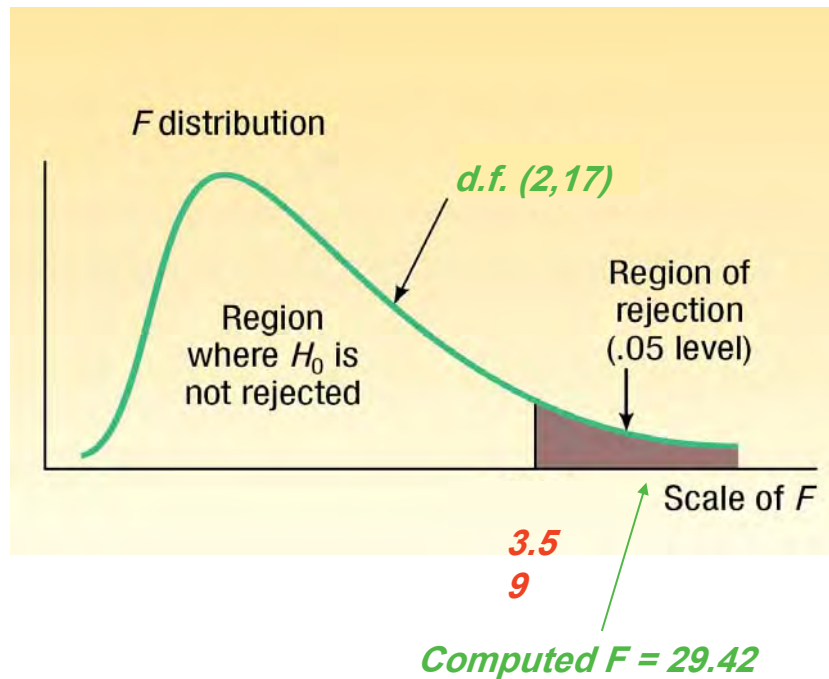
Critical t-stat for the New Slopes

For temperature:

$H_0: \beta_1 = 0$

$H_1: \beta_1 \neq 0$

For insulation:

$H_0: \beta_2 = 0$

$H_1: \beta_2 \neq 0$

□□□□□□$_0$ □□:

$$\frac{0}{\alpha\, □2□\ k\ 1} \qquad \frac{0}{\alpha\, □2□\ k\ 1}$$

$$\frac{0}{.0□□2□20\ 2\ 1} \qquad \frac{0}{.0□□2□20\ 2\ 1}$$

$$\frac{0}{.02□□1□} \qquad \frac{0}{.02□□1□}$$

$$\frac{0}{2.110} \qquad \frac{0}{2.110}$$

Region of
rejection
.025

Do not reject H_0

Region of
rejection
.025

.95

0

Scale of t

Critical value

Critical value

-2.110

2.110
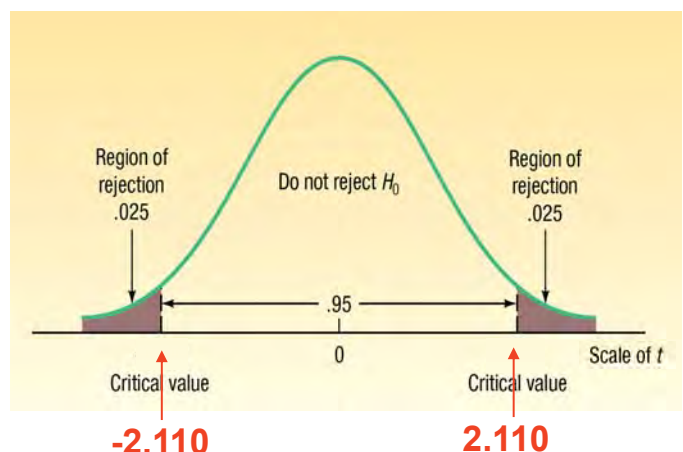
Conclusion on Significance of New Slopes

Region of rejection .025 Do not reject H_0 **Region of rejection** .025

.95

-2.110 Critical value 0 **2.110** Critical value Scale of t

-7.34 (Temp) **-2.98 Insulation**
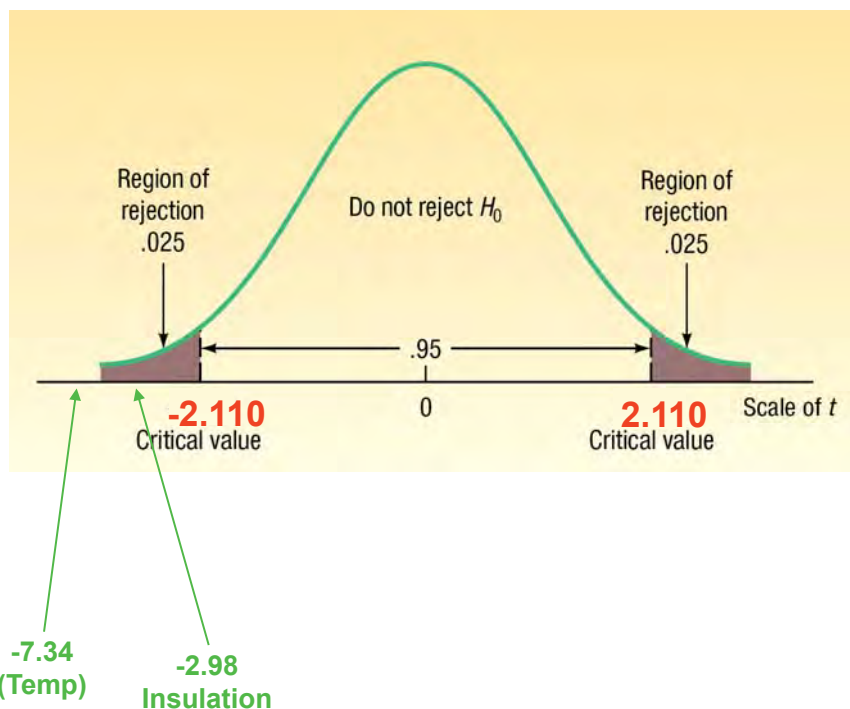
Evaluating the Assumptions of Multiple Regression

1. **There is a linear relationship.** □□t is, t□e□e is □ st□□i□□t-line □el□tions□i□ □et□een t□e □e□en□ent □□i□□le □n□ t□e set of in□e□en□ent □□i□□les□

□□**The variation in the residuals is the same for both large and small values of the estimated Y** □o □ut it □not□e□□□□, t□e □esi□u□ is un□el□te□ □□et□e□ t□e esti□□te□ □ is l□□□e o□ s□□ll□

□□**The residuals follow the normal probability distribution.**

□□**The independent variables should not be correlated.** □□□t is, □e □oul□ like to select □ set of in□e□en□ent □□i□□les t□□t □□e not t□e□ sel□es co□□el□te□□□

□□**The residuals are independent.** □□is □e□ns t□□t successi□e o□se□□□tions of t□e □e□en□ent □□i□□le □□e not co□□el□te□□□□□is □ssu□□tion is often □iol□te□ □□en ti□e is in□ol□e□ □it□ t□e s□□□le□ o□se□□□tions□

□ □esi□u□ is t□e □iffe□ence □et□een t□e □ctu□ □□lue of □ □n□ t□e □□e□icte□ □□lue of □□□

Scatter and Residual Plots

A plot of the residuals on the vertical corresponding $\hat{y}$ values is used for showing that there are no trends or patterns in the residuals.
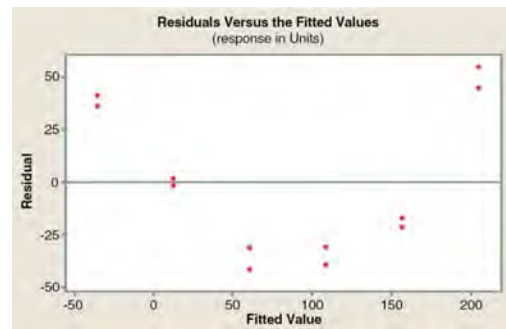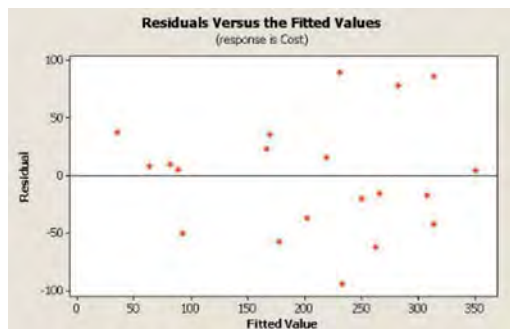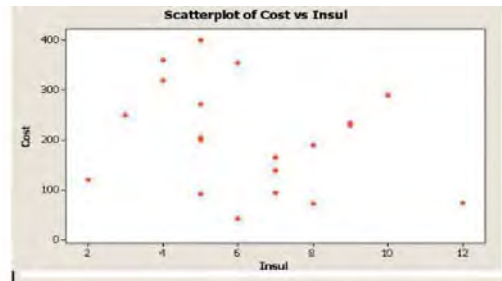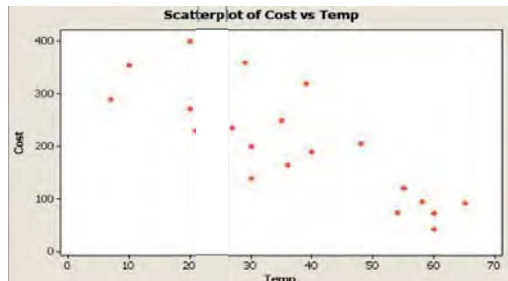
Distribution of Residuals
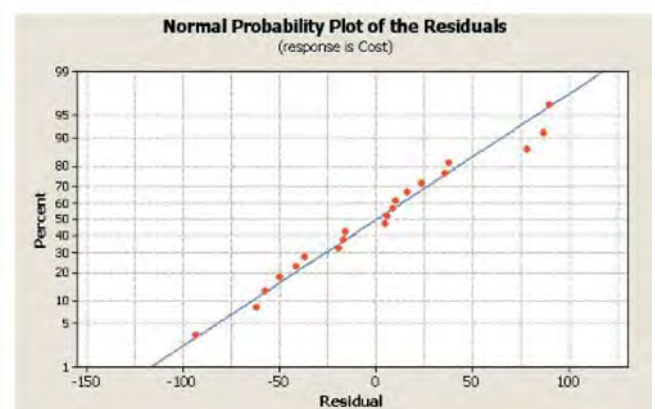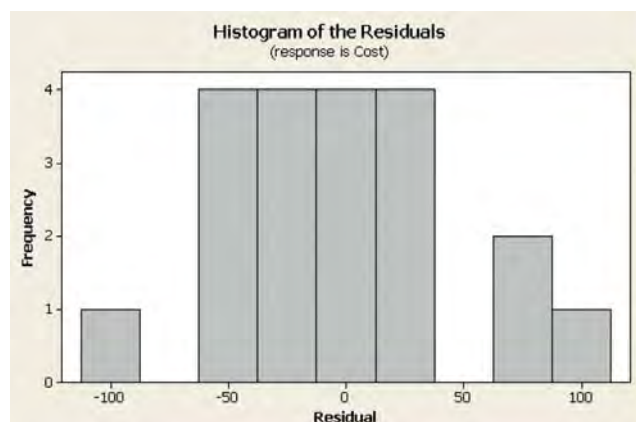
Both Minitab and Excel offer another diagram that helps to evaluate the assumption of normally distributed residuals. It is called a **normal probability plot** and is shown to the right of the histogram.

Multicollinearity

- Multicollinearity exists when independent variables (X's) are correlated.

- Effects of multicollinearity on the model:

  1. An independent variable known to be an important predictor ends up having a regression coefficient that is not significant.

  2. A regression coefficient that should have a positive sign turns out to be negative, or vice versa.

  3. When an independent variable is added or removed, there is a drastic change in the values of the remaining regression coefficients.

- However, correlated independent variables do not affect a multiple regression equation's ability to predict the dependent variable (Y).

1-

Variance Inflation Factor

- A general rule is if the correlation between two independent variables is between -0.70 and 0.70 there likely is not a problem using both of the independent variables.
- A more precise test is to use the **variance inflation factor (VIF).**
- A VIF > 10 is unsatisfactory. Remove that independent variable from the analysis.
- The value of VIF is found as follows:

$$VIF = \frac{1}{1 - R_j^2}$$

The term R_j^2 refers to the coefficient of determination, where the selected independent variable is used as a dependent variable and the remaining independent variables are used as independent variables.

1-

Multicollinearity – Example

Refer to the data in the table, which relates the heating cost to the independent variables outside temperature, amount of insulation, and age of furnace.

Develop a correlation matrix for all the independent variables.

Does it appear there is a problem with multicollinearity?

Find and interpret the variance inflation factor for each of the independent variables.

Home	Heating Cost ($)	Mean Outside Temperature (°F)	Attic Insulation (inches)	Age of Furnace (years)
1	$250	35	3	6
2	360	29	4	10
3	165	36	7	3
4	43	60	6	9
5	92	65	5	6
6	200	30	5	5
7	355	10	6	7
8	290	7	10	10
9	230	21	9	11
10	120	55	2	5
11	73	54	12	4
12	205	48	5	1
13	400	20	5	15
14	320	39	4	7
15	72	60	8	6
16	272	20	5	8
17	94	58	7	3
18	190	40	8	11
19	235	27	9	8
20	139	30	7	5

Correlation Matrix of the variables

```
              Cost       Temp      Insul
Temp       -0.812
Insul      -0.257    -0.103
Age         0.537    -0.486      0.064

Cell Contents:  Pearson correlation
```

1-□□

VIF – Minitab Example

```
Regression Analysis: Temp versus Insul, Age

The regression equation is
Temp = 58.0 - 0.51 Insul - 2.51 Age

Predictor     Coef     SE Coef        T        P     VIF
Constant     57.99       12.35     4.70    0.000
Insul       -0.509        1.488    -0.34    0.737     1.0
Age         -2.509        1.103    -2.27    0.036     1.0

S = 16.0311   R-Sq = 24.1%   R-Sq(adj) = 15.2%

Analysis of Variance
Source           DF        SS       MS       F       P
Regression        2    1390.3    695.1    2.70   0.096
Residual Error   17    4368.9    257.0
Total            19    5759.2
```

Coefficient of Determination

$$VIF = \frac{1}{1-R_1^2} = \frac{1}{1-.241} = 1.32$$

The VIF value of 1.32 is less than the upper limit of 10 this indicates that the independent variable temperature is not strongly correlated with the other.

1-□0

Independence Assumption

- The fifth assumption about regression and correlation analysis is that successive residuals should be independent.

- When successive residuals are correlated we refer to this condition as **autocorrelation.** Autocorrelation frequently occurs when the data are collected over a period of time.

Residual Plot versus Fitted Values: Testing the Independence Assumption

- When successive residuals are correlated we refer to this condition as **autocorrelation,** which frequently occurs when the data are collected over a period of time.

- Note the run of residuals above the mean of the residuals, followed by a run below the mean. A scatterplot such as this would indicate possible autocorrelation.
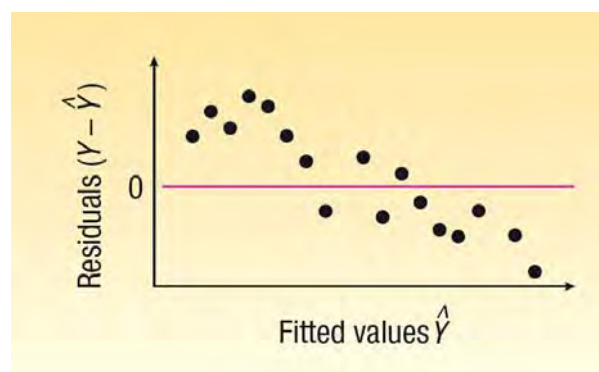
Qualitative Variable - Example

- Frequently we wish to use nominal-scale variables—such as gender, whether the home has a swimming pool, or whether the sports team was the home or the visiting team—in our analysis. These are called **qualitative variables**.

- To use a qualitative variable in regression analysis, we use a scheme of **dummy variables** in which one of the two possible conditions is coded 0 and the other 1.

EXAMPLE

Suppose in the Salsberry Realty example that the independent variable "garage" is added. For those homes without an attached garage, 0 is used; for those homes with an attached garage, a 1 is used. We will refer to the "garage" variable as The data from Table 1 - are entered into the MINITAB system.

Cost, y	Temperature, X_1	Insulation, X_2	Garage, X_4
$250	35	3	0
360	29	4	1
165	36	7	0
43	60	6	0
92	65	5	0
200	30	5	0
355	10	6	1
290	7	10	1
230	21	9	0
120	55	2	0
73	54	12	0
205	48	5	1
400	20	5	1
320	39	4	1
72	60	8	0
272	20	5	1
94	58	7	0
190	40	8	1
235	27	9	0
139	30	7	0

Qualitative Variable - Minitab

Garage is 'dummy' variable
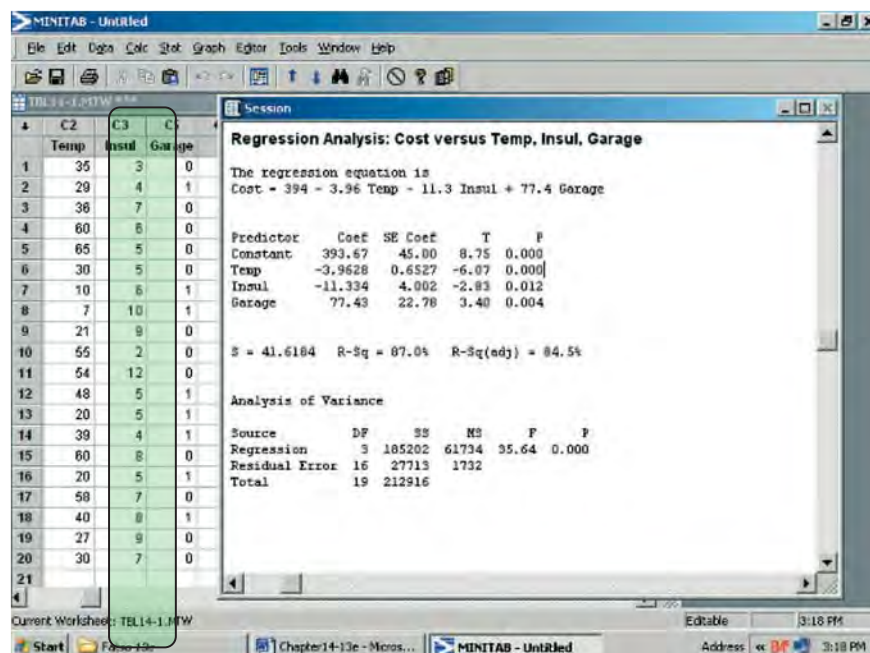
Using the Model for Estimation

What is the effect of the garage variable? Suppose we have two houses exactly alike next to each other in Buffalo, New York; one has an attached garage, and the other does not. Both homes have 3 inches of insulation, and the mean January temperature in Buffalo is 20 degrees.

For the house without an attached garage, a 0 is substituted for in the regression equation. The estimated heating cost is $280.90, found by:

$$\hat{Y} = 394 - 3.96X_1 - 11.3X_2 + 77.4X_4$$
$$= 394 - 3.96(20) - 11.3(3) + 77.4(0) = 280.90 \quad \text{Without garage}$$

For the house with an attached garage, a 1 is substituted for in the regression equation. The estimated heating cost is $358.30, found by:

$$\hat{Y} = 394 - 3.96X_1 - 11.3X_2 + 77.4X_4$$
$$= 394 - 3.96(20) - 11.3(3) + 77.4(1) = 358.30 \quad \text{With garage}$$

Evaluating Individual Regression Coefficients ($\beta_i = 0$)

- This test is used to determine which independent variables have nonzero regression coefficients.
- The variables that have zero regression coefficients are usually dropped from the analysis.
- The test statistic is the t distribution with n-(k+1) or n-k-1 degrees of freedom.
- The hypothesis test is as follows:

> H_0: $\beta_i = 0$
>
> H_1: $\beta_i \neq 0$
>
> Reject H_0 if $t > t_{\alpha/2,n-k-1}$ *or* $t < -t_{\alpha/2,n-k-1}$

$$t = \frac{b_i - 0}{s_{b_i}}$$

Testing Variable "Garage" for Significance

Reject H_0 if :

$t < -t_{\alpha/2, n-k-1}$ $t > t_{\alpha/2, n-k-1}$

$\dfrac{b_i - 0}{s_{b_i}} < -t_{\alpha/2, n-k-1}$ $\dfrac{b_i - 0}{s_{b_i}} > t_{\alpha/2, n-k-1}$

$\dfrac{b_i - 0}{s_{b_i}} < -t_{.05/2, 20-3-1}$ $\dfrac{b_i - 0}{s_{b_i}} > t_{.05/2, 20-3-1}$

$\dfrac{b_i - 0}{s_{b_i}} < -t_{.025, 16}$ $\dfrac{b_i - 0}{s_{b_i}} > t_{.025, 16}$

$\dfrac{b_i - 0}{s_{b_i}} < -2.120$ $\dfrac{b_i - 0}{s_{b_i}} > 2.120$

Region of rejection .025   Do not reject H_0 Region of rejection .025

.95

-2.120 Critical value   0   **2.120** Critical value   Scale of t
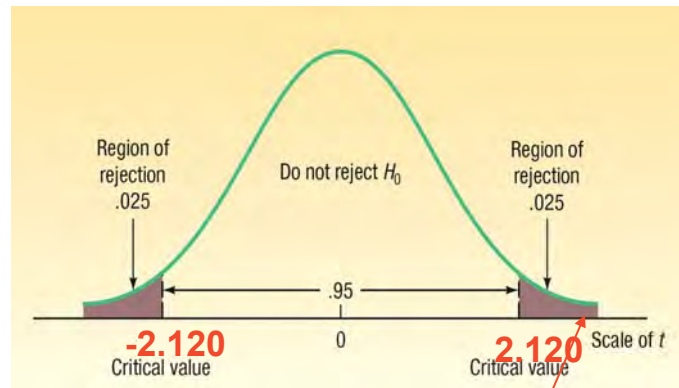
$$t = \frac{b_4 - 0}{s_{b_4}} = \frac{77.43 - 0}{22.78} = 3.40$$

Conclusion: The regression coefficient is not zero. The independent variable garage should be included in the analysis.

Stepwise Regression

> **STEPWISE REGRESSION** A step-by-step method to determine a regression equation that begins with a single independent variable and adds or deletes independent variables one by one. Only independent variables with nonzero regression coefficients are included in the regression equation.

The advantages to the stepwise method are:
1. □nly independent variables with significant regression coefficients are entered into the equation.
2. The steps involved in building the regression equation are clear.
3. It is efficient in finding the regression equation with only significant regression coefficients.
□. The changes in the multiple standard error of estimate and the coefficient of determination are shown.

Stepwise Regression – Minitab Example

The stepwise □INIT□B output for the heating cost problem follows.

Temperature is selected first. This variable explains more of the variation in heating cost than any of the other three proposed independent variables.

□arage is selected next, followed by Insulation.

Regression Models with Interaction

- In Chapter 12 interaction among independent variables was covered. Suppose we are studying weight loss and assume, as the current literature suggests, that diet and exercise are related. So the dependent variable is amount of change in weight and the independent variables are: diet (yes or no) and exercise (none, moderate, significant). We are interested in seeing if those studied who maintained their diet and exercised significantly increased the mean amount of weight lost?

- In regression analysis, interaction can be examined as a separate independent variable. □n interaction prediction variable can be developed by multiplying the data values in one independent variable by the values in another independent variable, thereby creating a new independent variable. □ two-variable model that includes an interaction term is:

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1 X_2$$

Refer to the heating cost example. Is there an interaction between the outside temperature and the amount of insulation? If both variables are increased, is the effect on heating cost greater than the sum of savings from warmer temperature and the savings from increased insulation separately?

Home	Heating Cost ($)	Mean Outside Temperature (°F)	Attic Insulation (inches)	Age of Furnace (years)
1	$250	35	3	6
2	360	29	4	10
3	165	36	7	3
4	43	60	6	9
5	92	65	5	6
6	200	30	5	5
7	355	10	6	7
8	290	7	10	10
9	230	21	9	11
10	120	55	2	5
11	73	54	12	4
12	205	48	5	1
13	400	20	5	15
14	320	39	4	7
15	72	60	8	6
16	272	20	5	8
17	94	58	7	3
18	190	40	8	11
19	235	27	9	8
20	139	30	7	5

Regression Models with Interaction - Example

Creating the Interaction Variable Using the information from the table in the previous slide, an interaction variable is created by multiplying the temperature variable by the insulation.

For the first sampled home the value temperature is 35 degrees and insulation is 3 inches so the value of the interaction variable is 35 × 3 = 105. The values of the other interaction products are found in a similar fashion.

Regression Models with Interaction - Example

The regression equation is:

$$\hat{Y} = 598.070 - 7.811X_1 - 30.161X_2 + 0.385X_1X_2$$

Is the interaction variable significant at 0.05 significance level?

$H_0: \beta_3 = 0$
$H_1: \beta_3 \neq 0$

There is $n - (k + 1) = 20 - (3 + 1) = 16$ degrees of freedom. Using the .05 significance level and a two-tailed test, the critical values of t are -2.120 and 2.120. We reject the null hypothesis if t is less than -2.120 or t is greater than 2.120. From the output, $b_3 = 0.385$ and $s_{b_3} = 0.291$. To find the value of t we use formula (14–6).

$$t = \frac{b_3 - 0}{s_{b_3}} = \frac{0.385 - 0}{0.291} = 1.324$$

END of Part 7

Applying statistical techniques in Decision Making

**Part 8
Time Series
and Forecasting**

Time Series and its Components

TIME SERIES is a collection of data recorded over a period of time (weekly, monthly, quarterly), **an analysis of history, that** can be used by management to make current decisions and plans based on long-term forecasting. It usually assumes **past pattern to continue into the future**

Components of a Time Series

➢ **Secular Trend** – the smooth long term direction of a time series

➢ **Cyclical Variation** – the rise and fall of a time series over periods longer than one year

➢ **Seasonal Variation** – Patterns of change in a time series within a year which tends to repeat each year

➢ **Irregular Variation** – classified into:
  ❑ **Episodic** – unpredictable but identifiable
  ❑ **Residual** – also called chance fluctuation and unidentifiable

Secular Trend – Examples
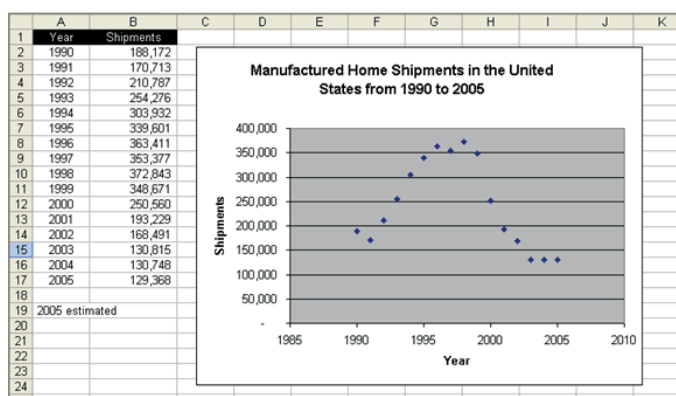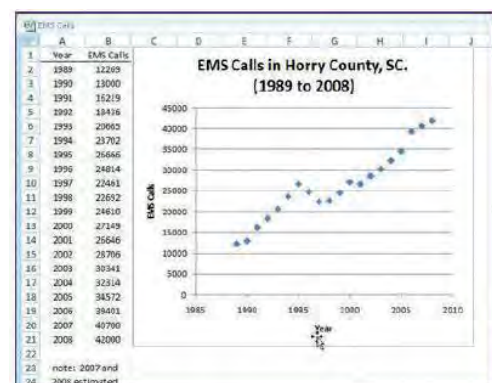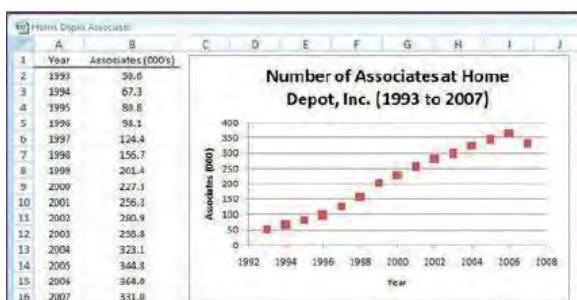
Cyclical Variation – Sample Chart
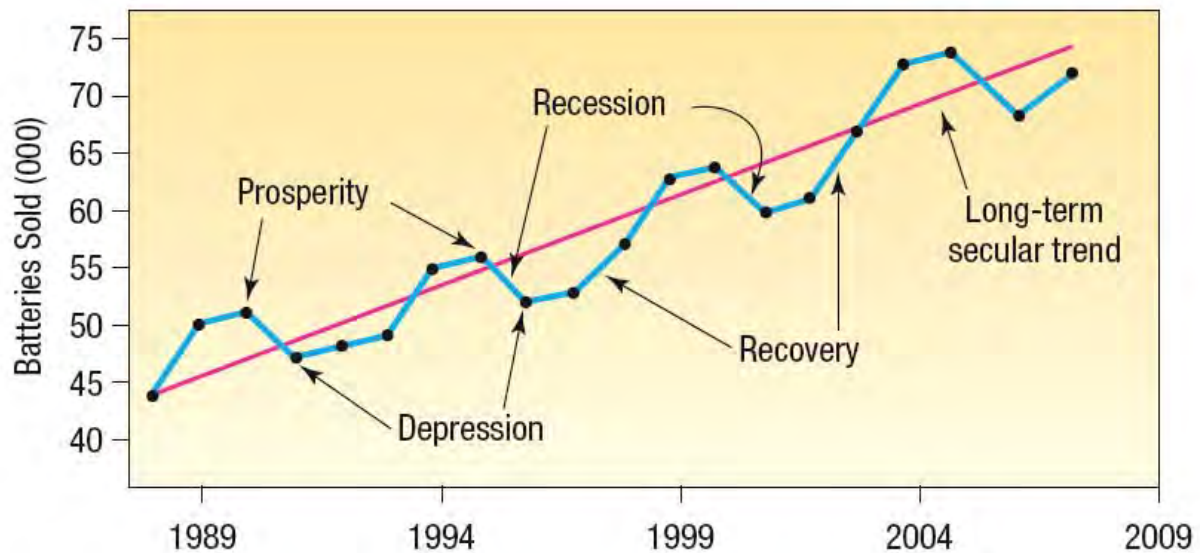
Seasonal Variation – Sample Chart
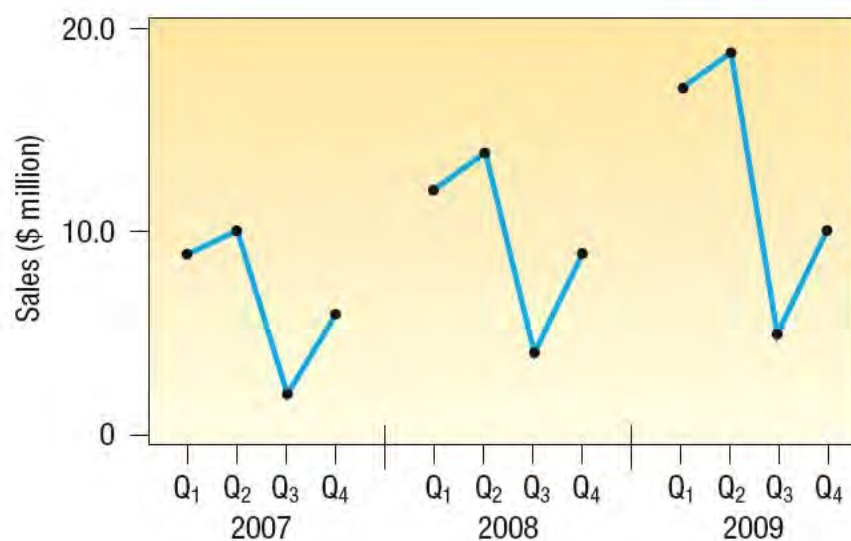
CHART 16–2 Sales of Baseball and Softball Equipment, Hercher Sporting Goods, 2007–2009 by Quarter

The Moving Average Method

> ➢ Useful in smoothing time series to see its trend
> ➢ Basic method used in measuring seasonal fluctuation
> ➢ Applicable when time series follows fairly linear trend that have definite rhythmic pattern

Moving Average Method - Example
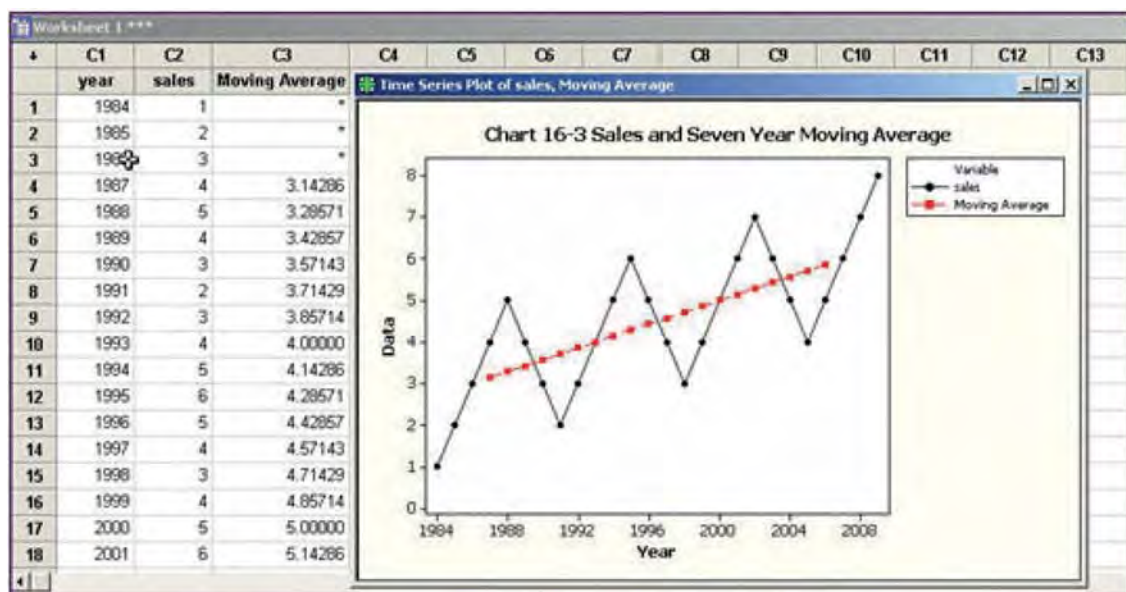
(Ex7_1)

Three-year and Five-Year Moving Averages

CHART 16–4 A Three-Year and Five-Year Moving Average 1991 to 2009

Weighted Moving Average

- ➢ A simple moving average assigns <u>the same weight</u> to each observation in averaging
- ➢ Weighted moving average assigns <u>different weights</u> to each observation
- ➢ Most recent observation receives the most weight, and the weight decreases for older data values
- ➢ In either case, the sum of the weights = 1

Weighted Moving Average - Example

Cedar Fair operates seven amusement parks and five separately gated water parks. Its combined attendance (in thousands) for the last 12 years is given in the following table. □ partner asks you to study the trend in attendance. Compute a three-year moving average and a three-year weighted moving average with weights of 0.2, 0.3, and 0.5 for successive years.

Year	Attendance (000)
1993	5,761
1994	6,148
1995	6,783
1996	7,445
1997	7,405
1998	11,450
1999	11,224
2000	11,703
2001	11,890
2002	12,380
2003	12,181
2004	12,557
2005	12,700
2006	19,300
2007	22,100

(Ex7_2)

Weighted Moving Average - Example

The three-year *weighted* moving average is:

Year	Attendance (000)	Weighted Moving Average	Found by
1993	5,761		
1994	6,148	6,388	.2(5,761) + .3(6,148) + .5(6,783)
1995	6,783	6,987	.2(6,148) + .3(6,783) + .5(7,445)
1996	7,445	7,293	.2(6,783) + .3(7,445) + .5(7,405)
1997	7,405	9,436	.2(7,445) + .3(7,405) + .5(11,450)
1998	11,450	10,528	.2(7,405) + .3(11,450) + .5(11,224)
1999	11,224	11,509	.2(11,450) + .3(11,224) + .5(11,703)
2000	11,703	11,701	.2(11,224) + .3(11,703) + .5(11,890)
2001	11,890	12,098	.2(11,703) + .3(11,890) + .5(12,380)
2002	12,380	12,183	.2(11,890) + .3(12,380) + .5(12,181)
2003	12,181	12,409	.2(12,380) + .3(12,181) + .5(12,557)
2004	12,557	12,553	.2(12,181) + .3(12,557) + .5(12,700)
2005	12,700	15,971	.2(12,557) + .3(12,700) + .5(19,300)
2006	19,300	19,380	.2(12,700) + .3(19,300) + .5(22,100)
2007	22,100		

Weighed Moving Average – An Example
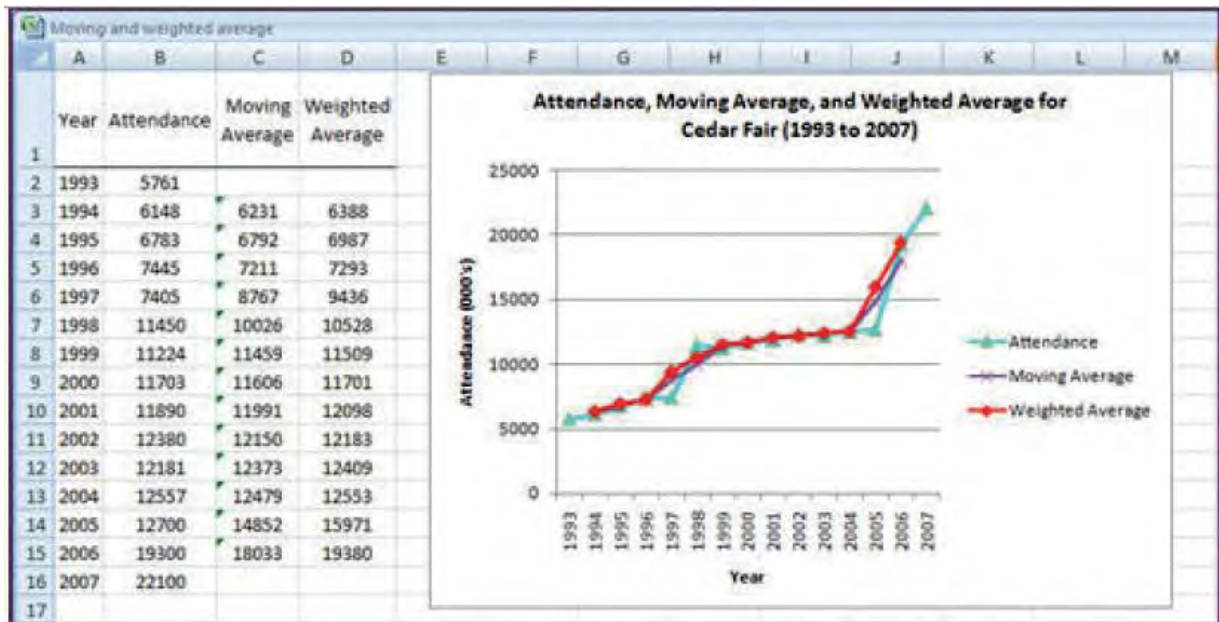
Linear Trend

● The long term trend of many business series often approximates a straight line

$$\text{Linear Trend } \square\square\square\text{ti}\square\square: \ \hat{Y} = a + bt$$

$\square\square e\square e:$

$\hat{Y} - \square e\square\square Y \ \square t\square, i\square t\square e \ \square\square j e c t e\square\square\square\square e \ \square f \ t\square e \ Y$
$\square\square i\square\square e \ f\square\square\square e\square e c t e\square \ \square\square\square e \ \square f \ t$

$a - t\square e \ Y \ i\square t e\square c e\square t$
$\square e\square t i\square\square t e\square \ \square\square\square e \ \square f \ Y \ \square\square e\square \ t = 0\square$

$b - t\square e \ \square\square\square e \ \square f \ t\square e \ \square i\square e$
$\square\square e\square\square e \ c\square\square\square\square e \ i\square Y \ f\square\square e\square c\square \ \square i t \ c\square\square\square\square e \ i\square t\square$

$t - \square\square\square \ \square\square\square e \ \square f \ t i\square e \ c\square\square e\square\square t\square\square t i\square\square e\square c t e\square$
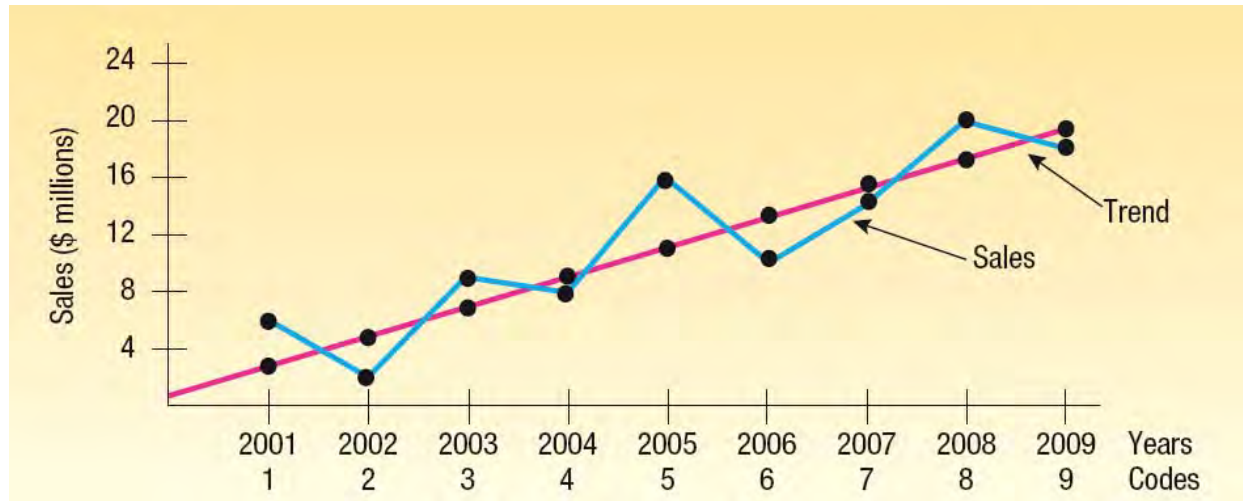
Linear Trend Plot

Linear Trend – Using the Least Squares Method

- Use the least squares method in Simple Linear Regression (Chapter 13) to find the best linear relationship between 2 variables
- Code time (t) and use it as the independent variable
- E.g. let t be 1 for the first year, 2 for the second, and so on (if data are annual)

Linear Trend – Using the Least Squares Method: An Example

The sales of Jensen Foods, a small grocery chain located in southwest Texas, since 2005 are:

Year	Sales ($ mil.)
2005	7
2006	10
2007	9
2008	11
2009	13

Year	t	Sales ($ mil.)
2005	1	7
2006	2	10
2007	3	9
2008	4	11
2009	5	13

(Ex7_3)

Linear Trend – Using the Least Squares Method: An Example Using Excel

Trend Analysis Plot for Sales

Chart 16-6; Trend Line for Jensen Food, 2005-2009
Linear Trend Model
Yt = 6.10 + 1.30*t

Variable
Actual
Fits

Accuracy Measures
MAPE   7.12592
MAD   0.68000
MSD   0.62000
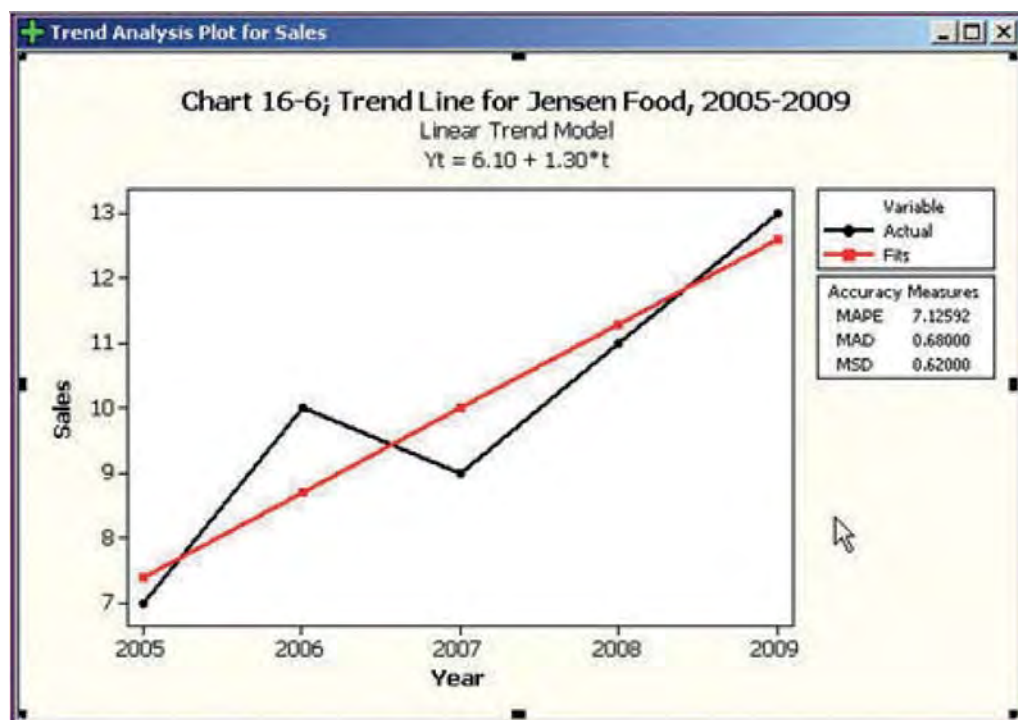
Nonlinear Trends

- A linear trend equation is used when the data are increasing (or decreasing) by <u>equal</u> amounts

- A nonlinear trend equation is used when the data are increasing (or decreasing) by <u>increasing</u> amounts over time

- When data increase (or decrease) by equal *percents or proportions* plot will show curvilinear pattern

Log Trend Equation – Gulf Shores Importers Example

- Graph on right is the log base 10 of the original data which now is linear
  (Excel function: =log(x) or log(x,10)
- Using Data Analysis in Excel, generate the linear equation
- Regression output shown in next slide

LOG TREND EQUATION	$\log \hat{Y} = \log a + \log b(t)$	[16–2]

	A	B
1	Year	Sales
2	1995	124.2
3	1996	175.6
4	1997	306.9
5	1998	524.2
6	1999	714.0
7	2000	1052.0
8	2001	1638.3
9	2002	2463.2
10	2003	3358.2
11	2004	4181.3
12	2005	5388.5
13	2006	8027.4
14	2007	10587.2
15	2008	13537.4
16	2009	17515.6
17		
18		

Chart 16-7 Sales for Gulf Shores Importers; 1995-2009
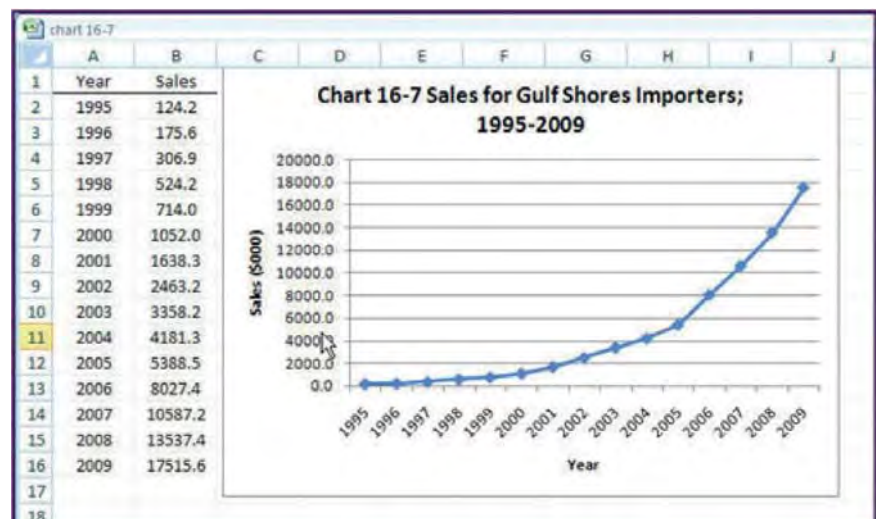
(Ex7_4)

Log Trend Equation – Gulf Shores Importers Example

The Linear equation is

$$\hat{} = \square\square\square\square\square\square + \square\square\square\square\square\square\,t$$

Log Trend Equation – Gulf Shores Importers Example

$\square\square$i$\square$a$\square$e $\square\square$ $\square\square$r $\square\square$r $\square$e $\square$ear $\square\square\square\square\square$in$\square$ $\square$e $\square$inear $\square$rend

$$\hat{} = \square\square\square\square\square\square + \square\square\square\square\square\square\,t$$

$\square\square\square\square$i$\square\square$e in $\square\square$e $\square$inear e$\square\square$a$\square$i$\square$n a$\square\square$e $\square$e $\square$de $\square\square\square\square\square$r $\square\square\square$

$$\hat{} = \square\square\square\square\square\square + \square\square\square\square\square\square\square\square\square$$

$$\hat{} = \square\square\square\square\square\square$$

T$\square$en $\square$ind $\square$e an$\square$i$\square\square\square\square \hat{} = \square\square^{\square\,Y}$

$$= \square\square^{\square\square\square\square\square\square}$$

$$= \square\square\square\square\square$$

Seasonal Variation

- One of the components of a time series
- Seasonal variations are fluctuations that coincide with certain seasons and are repeated year after year
- Understanding seasonal fluctuations help plan for sufficient goods and materials on hand to meet varying seasonal demand
- Analysis of seasonal fluctuations over a period of years help in evaluating current sales
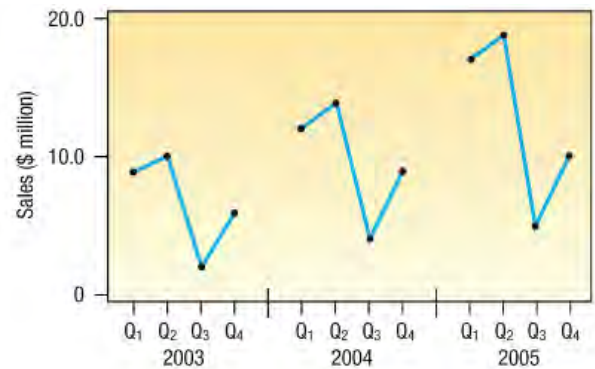
Seasonal Index

- A number, usually expressed in percent, that expresses the relative value of a season with respect to the average for the year (100%)

- Ratio-to-moving-average method

  - The method most commonly used to compute the typical seasonal pattern

  - It eliminates the trend (T), cyclical (C), and irregular (I) components from the time series

Seasonal Index – An Example

The table below shows the quarterly sales for Toys International for the years 2001 through 2006. The sales are reported in millions of dollars. Determine a quarterly seasonal index using the ratio-to-moving-average method.

Year	Winter	Spring	Summer	Fall
2004	6.7	4.6	10.0	12.7
2005	6.5	4.6	9.8	13.6
2006	6.9	5.0	10.4	14.1
2007	7.0	5.5	10.8	15.0
2008	7.1	5.7	11.1	14.5
~~2009~~	8.0	6.2	11.4	14.9

(Ex7_5)

Step (1) – Organize time series data in column form

Step (2) Compute the 4-quarter moving totals

Step (3) Compute the 4-quarter moving averages

Step (4) Compute the centered moving averages by getting the average of two 4-quarter moving averages

Step (5) Compute ratio by dividing actual sales by the centered moving averages

Year	Quarter	(1) Sales ($ millions)	(2) Four-Quarter Total	(3) Four-Quarter Moving Average	(4) Centered Moving Average	(5) Specific Seasonal
	Spring	4.6			8.513	0.540
			33.6	8.400		
			34.5	8.625		
	Summer	9.8			8.675	1.130
			34.9	8.725		
	Fall	13.6			8.775	1.550
			35.3	8.825		
2006	Winter	6.9			8.900	0.775
			35.9	8.975		
	Spring	5.0			9.038	0.553
			36.4	9.100		
	Summer	10.4			9.113	1.141
			36.5	9.125		
	Fall	14.1			9.188	1.535
			37.0	9.250		
2007	Winter	7.0			9.300	0.753
			37.4	9.350		
	Spring	5.5			9.463	0.581
			38.3	9.575		
	Summer	10.8			9.588	1.126
			38.4	9.600		
	Fall	15.0			9.625	1.558
			38.6	9.650		
2008	Winter	7.1			9.688	0.733
			38.9	9.725		
	Spring	5.7			9.663	0.590
			38.4	9.600		
	Summer	11.1			9.713	1.143
			39.3	9.825		
	Fall	14.5			9.888	1.466
			39.8	9.950		
2009	Winter	8.0			9.888	0.801
			40.1	10.025		
	Spring	6.2			10.075	0.615
			40.5	10.125		
	Summer	11.4				
	Fall	14.9				

Seasonal Index – An Example

Year	Winter	Spring	Summer	Fall	
2004			1.180	1.503	
2005	0.772	0.540	1.130	1.550	
2006	0.775	0.553	1.141	1.535	
2007	0.753	0.581	1.126	1.558	
2008	0.733	0.590	1.143	1.466	
2009	0.801	0.615			
Total	3.834	2.879	5.720	7.612	
Mean	0.767	0.576	1.144	1.522	4.009
Adjusted	0.765	0.575	1.141	1.519	4.000
Index	76.5	57.5	114.1	151.9	

CORRECTION FACTOR FOR ADJUSTING QUARTERLY MEANS

$$\text{Correction factor} = \frac{4.00}{\text{Total of four means}} \quad [16\text{–}3]$$

$$\text{Correction factor} = \frac{4.00}{4.009} = 0.997755$$

Adjusted Seasonal Indexes

Calculation of Seasonal Indexes

	1	2	3	4	
2004			1.180	1.503	
2005	0.772	0.540	1.130	1.550	
2006	0.775	0.553	1.141	1.535	
2007	0.753	0.581	1.126	1.558	
2008	0.733	0.590	1.143	1.466	
2009	0.801	0.615			
Mean:	0.767	0.576	1.144	1.522	4.009
Adjusted:	0.765	0.575	1.141	1.519	4.000

Actual versus Deseasonalized Sales for Toys International

Deseasonalized Sales = Sales / Seasonal Index

Centered Moving Average and Deseasonalization

t	Year	Quarter	Sales	Centered Moving Average	Ratio to CMA	Seasonal Indexes	Sales Deseasonalized
1	2004	1	6.70			0.765	8.759
2	2004	2	4.60			0.575	8.004
3	2004	3	10.00	8.475	1.180	1.141	8.761
4	2004	4	12.70	8.450	1.503	1.519	8.361
5	2005	1	6.50	8.425	0.772	0.765	8.498
6	2005	2	4.60	8.513	0.540	0.575	8.004
7	2005	3	9.80	8.675	1.130	1.141	8.586
8	2005	4	13.60	8.775	1.550	1.519	8.953
9	2006	1	6.90	8.900	0.775	0.765	9.021
10	2006	2	5.00	9.038	0.553	0.575	8.700
11	2006	3	10.40	9.113	1.141	1.141	9.112
12	2006	4	14.10	9.188	1.535	1.519	9.283
13	2007	1	7.00	9.300	0.753	0.765	9.151
14	2007	2	5.50	9.463	0.581	0.575	9.570
15	2007	3	10.80	9.588	1.126	1.141	9.462
16	2007	4	15.00	9.625	1.558	1.519	9.875
17	2008	1	7.10	9.688	0.733	0.765	9.282
18	2008	2	5.70	9.663	0.590	0.575	9.918
19	2008	3	11.10	9.713	1.143	1.141	9.725
20	2008	4	14.50	9.888	1.466	1.519	9.546
21	2009	1	8.00	9.988	0.801	0.765	10.459
22	2009	2	6.20	10.075	0.615	0.575	10.788
23	2009	3	11.40			1.141	9.988
24	2009	4	14.90			1.519	9.809

Actual versus Deseasonalized Sales for Toys International – Time Series Plot using Minitab
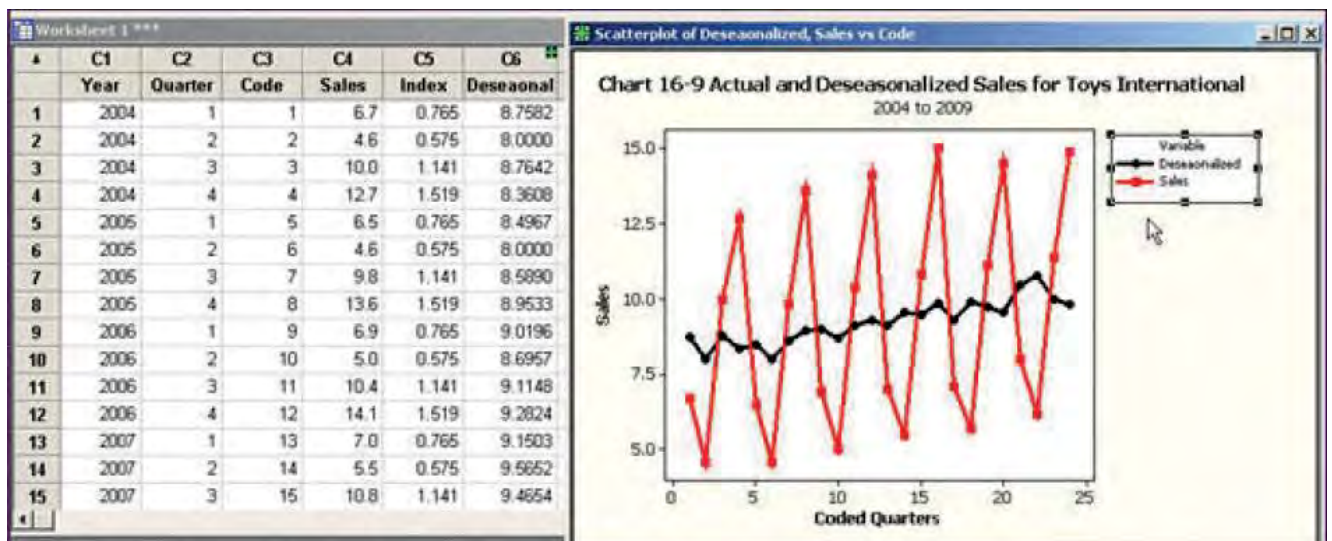
Seasonal Index – An Example Using Excel

Given the deseasonalized linear equation for Toys International sales as $\hat{Y} = 8.109 + 0.0899t$, generate the seasonally adjusted forecast for each of the quarters of 2010

	A	B	C	D	E	F	G
1							
2							
3			Quarterly Forecast for Toys International				
4			2010				
5							
6		Quarter	t value	Estimated Sales	Seasonal Index	Quarterly Forecast	
7		Winter	25	10.3565	0.765	7.923	
8		Spring	26	10.4464	0.575	6.007	
9		Summer	27	10.5363	1.141	12.022	
10		Fall	28	10.6262	1.519	16.141	
11							

$\hat{Y} \times SI = 10.62648 \times 1.519$

$\hat{Y} = 8.10 + 0.0899(28)$

Durbin-Watson Statistic

- Tests the autocorrelation among the residuals
- The Durbin-Watson statistic, d, is computed by first determining the residuals for each observation: $e_t = (Y_t - \hat{Y}_t)$
- Then compute d using the following equation:

DURBIN-WATSON STATISTIC

$$d = \frac{\sum\limits_{t=2}^{n}(e_t - e_{t-1})^2}{\sum\limits_{t=1}^{n}(e_t)^2}$$

[16–4]

Durbin-Watson Test for Autocorrelation – Interpretation of the Statistic

- Range of d is 0 to 4

$d = 2$	No autocorrelation
d close to 0	Positive autocorrelation
d beyond 2	Negative autocorrelation

- Hypothesis Test:

  H_0: No residual correlation ($\rho = 0$)
  H_1: Positive residual correlation ($\rho > 0$)

- Critical values for d are found in *Appendix B.10* using
  - α - significance level
  - n – sample size
  - K – the number of predictor variables

Durbin-Watson Critical Values (=.05)

n	k = 1 d_L	k = 1 d_U	k = 2 d_L	k = 2 d_U	k = 3 d_L	k = 3 d_U	k = 4 d_L	k = 4 d_U
15	1.08	1.36	0.95	1.54	0.82	1.75	0.69	1.97
16	1.10	1.37	0.98	1.54	0.86	1.73	0.74	1.93
17	1.13	1.38	1.02	1.54	0.90	1.71	0.78	1.90
18	1.16	1.39	1.05	1.53	0.93	1.69	0.82	1.87
19	1.18	1.40	1.08	1.53	0.97	1.68	0.86	1.85
20	1.20	1.41	1.10	1.54	1.00	1.68	0.90	1.83
21	1.22	1.42	1.13	1.54	1.03	1.67	0.93	1.81
22	1.24	1.43	1.15	1.54	1.05	1.66	0.96	1.80
23	1.26	1.44	1.17	1.54	1.08	1.66	0.99	1.79
24	1.27	1.45	1.19	1.55	1.10	1.66	1.01	1.78
25	1.29	1.45	1.21	1.55	1.12	1.66	1.04	1.77
26	1.30	1.46	1.22	1.55	1.14	1.65	1.06	1.76
27	1.32	1.47	1.24	1.56	1.16	1.65	1.08	1.76
28	1.33	1.48	1.26	1.56	1.18	1.65	1.10	1.75
29	1.34	1.48	1.27	1.56	1.20	1.65	1.12	1.74
30	1.35	1.49	1.28	1.57	1.21	1.65	1.14	1.74
31	1.36	1.50	1.30	1.57	1.23	1.65	1.16	1.74
32	1.37	1.50	1.31	1.57	1.24	1.65	1.18	1.73
33	1.38	1.51	1.32	1.58	1.26	1.65	1.19	1.73
34	1.39	1.51	1.33	1.58	1.27	1.65	1.21	1.73
35	1.40	1.52	1.34	1.58	1.28	1.65	1.22	1.73
36	1.41	1.52	1.35	1.59	1.29	1.65	1.24	1.73
37	1.42	1.53	1.36	1.59	1.31	1.66	1.25	1.72
38	1.43	1.54	1.37	1.59	1.32	1.66	1.26	1.72
39	1.43	1.54	1.38	1.60	1.33	1.66	1.27	1.72
40	1.44	1.54	1.39	1.60	1.34	1.66	1.29	1.72
45	1.48	1.57	1.43	1.62	1.38	1.67	1.34	1.72
50	1.50	1.59	1.46	1.63	1.42	1.67	1.38	1.72
55	1.53	1.60	1.49	1.64	1.45	1.68	1.41	1.72
60	1.55	1.62	1.51	1.65	1.48	1.69	1.44	1.73
65	1.57	1.63	1.54	1.66	1.50	1.70	1.47	1.73
70	1.58	1.64	1.55	1.67	1.52	1.70	1.49	1.74
75	1.60	1.65	1.57	1.68	1.54	1.71	1.51	1.74
80	1.61	1.66	1.59	1.69	1.56	1.72	1.53	1.74
85	1.62	1.67	1.60	1.70	1.57	1.72	1.55	1.75
90	1.63	1.68	1.61	1.70	1.59	1.73	1.57	1.75
95	1.64	1.69	1.62	1.71	1.60	1.73	1.58	1.75
100	1.65	1.69	1.63	1.72	1.61	1.74	1.59	1.76

Durbin-Watson Test for Autocorrelation: An Example

The Banner Rock Company manufactures and markets its own rocking chair. The company developed special rocker for senior citizens which it advertises extensively on TV. Banner's market for the special chair is the Carolinas, Florida and Arizona, areas where there are many senior citizens and retired people The president of Banner Rocker is studying the association between his advertising expense (X) and the number of rockers sold over the last 20 months (Y). He collected the following data. He would like to use the model to forecast sales, based on the amount spent on advertising, but is concerned that because he gathered these data over consecutive months that there might be problems of autocorrelation.

Month	Sales (000)	Ad ($millions)
1	153	5.5
2	156	5.5
3	153	5.3
4	147	5.5
5	159	5.4
6	160	5.3
7	147	5.5
8	147	5.7
9	152	5.9
10	160	6.2
11	169	6.3
12	176	5.9
13	176	6.1
14	179	6.2
15	184	6.2
16	181	6.5
17	192	6.7
18	205	6.9
19	215	6.5
20	209	6.4

(Ex7_6)

Durbin-Watson Test for Autocorrelation: An Example

- Step 1: Generate the regression equation
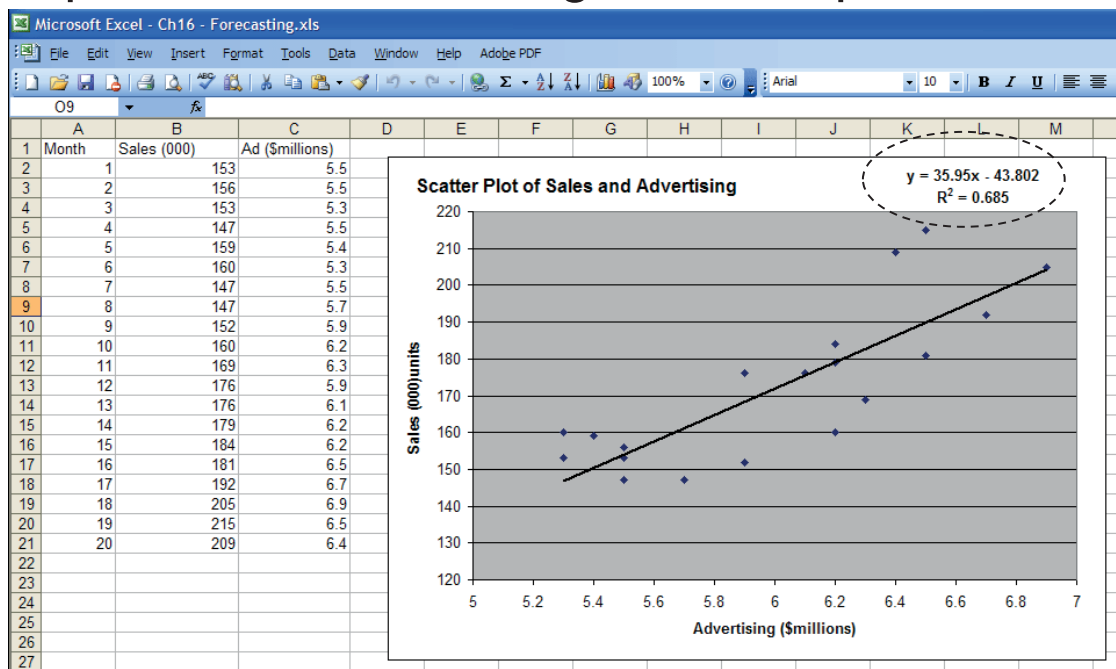
Durbin-Watson Test for Autocorrelation: An Example

- The resulting equation is: $\hat{Y} = -43.802 + 35.95X$
- The coefficient (r) is 0.828
- The coefficient of determination (r^2) is 68.5%

  (note: Excel reports r^2 as a ratio. Multiply by 100 to convert into percent)

- There is a strong, positive association between sales and advertising
- Is there potential problem with autocorrelation?

Durbin-Watson Test for Autocorrelation: An Example

Excel worksheet "Ch16 - Forecasting":

	A	B	C	D	E	F	G	H
1	Month	Sales (000)	Ad ($millions)	Predicted Sales (000)	Residuals	Lagged		
2		Y	X	$\hat{Y}$	$e_i = Y - \hat{Y}$	e_{i-1}	$(e_i - e_{i-1})^2$	$(e_i)^2$
3	1	153	5.5	153.923	-0.923			0.8519
4	2	156	5.5	153.923	2.077	-0.923	9.0000	4.3139
5	3	153	5.3	146.733	6.267	2.077	17.5561	39.2753
6	4	147	5.5	153.923	-6.923	6.267	173.9761	47.9279
7	5	159	5.4	150.328	8.672	-6.923	243.2048	75.2036
8	6	160	5.3	146.733	13.267	8.672	21.1140	176.0133
9	7	147	5.5	153.923	-6.923	13.267	407.6361	47.9279
10	8	147	5.7	161.113	-14.113	-6.923	51.6961	199.1768
11	9	152	5.9	168.303	-16.303	-14.113	4.7961	265.7878
12	10	160	6.2	179.088	-19.088	-16.303	7.7562	364.3517
13	11	169	6.3	182.683	-13.683	-19.088	29.2140	187.2245
14	12	176	5.9	168.303	7.697	-13.683	457.1044	59.2438
15	13	176	6.1	175.493	0.507	7.697	51.6961	0.2570
16	14	179	6.2	179.088	-0.088	0.507	0.3540	0.0077
17	15	184	6.2	179.088	4.912	-0.088	25.0000	24.1277
18	16	181	6.5	189.873	-8.873	4.912	190.0262	78.7301
19	17	192	6.7	197.063	-5.063	-8.873	14.5161	25.6340
20	18	205	6.9	204.253	0.747	-5.063	33.7561	0.5580
21	19	215	6.5	189.873	25.127	0.747	594.3844	631.3661
22	20	209	6.4	186.278	22.722	25.127	5.7840	516.2893
23								
24							2338.5702	2744.2686
25								
26								
27								

Cell E3 fx =B3-D3

Annotations:
- =-43.802+35.95*C3
- =(E4-F4)^2
- =E4^2
- =B3-D3
- =E3
- $\sum(e_i - e_{i-1})^2$ → 2338.5702
- $\sum(e_i)^2$ → 2744.2686

Durbin-Watson Test for Autocorrelation: An Example

- Hypothesis Test:

  H_0: No residual correlation ($\rho = 0$)

  H_1: Positive residual correlation ($\rho > 0$)

- Critical values for d given $\alpha=0.5$, $n=20$, $k=1$ found in Appendix B.10

  $d_l=1.20$ $d_u=1.41$
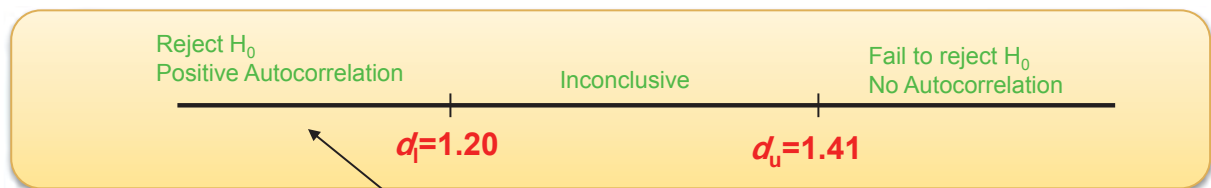
Reject H_0 Positive Autocorrelation	Inconclusive	Fail to reject H_0 No Autocorrelation
d_l=1.20		d_u=1.41

$$= \frac{\sum\limits_{t=0} \left(\square_t - \square_{t-\square}\right)^{\square}}{\sum\limits_{t=\square} \square_t{}^{\square}} = \frac{\square\square\square\square\square\square\square}{\square\square\square\square\square\square} \neq \square\square\square\square\square$$

END of Part 8

Applying statistical techniques in Decision Making

Part 9
Process Control
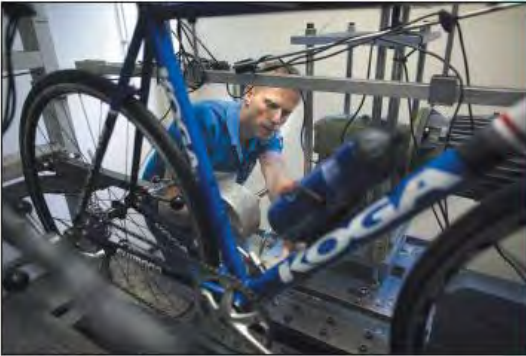
Control Charts

Statistical Quality Control (SQC): emphasizes in-process control with the objective of **controlling the quality of a manufacturing process** or **service operation** using **sampling techniques**.

- ➢ **Statistical sampling techniques** are used to **aid** in the **manufacturing of a product to specifications** rather than attempt **to inspect quality into the product after it is manufactured.**

- ➢ **Control Charts** are useful for **monitoring** a process.

Causes of Variation

All parts produced by a manufacturing process contain variation. The two sources of variation are:

Chance Variation is random in nature and cannot be entirely eliminated unless there is a major change in the techniques, technologies, methods, equipment, or materials used in the process.

Assignable Variation is nonrandom in nature and can be reduced or eliminated by investigating the problem and finding the cause.

Diagnostic Charts

There are a variety of diagnostic techniques available to investigate quality problems. Two of the more prominent of these techniques are Pareto charts and fishbone diagrams.
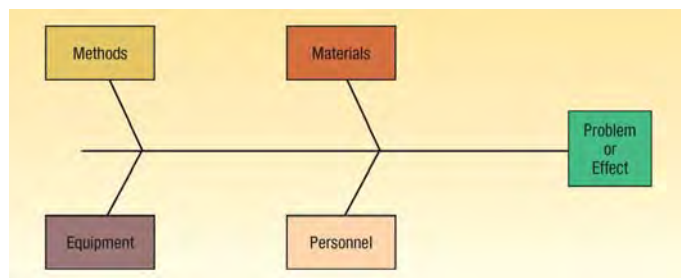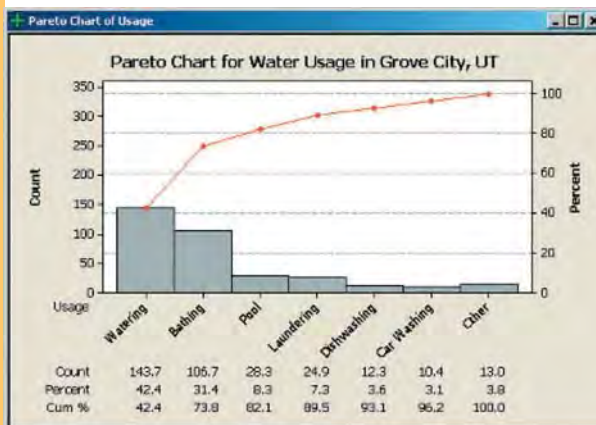
Pareto Charts Example (1)

- ➢ **Pareto analysis is a technique for tallying the number and type of defects that happen within a product or service.**

- ➢ **The chart is named after a nineteenth-century Italian scientist, Vilfredo Pareto. He noted that most of the "activity" in a process is caused by relatively few of the "factors."**

- ➢ **Pareto's concept, often called the 80–20 rule, is that 80 percent of the activity is caused by 20 percent of the factors. By concentrating on 20 percent of the factors, managers can attack 80 percent of the problem.**

Fishbone Diagrams

Another diagnostic chart is a cause-and-effect diagram or a fishbone diagram. It is called a cause-and-effect diagram to emphasize the relationship between an effect and a set of possible causes that produce the particular effect.

This diagram is useful to help organize ideas and to identify relationships. It is a tool that encourages open brainstorming for ideas. By identifying these relationships we can determine factors that are the cause of variability in our process.
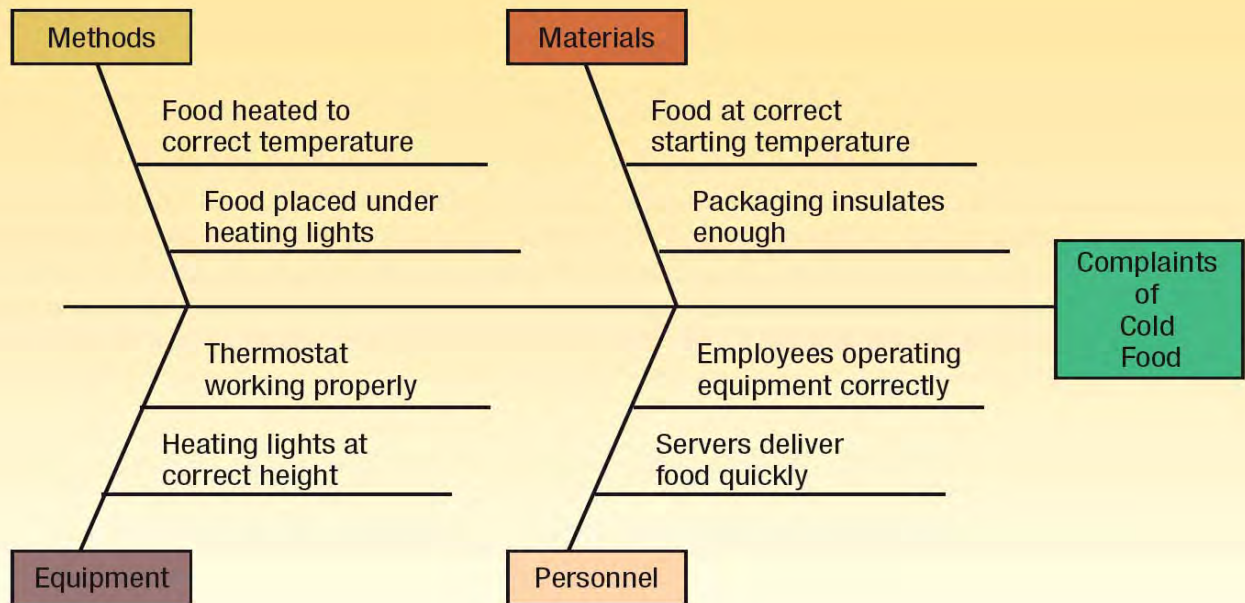
Fishbone Diagrams

Fishbone Diagram for a Restaurant Investigation of Cold Food Complaints

Purpose of Quality Control Charts

➢ **The purpose of quality-control charts is to portray graphically when an assignable cause enters the production system so that it can be identified and corrected.**

➢ **This is accomplished by periodically selecting a random sample from the current production.**

Mean and Range Chart for Variables **Examples (2 & 3)**

A **mean** or the **x-bar chart** is designed to control variables such as weight, length, etc. The upper control limit (*UCL*) and the lower control limit (*LCL*) are obtained from the equation:

$$= \overline{\overline{}} + \overline{}_{\square}\, a \qquad\qquad = \overline{\overline{}} - \overline{}_{\square}$$

A **range chart** shows the **variation** in the sample ranges.

$$= {}_{\square}\overline{\square}\, a \qquad\qquad = {}_{\square}\overline{\square}$$

Where:
<u>*n*</u> is the sample size
    $\overline{}$ is the mean of the sample means
     $\overline{}$ is the mean of the ranges
D_3 and D_4 values are found in Appendix B.8

A portion of Appendix B.8

n	A_2	D_2	D_3	D_4
2	1.880	1.128	0	3.267
3	1.023	1.693	0	2.575
4	0.729	2.059	0	2.282
5	0.577	2.326	0	2.115
6	0.483	2.534	0	2.004

In-Control Situation
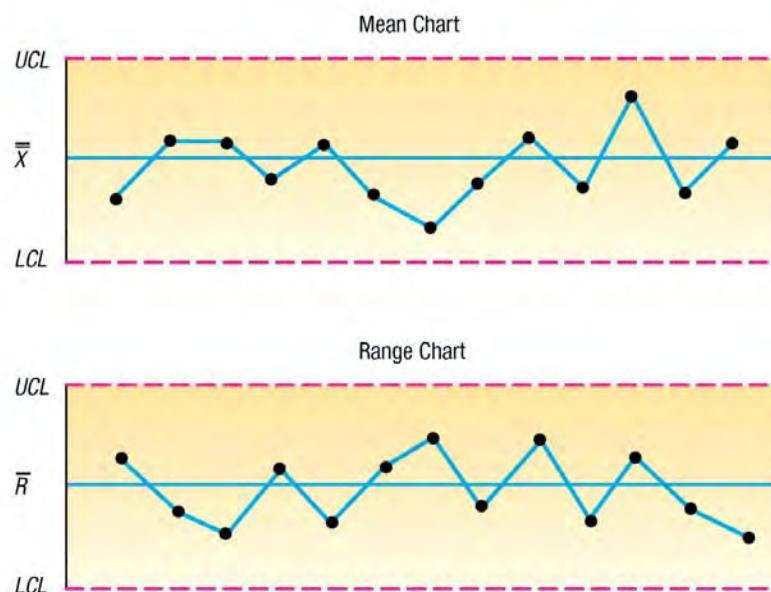
Mean In-control, Range Out-of-control

Mean Chart
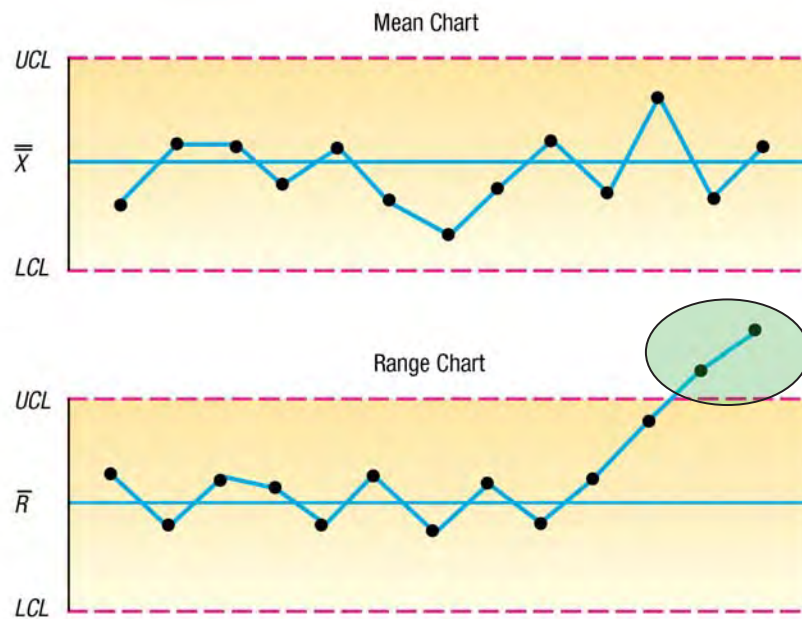
Range Chart

Mean Out-of-control, Range In-control

Mean Chart

Range Chart

The **percent defective chart** is also called a *p*-chart or the *p*-bar chart. It graphically shows the proportion of the production that is not acceptable. The proportion of defectives is found by:

$$\bar{p} = \frac{\text{Total number defective}}{\text{Total number sampled}}$$

The *UCL* and *LCL* are computed as the mean percent defective plus or minus 3 times the **standard error of the percents**:

$$\sigma_{\bar{p}} = \sqrt{\frac{\bar{p}(1-\bar{p})}{n}}$$

1-52

Attribute Control Chart : The c-Chart Example (5)

The *c*-chart or the *c*-bar chart is designed to control the number of defects per unit. The *UCL* and *LCL* are found by:

$$\bar{c} \pm \sqrt{\bar{c}}$$

Acceptance Sampling

Acceptance sampling is a **method** of **determining** whether **an incoming lot** of a product **meets specified standards.**

➢ It is based on random sampling techniques.

➢ A random sample of **n units** is obtained from the entire **lot**.

➢ **c** is the maximum number of **defective** units that may be found in the sample for the lot to still be considered acceptable.

Acceptance Sampling Procedure

Accept shipment or reject shipment? The usual procedure is to screen the quality of incoming parts by using a statistical sampling plan. According to this plan:

➢ A sample of *n* units is randomly selected from the lots of *N* units (the population). This is called **acceptance sampling.**

➢ The inspection will determine the number of **defects** in the sample.

➢ This number is compared with a predetermined number called the **critical number** or the acceptance number usually designated *c.*

  ❑ If the number of defects in the sample of size *n* is less than or equal to *c,* the lot is **accepted**.

  ❑ If the number of defects **exceeds** *c,* the lot is **rejected** and returned to the supplier, or **perhaps submitted to 100 percent inspection.**

Consumer's Risk vs. Producer's Risk in Acceptance Sampling

Type II Error

	States of Nature	
Decision	**Good Lot**	**Bad Lot**
Accept lot	Correct	Consumer's risk
Reject lot	Producer's risk	Correct

Type I Error

Operating Characteristic Curve Example (6)

An OC curve, or **operating characteristic curve**, is developed using the **binomial probability distribution** in order to determine the probabilities of **accepting** lots of various quality level .

END of Part 9

Applying statistical techniques in Decision Making

Chapter 10

Introduction to Decision Theory
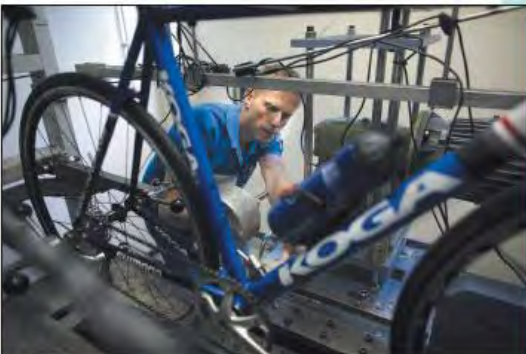
Statistical Decision Theory

- Classical statistics focuses on estimating a parameter, such as the population mean, constructing confidence intervals, or hypothesis testing.

- Statistical Decision Theory (Bayesian statistics) is concerned with determining which decision, from a set of possible decisions, is optimal.

Elements of a Decision

There are three components to any decision-making situation:

1. The available choices (alternatives or acts).
2. The states of nature, which are not under the control of the decision maker - uncontrollable future events.
3. The payoffs - needed for each combination of decision alternative and state of nature.

Decision Making

Explanatory Statements	
Event	Uncertainty regarding future demand. State of nature (future demand) unknown. Decision maker has no control over state of nature.
Act	Two or more courses of action open to decision maker. Decision maker must evaluate alternatives. Decision maker selects a course of action based on certain criteria. Depending on the set of circumstances, these criteria may be quantitative, psychological, sociological, and so on.
Outcome Payoff Consequence	Profit. Breakeven. Loss.

Payoff Table and Expected Payoff

- A Payoff Table is a listing of all possible combinations of decision alternatives and states of nature.

- The Expected Payoff or the Expected Monetary Value (*EMV*) is the expected value for each decision.

Calculating the EMV

$$\square \;\; \square = \;\; \square \;\; \square \;\; \square \;\; \square \;\; \square \;\; \square$$

- Let A_i be the ith decision alternative.
- Let $P(S_j)$ be the probability of the jth state of nature.
- Let $V(A_i, S_j)$ be the value of the payoff for the combination of decision alternative A_i and state of nature S_j.
- Let $EMV(A_i)$ be the expected monetary value for the decision alternative A_i.

Decision Making Under Conditions of Uncertainty - Example

Bob Hill, a small investor, has $1,100 to invest. He has studied several common stocks and narrowed his choices to three, namely, Kayser Chemicals, Rim Homes, and Texas Electronics. He estimated that, if his $1,100 were invested in Kayser Chemicals and a strong bull market developed by the end of the year (that is, stock prices increased drastically), the value of his Kayser stock would more than double, to $2,400. However, if there were a bear market (i.e., stock prices declined), the value of his Kayser stock could conceivably drop to $1,000 by the end of the year. His predictions regarding the value of his $1,100 investment for the three stocks for a bull market and for a bear market are shown below. A study of historical records revealed that during the past 10 years stock market prices increased six times and declined only four times. According to this information, the probability of a market rise is .60 and the probability of a market decline is .40.

Purchase	Bull Market, S_1	Bear Market, S_2
Kayser Chemicals (A_1)	$2,400	$1,000
Rim Homes (A_2)	2,200	1,100
Texas Electronics (A_3)	1,900	1,150

(Ex10_1)

EMV- Example

Purchase	Bull Market, S_1 (.60)	Bear Market, S_2 (.40)	Expected Payoff
Kayser Chemicals (A_1)	$2,400	$1,000	$1,840
Rim Homes (A_2)	2,200	1,100	1,760
Texas Electronics (A_3)	1,900	1,150	1,600

⭐ $(A1)=(.6)(\$2,400)+(.4)(\$1,000) =\$1,840$

$(A2)=(.6)(\$2,400)+(.4)(\$1,000) =\$1,760$

$(A3)=(.6)(\$2,400)+(.4)(\$1,000) =\$1,600$

Opportunity Loss

Opportunity Loss or Regret is the loss because the exact state of nature is not known at the time a decision is made.

- The opportunity loss is computed by taking the difference between the optimal decision for each state of nature and the other decision alternatives.

Expected Opportunity Loss

$$=$$

where
    $EOL(A_i)$ refers to the expected opportunity loss for a particular decision alternative.
      $P(S_j)$ refers to the probability associated with the states of nature j.
    $R(A_i, S_j)$ refers to the regret or loss for a particular combination of a state of nature and a decision alternative.

Opportunity Loss - Example

Purchase	Bull Market, S_1	Bear Market, S_2
Kayser Chemicals (A_1)	$2,400	$1,000
Rim Homes (A_2)	2,200	1,100
Texas Electronics (A_3)	1,900	1,150

Purchase	Opportunity Loss	
	Market Rise	Market Decline
Kayser Chemicals	$ 0	$150
Rim Homes	200	50
Texas Electronics	500	0

Opportunity Loss when Market Rises
Kayser:
$2,400 - $2,400= $0

Rim Homes:
$2,400 - $2,200 = $200

Texas Electronics:
$2,400 - $1,900 = $500

Opportunity Loss when Market Declines
Kayser:
$1,150 - $1,000= $150

Rim Homes:
$1,150 - $1,100 = $50

Texas Electronics:
$1,150 - $1,150 = $0

(Ex10_2)

Expected Opportunity Loss

$$=$$

Purchase	Opportunity Loss		Expected Opportunity Loss
	0.60 **Market Rise**	0.40 **Market Decline**	
Kayser Chemicals	$ 0	$150	$ 60
Rim Homes	200	50	140
Texas Electronics	500	0	300

⭐ (A1)=(.6)($0)+(.4)($150) =$60

(A2)=(.6)($200)+(.4)($50) =$140

(A3)=(.6)($500)+(.4)($0) =$300

Maximin, Maximax, and Minimax Regret Strategies

Payoff Table

Purchase	Bull Market, S_1	Bear Market, S_2	Maximin	Maximax
Kayser Chemicals (A_1)	$2,400	$1,000	1,000	2,400
Rim Homes (A_2)	2,200	1,100	1,100	2,200
Texas Electronics (A_3)	1,900	1,150	1,150	1,900

Opportunity Loss Table

Purchase	Opportunity Loss		Minimax Regret
	Market Rise	Market Decline	
Kayser Chemicals	$ 0	$150	150
Rim Homes	200	50	200
Texas Electronics	500	0	500

Maximin, Maximax, and Minimax Regret Strategies

Maximin strategy maximizes the minimum gain. It is a pessimistic strategy.

Maximax strategy maximizes the maximum gain. Opposite of a maximin approach, it is an optimistic strategy

Minimax regret strategy minimizes the maximum regret (opportunity loss). This is another pessimistic strategy

Value of Perfect Information

What is the worth of information known in advance before a strategy is employed?

Expected Value of Perfect Information (*EVPI*) is the difference between the expected payoff if the state of nature were known and the optimal decision under the conditions of uncertainty.

EVPI Example

EVPI = Expected value under conditions of certainty
  − Expected value under conditions of uncertainty

Step 1: Compute the Expected Value Under Certainty

State of Nature	Decision	Payoff	Probability of State of Nature	Expected Payoff
Market rise, S_1	Buy Kayser	$2,400	.60	$1,440
Market decline, S_2	Buy Texas Electronics	1,150	.40	460
				$1,900

Expected Value Under Certainty

(Ex10_3)

EVPI Example

Step 2: Compute the Expected Value Under Uncertainty

Purchase	Bull Market, S_1 (.60)	Bear Market, S_2 (.40)	Expected Payoff
Kayser Chemicals (A_1)	$2,400	$1,000	$1,840
Rim Homes (A_2)	2,200	1,100	1,760
Texas Electronics (A_3)	1,900	1,150	1,600

Step 3: Subtract the Expected Value Under Uncertainty from the Expected Value Under Certainty

$1,900 Expected value of stock purchased under conditions of certainty
−1,840 Expected value of purchase (Kayser) under conditions of uncertainty
$ 60 Expected value of perfect information

Sensitivity Analysis and Decision Trees

- Sensitivity Analysis examines the effects of various probabilities for the states of nature on the expected values for the decision alternatives.

- Decision Trees are useful for structuring the various alternatives. They present a picture of the various courses of action and the possible states of nature.
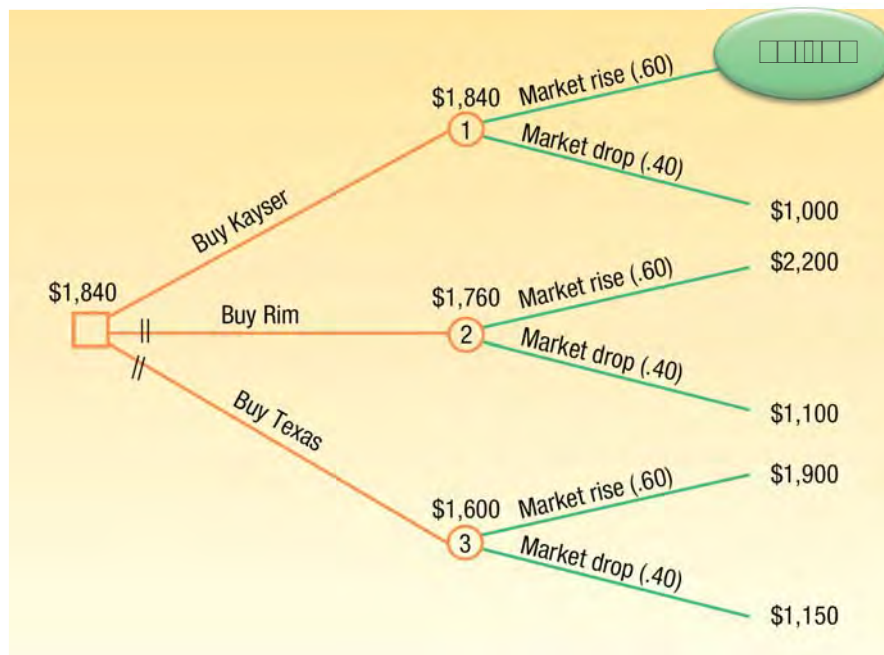
Decision Tree

A **decision tree** is a picture of all the possible courses of action and the consequent possible outcomes.

- A box is used to indicate the point at which a decision must be made,

- The branches going out from the box indicate the alternatives under consideration

		$1,840 Market rise (.60)
	1	
		Market drop (.40)
		$1,000
Buy Kayser		
		$2,200
$1,840	Buy Rim	$1,760 Market rise (.60)
	2	
		Market drop (.40)
		$1,100
Buy Texas		$1,900
		$1,600 Market rise (.60)
	3	
		Market drop (.40)
		$1,150

END of Part 10

Water conservation intiatives

Eng. Mohamed Abu Taleb

Utipities Dept. Manager
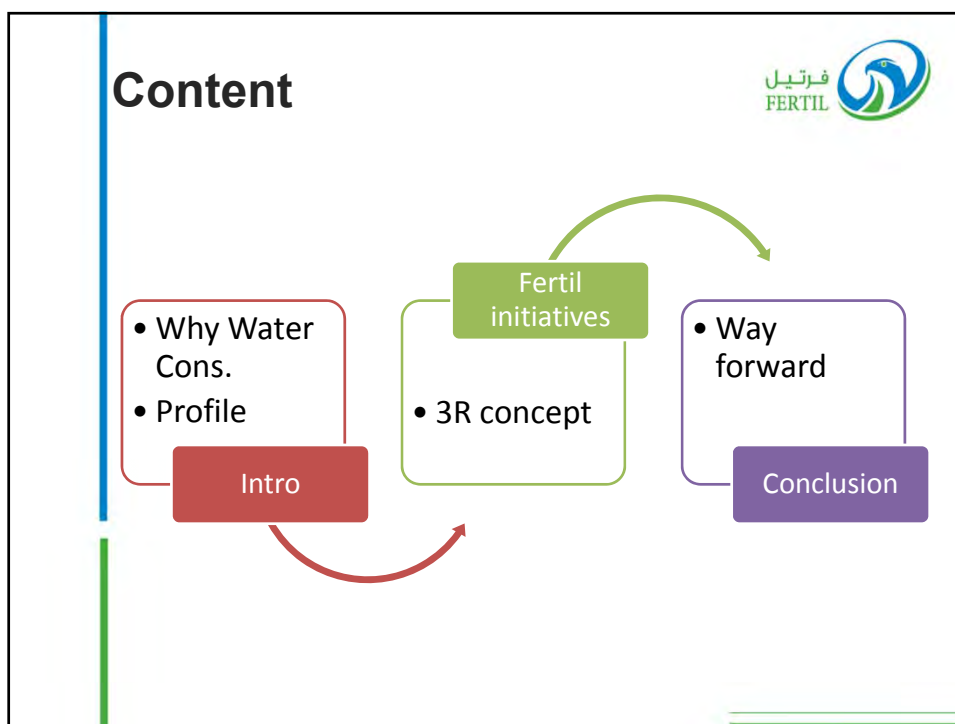Fertil - UAE

FERTIL
فـرتـيـل

Water Conservation Initiatives
FERTIL

Presented in : AFA Workshop
Water Treatment & water quality in Fertilizer and Petrochemical Industries
23- 25 Dec. 2013 – Aswan , Egypt

Presenter:

www.fertil.com

Content

FERTIL
فـرتـيـل

Fertil initiatives

- Why Water Cons.
- Profile

Intro

- 3R concept

- Way forward

Conclusion

FERTIL's Profile

Location	Ruwais (250 km west of Abu Dhabi)		
Established	1980		
Shareholders	ADNOC (2/3) & TOTAL (1/3)		
Plants		FERTIL 1	FERTIL 2
Established/ Started Up		Oct.1980 / Nov.1983	Nov. 2009 / June 2013
Products, Name plate capacity	Ammonia (MT/Day)	1,300	2,000
	Urea (MT/Day)	2,300	3,500

Plant's Photos

FERTIL-1

FERTIL-2

FERTIL's Awards
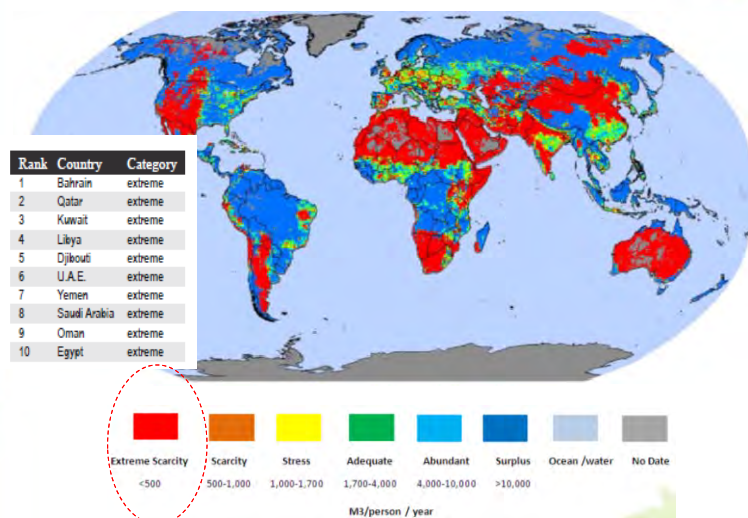
✓ Several Awards in ADNOC HSE Performance

✓ Occupational Health & Safety certification (OHSAS 18001)

✓ Several Awards of Royal Society for the Prevention of Accidents (RoSPA) including Sector Award

✓ Environmental Quality Certification (ISO 14001)

✓ 12 years without Lost Time Incident (LTI) Award

✓ (ISO 9001) for Quality Management System

✓ Dubai Quality Appreciation Program Award for industrial sector
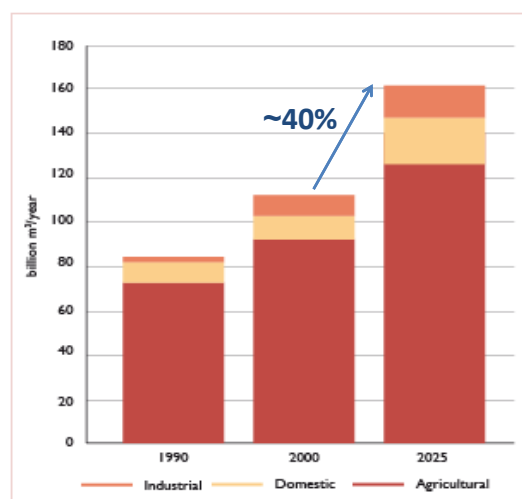
✓ Sheikh Khalifa Excellence Award for industrial sector
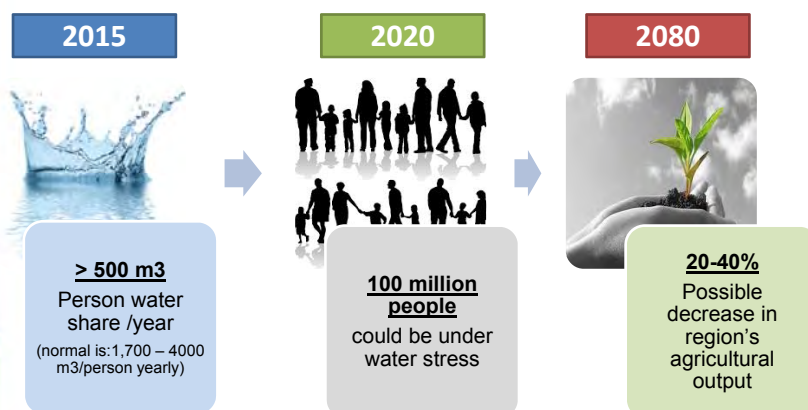
Why water conservation ?

Water Stress Index 2012

فرتيـل
FERTIL

Rank	Country	Category
1	Bahrain	extreme
2	Qatar	extreme
3	Kuwait	extreme
4	Libya	extreme
5	Djibouti	extreme
6	U.A.E.	extreme
7	Yemen	extreme
8	Saudi Arabia	extreme
9	Oman	extreme
10	Egypt	extreme

Extreme Scarcity	Scarcity	Stress	Adequate	Abundant	Surplus	Ocean /water	No Date
<500	500-1,000	1,000-1,700	1,700-4,000	4,000-10,000	>10,000		

M3/person / year

فرتيـل
FERTIL

Trend and Projection in <u>Water Demand</u> in Arab Region
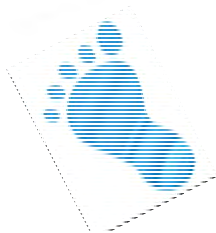
~40%

billion m³/year

1990 2000 2025

Industrial   Domestic   Agricultural

Water Stress future outlook

2015 | 2020 | 2080

> 500 m3
Person water share /year
(normal is:1,700 – 4000 m3/person yearly)

100 million people
could be under water stress

20-40%
Possible decrease in region's agricultural output

Water Conservation Drivers

FERTIL's Commitments

Conserve energy, water and other resources for the future

Reduce industrial footprints

Leave a healthy environment

FERTIL's Approach toward water conservation

Phase 1 / Phase 2

- Smart 3R concept
- All wastewater streams are identified
- Recovery options are studied and implemented
- Apply suitable technology to treat the remaining streams
- ZERO LIQUID DISCHARGE

Fertil's Water Conservation Initiatives

Water conservation
- Reduce
  - 1-condensing surplus LP steam
- Reuse
  - 2-Excess Urea Process condensate reuse in F2 D-plant
  - 3-Reuse Pr. Air comp suction wash water
- Recycle
  - 4-Boiler BD recycle after polishers upgrade

1. Condensing Surplus LP steam

FERTIL فــرتـيـل

Surplus low pressure (LP) steam was vented

Loss of heat and water

FERTIL identified one unused heat exchanger/cooler in ammonia plant

Excess LP steam (about 14 T/hr) was condensed in this cooler recovering valuable water

Equivalent quantity of desalinated water import is being reduced

---

2- Reuse of excess Urea Process condensate in FERTIL 2 plant

FERTIL فــرتـيـل

F2 BFW

Urea-1 effluent process Condensate

Analyzers

Within the range

Tie-in

F2 Demine. Plant

45 M3/hr

Out of the range

F2 Urea off spec tank

Controlled reprocessing

F2 Desorption Unit

Analyzers
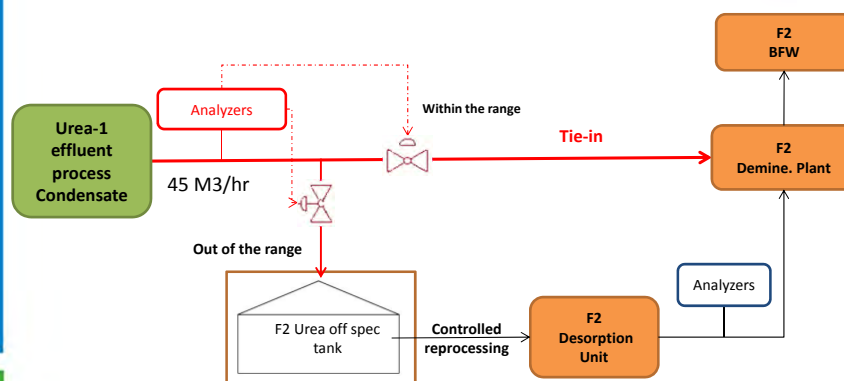
Benefits:
1. Save the import of about 45 m³/hr desalinated water.
2. Reduce effluent to sea

3- Recovery of process water from air compressor suction washing unit

FERTIL فرتيل

The demineralised water used for washing in the Air Intake Stack of Process Air Compressor (8 M3/hr)

| Recovered | Treated | Reused as raw water make up |
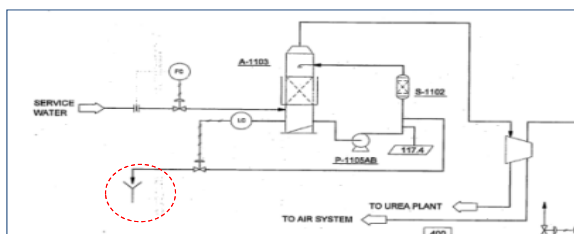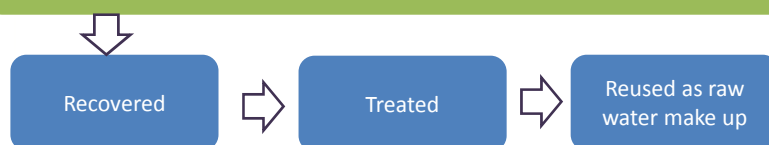
4. Boiler blow down (CBD) condensate

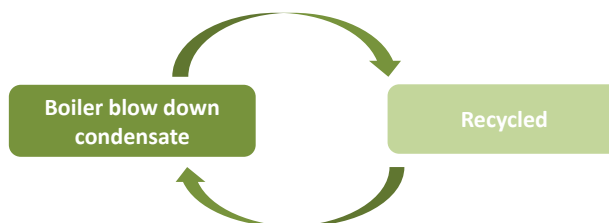FERTIL فرتيل

Currently: Boiler blow down condensate 9 M3/hr → Dumped

Planned: Boiler blow down condensate → Recycled

After increasing the capacity of condensate polishing unit

F-1 Effluent Treatment System

FERTIL فـرتـيـل

Water Conservation Benefits

FERTIL فـرتـيـل

Benefits

- Cost optimization
- Improve performance
- Reduce footprints
- 55% of FERTIL-1 wastewater Recovery
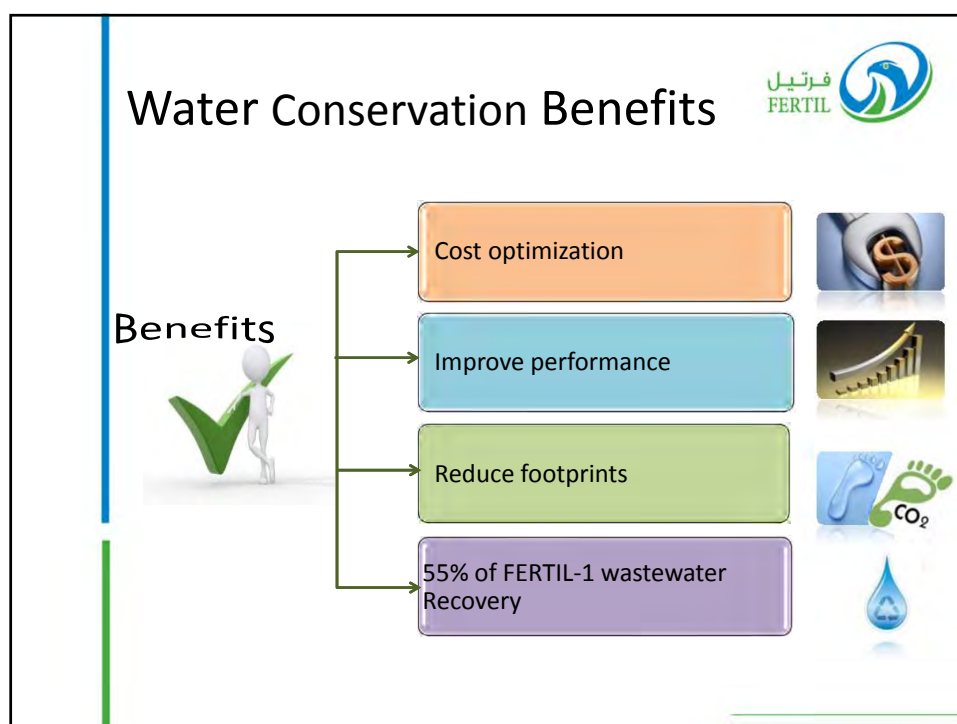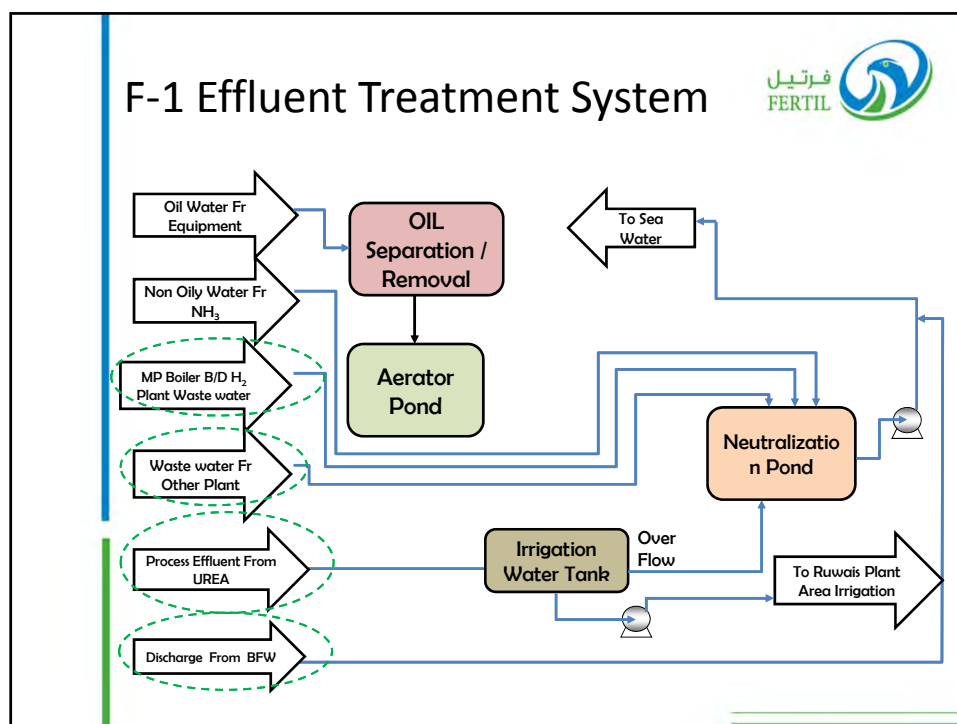
Way forward

- Continual exploration (PROFLEX).
- Start phase 2: ZLD
- Awareness campaigns, improve attitude.
- Rewarding system for energy/water saving proposals as FERTIL EnMs. (ISO 50001).

Save water Today,

Keep Their SmileTomorrow

THANK YOU

AFA
WORKSHOP
Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Case Study 《 effect of scale inhibitor addition in cooling water of synthesis gas compressor inter cooler 》

Eng. Hassan Mostafa Ahmed

Head of Mechanical Engineering Sector– KIMA ~ Egypt

EGYPTIAN CHEMICAL INDUSTRIES

KIMA

Case study:

EFFECT
OF
SCALE INHIBITOR ADDITION IN COOLING WATER OF SYNTHESES GAS COMPRESSOR INTERCOOLERS

Prepared by
Eng. Hassan Mostafa Ahmad

1 1

ABSTRACT

The fouling is a great problem in the industrial applications especially for heat exchangers. In Kima company six-stages reciprocating compressors are used to deliver the synthesis gas ($3H_2 + N_2$), Compressors inter-coolers were cooled by open recirculation system.

Two cases were considered in this study, in each one the overall heat transfer coefficient and consequently the fouling resistance values were recorded.

In the first case artesian water was used, while Sc.I.A. material was added to the cooling system in the second case. Results of this study showed that 6000 hours is a maximum operating time (inter-cooler life time) for the artesian water case. In the other case, for treated cooling water with Sc.I.A, a fouling resistance of 0.385 m2 K/Kw was obtained after 10,000 hours, this value was approximately constant till 30,000 hours of operating time which means that this value can be considered the fouling factor in the second case.

2

COMPRESSOR SPECIFICATIONS

DEMAG compressor six stages

Medium: Synthesis gas ($N+3H_2$)
Suction pressure :   1.02 ata
Suction temperature: 45 °C
Capacity: 13150 m³/hr
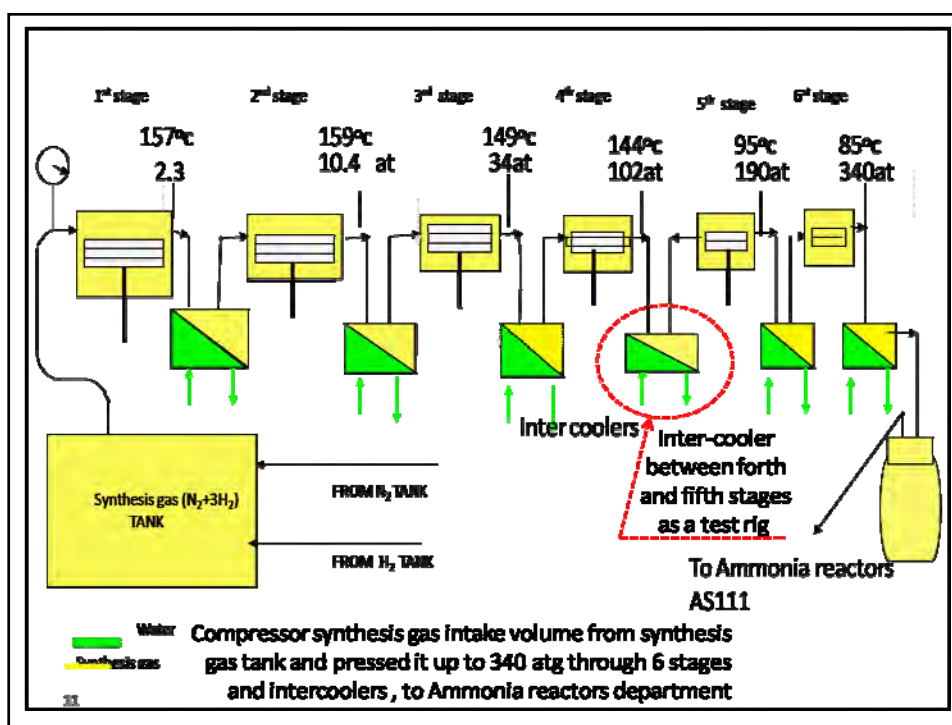Discharge pressure: 341 ata
Speed   125 rpm
Power   4300 KW

3

1st stage	2nd stage	3rd stage	4th stage	5th stage	6th stage
157°c 2.3	159°c 10.4 at	149°c 34at	144°c 102at	95°c 190at	85°c 340at

Synthesis gas (N_2+3H_2) TANK

FROM N_2 TANK

FROM H_2 TANK

Inter coolers

Inter-cooler between forth and fifth stages as a test rig

To Ammonia reactors AS111

Water

Synthesis gas

Compressor synthesis gas intake volume from synthesis gas tank and pressed it up to 340 atg through 6 stages and intercoolers , to Ammonia reactors department

11

1-Introduction

The surface heat transfer exchangers are commonly used for heat transfer processes in industrial applications. The use of impure fluids form a layer of scales and foulants covering heat transfer surfaces. This layer impedes the heat flow across the surface, and promotes chemical reactions at the surface affecting the rate of corrosion or erosion. In some cases, the layer is too thick to block the passages of the fluids. Thus, it is important to clean these heat exchangers from time to time. There are many researches concerned with this problem. Some of these researches focused on the mechanism of fouling formation under different fluid conditions of temperature, velocity, and impurities concentration, (1-4). Also the effect of tube material on the fouling rate was investigated in some researches, (4 , 5). On the other hand there are many studies for the effect of the transfer surface geometry on the fouling rates, (6 – 13) .

5

the treatment of the fouling problem, usually is done by two methods , mechanical or chemical. In the first method a frictional force is applied on the layer to remove the deposition. While the second one depends upon the conversion of depositions to soluble material or suspended solids.

In the present study the forth inter-cooler for a reciprocating compressor in Kima company was selected as a test rig and equipped with recovery instruments. The temperature of inlet and outlet, and the flow rate of cooling water and synthesis gas were recorded with time. Also, the corrosion rate was measured for the cooling water. These measurements were in the normal condition and after chemical treatment.

6

1.1- Heat transfer resistance

☐ For double-pipe heat exchanger, the heat transfer is defined by an integrated modification of Fourier's law,[9].:

$$Q = U \, A_s \, \Delta T$$

➢ At clean condition, the overall heat transfer resistance is expressed by:

$$\sum R_c = 1/U_c = 1/h_o + R_{mo} + (1/h_i) * A_o / A_i$$

➢ It is necessary to provide for the accumulation of fouling substances at the heat transfer surfaces the overall fouled resistance as shown in fig.
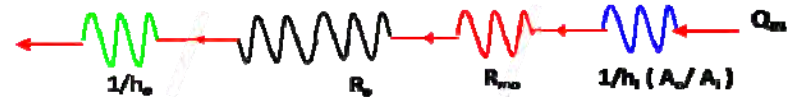
$$\sum R_f = 1/U_f = 1/h_o + R_o + R_{mo} + (1/h_i) * A_o / A_i$$

7

☐ **Thermal conductivity of some metals, [17] :**

• Copper	3980	mW/cm^{o}K
• Aluminum	2370	mW/cm^{o}K
• Iron	803	mW/cm^{o}K
• Steel	447	mW/cm^{o}K

☐ **Thermal conductivity of various scals , [17] :**

• CaCO$_3$	30	mW/cm^{o}K
• Silicate scale	0.86	mW/cm^{o}K
• Other scale	11.54 to 36.05	mW/cm^{o}K

8

Results of fouling layer analyses shows that :

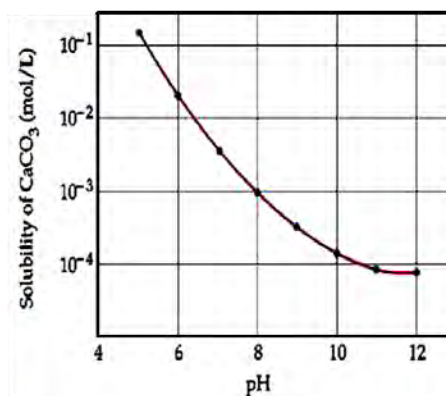(as given by the chemical laboratory of kima company.)

CaCO$_3$ scale forms 84.02% of the fouling layers

on the outside surface area of inter- coolers inner pipes

Calcium carbonate has inverse solubility with temperature
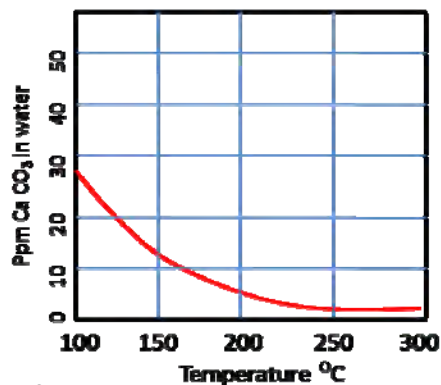
Calcium carbonate solubility with pH.

9

Effective factors on the asymptotic fouling resistance and fouling rates

The most common fouling curves found experimentally are shown in Fig. (1b)

In principle the net overall rate of fouling at any time,ζ can be expressed as the difference between the deposition rate, ϕ_D, and the removal rate, ϕ_g.

The linear mode is indicative of either a constant ϕ_D with ϕ_g Being negligible or ($\phi_D - \phi_g$) is constant.

The falling rate mode results from either decreasing with ϕ_g and ϕ_D being constant or decreasing ϕ_D and increasing ϕ_g.

The asymptotic mode is indicative of a constant ϕ_D and ϕ_g being directly proportional to Rf until $\phi_g = \phi_D$ at the asymptote
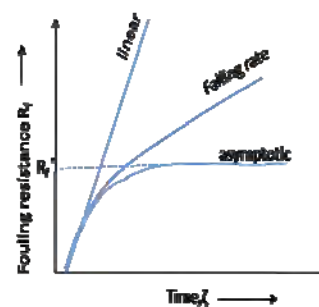

Fig.(1b) Fouling curves, (1)

11

2-EXPEREMENTAL WORK

This experimental study is carried out in kima company at Aswan city. An inter-cooler of the compressor of synthesis gases was prepared as test rig and equipped with the instruments .
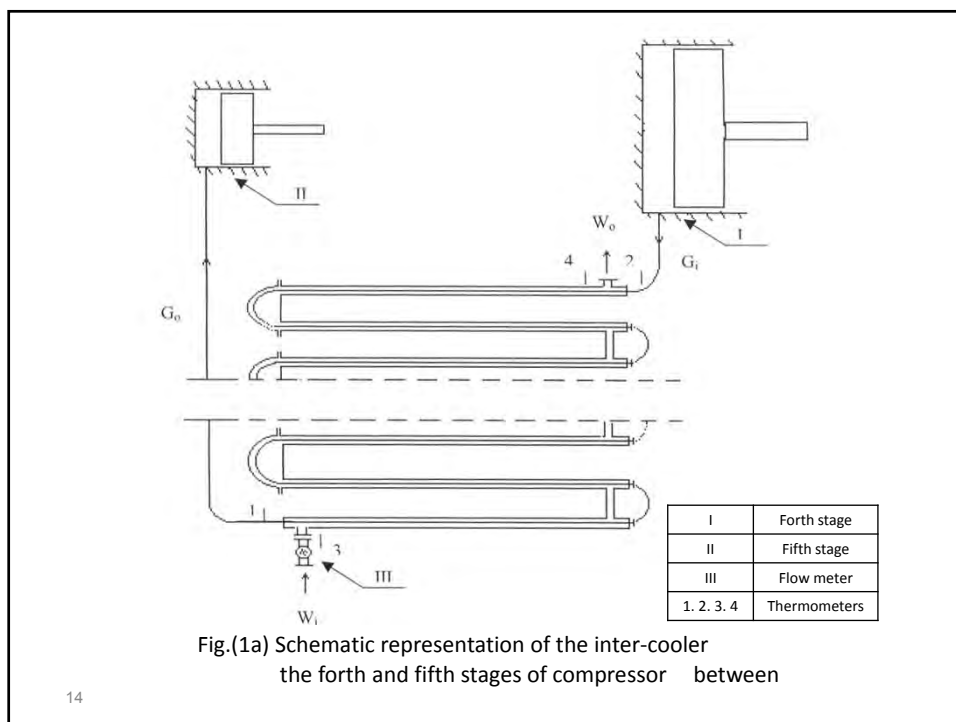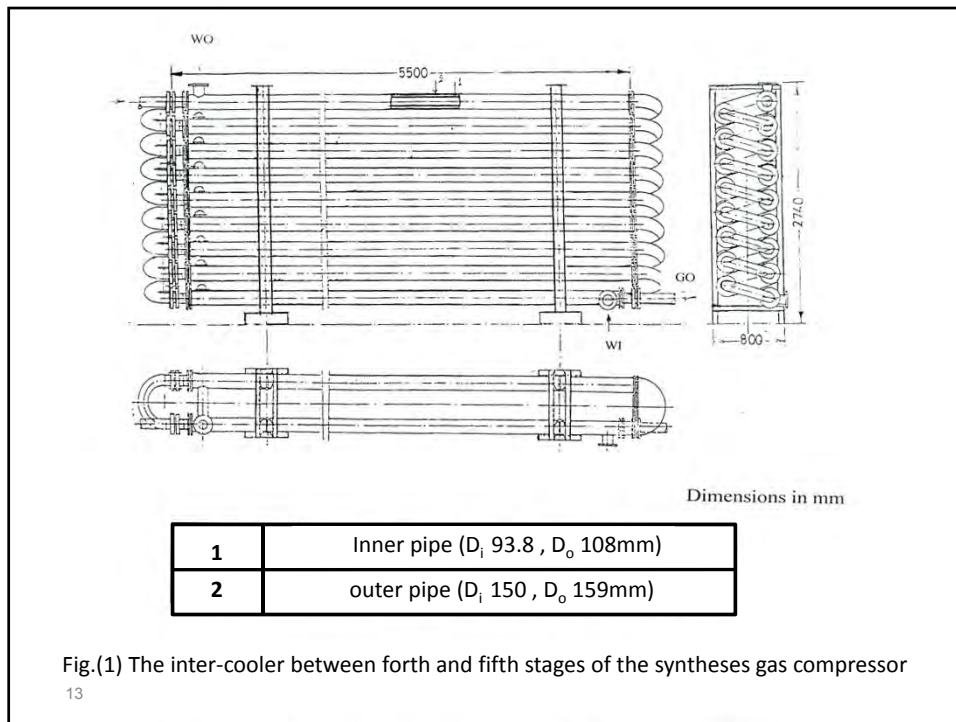
2-1 Test rig

In kima company six stage-reciprocating compressors are used to compress the synthesis gas from 1. 0 to 325 atm. Five intercoolers are used in between these stages. Also, an additional cooler is used to cool the gas after the compression process. The first and second inter-coolers are shell and tube bundle with cross-flow type. The third one is shell and tube bundle with counter-flow type. For the last two inter-coolers the synthesis gas passes through the inside pipe while the water passes through the annulus. Also, the additional cooler has the same specifications of the last two inter-coolers. The fourth inter-cooler consists of eight pipes each pipe is U-shaped, Fig. (1) .
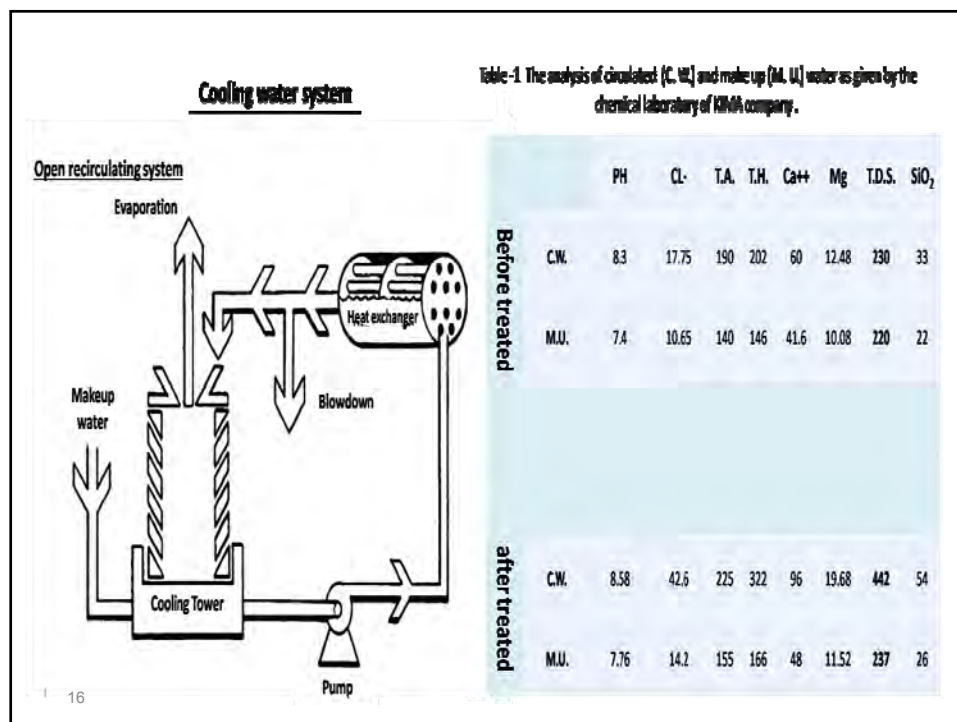
11

12

| 1 | Inner pipe (D_i 93.8 , D_o 108mm) |
| 2 | outer pipe (D_i 150 , D_o 159mm) |

Fig.(1) The inter-cooler between forth and fifth stages of the syntheses gas compressor

13

I	Forth stage
II	Fifth stage
III	Flow meter
1. 2. 3. 4	Thermometers

Fig.(1a) Schematic representation of the inter-cooler
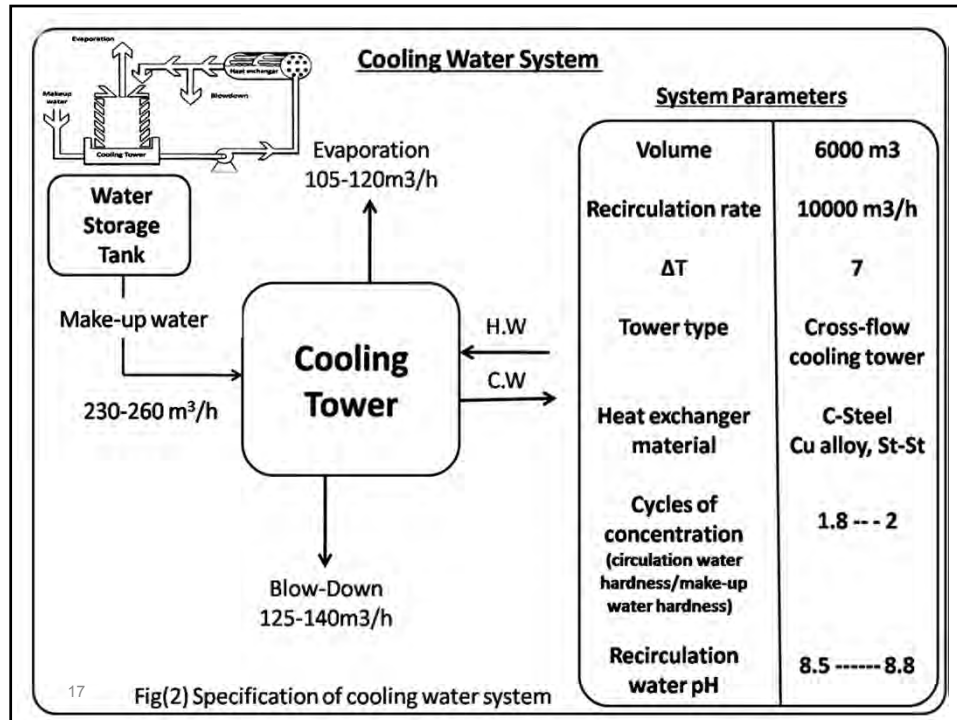   the forth and fifth stages of compressor   between

14

The total length of pipes is 105 m while the wetted length is 85.5 m. (The inner and outer diameters for the inside pipe are 93.8 and 108 mm, respectively. While they are for the outside pipe (shell) 150 and 159 mm, respectively The cooling surface area is 29 M^2). Pipes are made of carbon steel .

The inlet and outlet temperatures of cooling water and gas were recorded against the operating time. Aswan city water (artesian water) is used as a coolant in a opened-loop cycle, fig. (2). The circulated and make up water are analyzed periodically (daily) in the chemical laboratory of kima company. This analysis determines the pH number and concentration of calcium (Ca), chlorine (Cl), Magnesium (Mg), and Silicon oxide (Si O_2). Also, the total dissolved solids (T. D. S.), total hardness (T. H.) and total alkalinity (T. A.) are included in this analysis, as in table -1 .

15

Cooling water system

Open recirculating system

Table-1 The analysis of circulated (C. W.) and make up (M. U.) water as given by the chemical laboratory of KIMA company.

		PH	Cl-	T.A.	T.H.	Ca++	Mg	T.D.S.	SiO₂
Before treated	C.W.	8.3	17.75	190	202	60	12.48	230	33
	M.U.	7.4	10.65	140	146	41.6	10.08	220	22
after treated	C.W.	8.58	42.6	225	322	96	19.68	442	54
	M.U.	7.76	14.2	155	166	48	11.52	237	26

16

Fig(2) Specification of cooling water system

2-2 Fouling Resistance :- The overall heat transfer coefficient based on the outside surface area of the inner pipe was calculated as follows ;

$$U_O = q_W / (A_O \, \Delta T_{LMTD}) \qquad (1)$$

Where $\qquad A_O = \pi D_O L \qquad (2)$

At the beginning of the operation , $(\tau = 0)$;

$$U_C = U_O \qquad (3)$$

At any time, the fouling resistance is obtained from the following relation ;

$$R_F = 1/U_F - 1/U_C \qquad (4)$$

To determine the overall heat transfer coefficient, the heat added to the cooling water should be calculated from the following relation;

$$q_w = m_w \, cp_w (T_{wo} - T_{wi}) \qquad (5)$$

For the synthesis gas the heat rejected is given by;

$$q_g = m_g \, Cp_g (T_{gl} - T_{go}) \qquad (6)$$

18

The difference between the values of q_g and q_w is considered as heat rejected from the inter-cooler to the surrounding by convection and radiation especially from the bends of tubes (not wetted parts) . This heat difference, (q_g / q_w) is presented as a ratio of q_g as follows ;

$$q_r = 1-(q_w / q_g) \qquad (7)$$

The value of q_r was varied from 0.1 to 0.2 for artesian water (case – I), while for treated water (case – II) , it was from 0.1 to 0.15 .

2 -3 Corrosion Rate :- A special coupon, (plate of carbon steel) is used to determine the corrosion rate, " CR " . The manufacturer of the coupon recommended the following relations;

$$CR = \frac{B \ * \ \text{weight loss,} \ \ \text{(grams)} \ * \ 1000.}{\text{Operating time,} \ \ \text{(days)}} \qquad (8)$$

Where the area factor, B is equal to 1.11 for carbon steel coupon as detected by the manufacturer .

19

RESULTS AND DISCUSSION

- The heat transfer values for gas and cooling water were calculated at different operation times, (Eq. (5 & 6)). Then , the overall heat transfer coefficient was obtained, (Eq . (1)). Also, the corrosion rate was determined, (Eq. (8)). These values were recorded for the following two cases ;

20

1 – **Case – I :-**

In this case the artesian water was used as a cooling water for the inter-cooler . Fig. (3) shows the values of overall heat transfer coefficient versus time for inter-cooler. The minimum value for overall heat transfer coefficient, U_{min} , was about 0. 31 kw/m^2 k. At this value the inter-cooler was rejected for cleaning process where the volumetric efficiency was decreases to about 82% from the actual intake volume as shown in Appendix–B. The operating time corresponding to U_{min} was about 6,000 hours At these operating times, the corresponding values of fouling resistance are 1.68 m^2 k/kw, Fig. (4) . It should be mentioned that the inter-cooler was rejected (it partially blocked at the cooling water annular last pass, as in picture) before the asymptotic time was achieved. The maximum value for corrosion rate in this case was about 14.9 mpy in the circulated cooling water
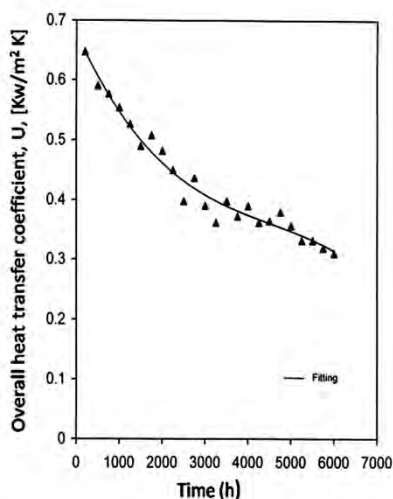
21

Fig.(3) Variation of overall heat transfer coefficient, U, versus operating time in case-1,
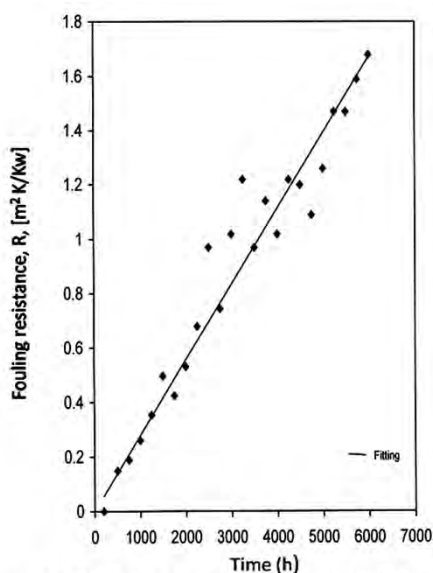
Fig.(4) Fouling resistance, R, as depicted along operating time in case-1,

22   **Case-1, cooling water without scale inhibitor addition, S. I. A.**

Photo of fouled inter-cooler

23

2- Case – II

Treated water (with Sc.I.A) was used in this case for the inter-cooler under test. The asymptotic time was obtained after about 10,000 hours where the value of overall heat transfer coefficient was 0.616 kW/ m² k, Fig. (5). At this time the fouling resistance was about 0.385 m² k/kW which is considered the fouling factor for this case, Fig. (6) . The maximum value for corrosion rate in this case was about 6 mpy .
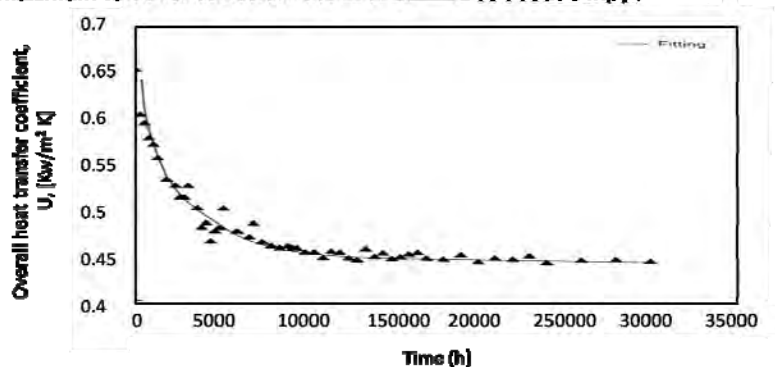

Fig.(5) Variation of overall heat transfer coefficient, U, versus operating time in case-2, cooling water with scale inhibitor addition, S. I. A.
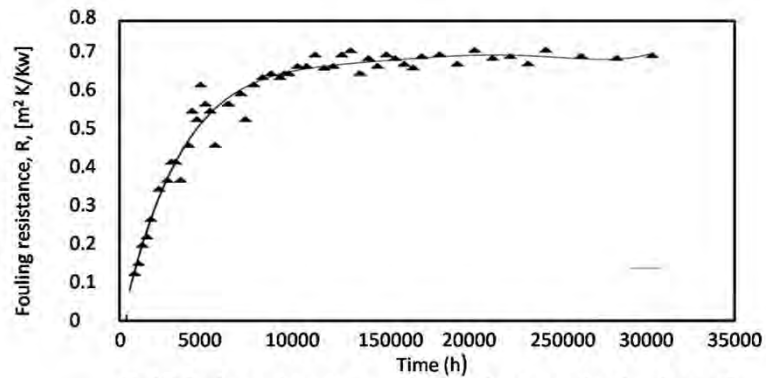
24

Fig.(6) Fouling resistance, R, as depicted along operating time in case-2, cooling water with scale inhibitor addition, S. I. A.

25

Table (4-1) Comparison of results for two cases of field measurements work

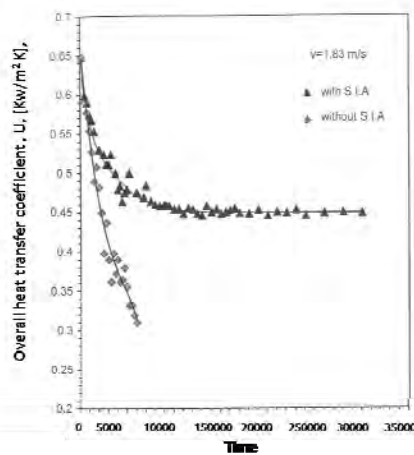|	Case-1 Without S.I.A	Case-2 With S.I.A
Water flow rate m³/h	56	56
Cooling water velocity m/s	1.83	1.83
U_c kW/m² K	0.64	0.64
U_f kW/m² K	0.31	0.45
R_f m² K/kW	1.68	0.658
Reduction in U %	51	29.6
Inter-cooler operating hours (Inter-cooler service life) h	6,000 (The Inter-cooler was partially blocked and become out of service)	30,000 (The Inter-cooler still continues in operation)

26

Fig.|7 Variation of overall heat transfer coefficient, U, along operating time in two cases of field measurements work
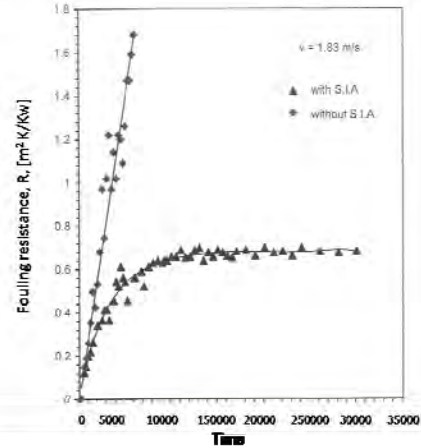
Fig 8) Variation of fouling resistance, R, along operating time in two cases of field measurements work

27

4 - CONCLUSIONS

In this study the fourth inter-cooler for a six-stage reciprocating compressor in Kima company was tested under two cases. In the first case (artesian water) was used as a cooling water, a fouling resistance equal to 1. 091 m^2 ^{O}K / kW was obtained. At this value the inter-cooler was rejected (6,000 hours) for cleaning process before the fouling factor was recorded. For the second case treated cooling water (with Sc.I.A) was used, the asymptotic value (fouling factor) was obtained after 10,000 hours. The compressor is in operation, (about 30,000 hours). The maximum recorded value of corrosion rate was 14.9 and 6.0 mpy for the first and second cases, respectively.

In the second case, the economic study shows that the direct total cost of water treatment and maintenance represent about 35% of the maintenance cost in the first case , with addition to decreased in number of compressor stopped times due to intercoolers cleaning or changing. Also, increased in compressor volumetric efficiency.

28

5 - NOMENCLATURE

A   area, mm^2

B   area constant, Eq. $(8)^s$, (mils . Days) / (mg . Year) .

Cp   specific heat, kw / kg K.

CR   corrosion rate, mpy (mils per year) .

C. W.   Cooling water

D   diameter, mm.

L   tube length, mm.

m   Mass flow rate, kg / s .

M . U.   Make up water .

q   rate of heat transfer, kw .

R_f fouling resistance for heat transfer, m^2 k / kw .

R·   Asymptotic value of R , m^2 k / kw.

T   temperature . K

T . A .   Total alkalinity

T . D . S.   Total dissolved solids .

T . H .   Total hardness .

U   overall heat transfer coefficient, kw / m^2 k.

Subscripts

c   clean

f   fouling

g   gas

i   inner or inlet

o   outer or outlet

r   relative heat difference

w   cooling water

29

7 - REFERENCES

1. watkinson, A. P. And O. Martinez, " Scaling of spirally indented heat exchanger tubes", Transaction of the ASME, Series C, pp. 490 – 492, 1975.

2. watkinson, A. P. And O. Martinez, " Scaling of heat Exchanger Tubes by Calcium Carbonate", Transaction of the ASME, Series C, pp . 504 – 508, 1975.

3. Bansal, B., Muller- Steinhagen, H., and Chen, x. D. , "Effect of Suspended particles on crystallization Fouling in plate Heat Exchanger" , ASME Transaction, vol. 119, No. 3, pp. 586 – 574, 1997.

4. Lee, S . H . , and Knudsen, J. G. , " Scaling Characteristics of cooling Tower Water" , ASHRAE Trans., vol. 85, part – 1, pp. 281 – 302, 1979

5. Zelever, N . , et al, "Tube Material, Fluid Velocity, Surface Temperature and Fouling " Cooling Tower Inst. , Houston, TX, CTI paper No. TP – 84 – 16 , 1984 .

6. Sheikholesami , R. And watkinson, A . P . , " Scaling of plain and Externally Finned Heat Exchanger Tubes" , Trans. Of the ASME, Series C, vol. 108. pp. 174 – 152, 1986 .

7. El- Moghazy, I. M. M. , and M. B. Abu El – Hassan, " The effect of inter-fin spacing and fin- height on heat transfer coefficient considering fouling " , J. Of Eng. And Applied science, Faculty of Eng. , Cairo University, vol. 39, No. 1, pp. 87 – 99, 1992 .

8. Watkinson, A. P. , L. Louis, and R. Brent, " Scaling of Enhanced Heat Exchanger Tubes " Canadian J. Of Chemical Engineering, vol. 52, pp. 558 – 562, 1974 .

9. kim, N – H., and R. L Webb, "Experimental study of particulate Fouling in Enhanced water chiller Condenser Tubes" , ASHRAE Transaction, Vol. 95, part – 1, pp. 507 – 514, 1989.

30

10. kim, N – H. , and R. L. Webb, "particulate Fouling of water in Tubes Having a Two-Dimensional Roughness Geometry" , Int. J. Heat Mass Transfer, Vol. 34, No. 11, pp. 2727 – 2738, 1991 .

11. El- Moghazy, I. M. M. "Experimental study of fouling inside internally Finned Tubes" , J. Of Eng. And Applied Science, Faculty of Eng., Cairo University, Vol. 42, No. 5, pp. 945 – 960, 1995.

12. El- Moghazy, I. M. M. "Enhancing Heat Transfer for Condensation of saturated steam on Helically Grooved Tubes" , Bulletin of the Faculty of Eng. , Assuit University , Vol. 42, pp. 49 – 56, 1996 .

13. Epstein, N. , and Sandhu, k. , "Effect of Uniform Fouling Deposit on Total Efficiency of Extended Heat Transfer Surface" , Sixth Int' l Heat Transfer Conf. , Toronto, Vol. 4, pp. 307 – 402, 1978 .

14. Kern, D. Q. , and R. E. Seaton, "A Theoretical Analysis of Thermal Surface Fouling" Br. Chem. Engineering Vol. 14, No. 3, Pp. 258 – 262, 1959 .

15. Characklis, W. G., Zelever, N. , and Turakhia, M. , "Fouling and Heat Transfer in Fouling in Heat Exchange Equipment" , ASME, HTD, 17, pp. 1 - `15, 1981 .

16. Ibrahim, M. K. , " Fouling Prediction in Heat Transfer Equipment" , The 10 th Int. Conf. Of Mechanical power Engineering, Assuit, Egypt, 16 – 18 Dec. 1997 .

17. RCG/ Hagler, Bailly, Inc. Washington, D.C. USA "BOILER WATER TREATMENT" Published by Energy Conservation and Efficiency Program (ECEP) December, 1994.

31

Compressor curves for intake volume
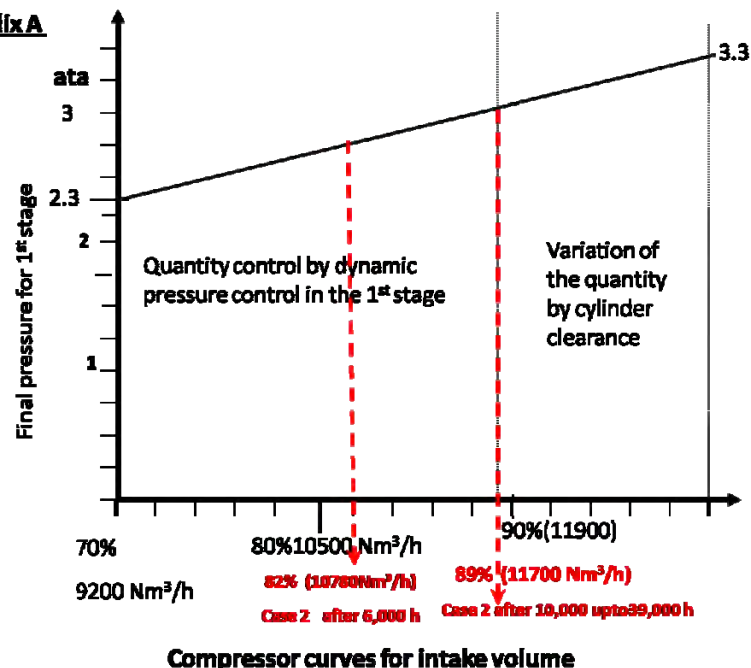
Session III

AFA
WORKSHOP
Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Pretreatment Technology for surface water and well water

Dr. Abdel Aziz Konsowa~ Chairman – Environmental Engineering Consultants - Egypt

Evaluation Removal of Nanoparticles from Water by Coagulation and Ultrafiltration Process

Xuezhi Zhang[a], A. H. Konsowa[c], Yongsheng Chen [a,b*], Xiaoshan Zhu[a] and John C. Crittenden[b]

[a]Department of Civil and Environmental Engineering, Arizona State University, Tempe, Arizona, USA

[b]School of Civil, Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

[c] Chemical Engineering Department, Alexandria University, Alexandria, 21544, Egypt.

Abstract: The removal of nanoparticles (NPs) is a challenging due to their smaller size. In this study the removal of NPs using coagulation/-flocculation/sedimentation as well as ultrafiltration process were evaluated. Synthetic hematite NPs with different size (53, 98, and 205 nm), commercial silver and SiO_2 NPs were used as model contaminants. Standard jar test was performed to evaluate NPs removal by coagulation/flocculation/sedimentation process with 20 and 60 mg/l aluminum sulfate. For the ultrafiltration process, a PVC UF membrane with a Molecular weight cut off (MWCO) of 50K Dalton was employed. GF-AAS was used to analyze the metal ion concentration. SEM-EDX was also used to understand the filtration mechanism of NPs by the UF membrane process. Practicability of NPs removal using UF membrane was evaluated by studying the membrane fouling by hematite NPs.

The results show natural sedimentation of NPs is very slowly due to their small particle size. Coagulation/flocculation/sedimentation process is not efficient for hematite NPs removal due to the small size of NPs. At lower aluminum sulfate concentration of 20 mg/L, about 12 hours are needed to remove 58%~80% of the NPs. Removal rate for smaller particles was found to be lower than those of larger particles. Higher alum concentration (60 mg/L) enhances NPs removal, however, there are still 3%~ 5% NPs in water even after 24 hours sedimentation. Comparing with coagulation/flocculation/sedimentation, UF is very effective for hematite NPs removal in view of higher removal rates. Removal of 99.95% of hematite, 99.90% of silver and 99.70% of SiO2 were achieved... SEM mapping shows that all hematite NPs were

* Corresponding author. Y. Chen; phone: +1 404-894-3089; fax: +1 404-894-2278; email: yongsheng.chen@ce.gatech.edu

rejected on the active filter layer of the hollow fiber membrane and no hematite presents in the inside pores of the membrane. The primary mechanism for removing particles from solution in membrane filtration is straining and cake filtration for hematite and SiO_2 NPs while attachment and cake filtration for silver NPs. Fouling of the membrane by hematite NPs is mainly due to the cake formation which is 95.61% of the total membrane resistance, and membrane permeability can be easily resorted by backwash.

Keywords: Nanoparticles; removal; coagulation; membrane; fouling

1 Introduction

Production, use, and disposal of nanomaterials (NPs) will inevitably cause humans and other environmental receptors to be exposed to NPs. Recent research suggests that when normally harmless bulk materials are made into NPs, they tend to become toxic. Researchers have found fullerene-related photo-induced lipids, proteins and cells damage, brain damage, severe organ damage, skin inflammation, alteration of biochemical functions, and distribution into cells and tissues [1-4]. Other NPs such as metals and metal oxides have also been shown to have inflammatory and toxic effects on cells, including DNA damage and chromosomal aberrations [5-7].

It is very urgent to evaluate the removal efficiency of NPs by the present water treatment technology (such as coagulation/flocculation/sedimentation and filtration). There are only few papers studied the remove of NPs using coagulation, membrane filtration etc. However, the NPs used in these studies are relatively large the membrane used is not scale up for water treatment process [8-11]. In this study the removal of silver and SiO_2 NPs and lab-made hematite NPs with different size (53, 98, and 205 nm) were studied by comparing coagulation/-flocculation/sedimentation as well as UF process were evaluated, and the removal mechanism and the feasibility of NPs removal by UF was discussed.

2 Material and method

2.1 Material

Silver NPs (1-10 nm particle size, Northern Nanotechnologies, Inc.), SiO_2 (10 nm, Sigma-Aldrich) and hematite particles (self-make) were used as contaminants.

Three hematite NPs sizes 53, 98 and 205 nm were synthesized. 53 nm hematite (a-Fe_2O_3) NPs were synthesized by the forced hydrolysis of $FeCl_3$ using the method described by Penners et. al [12]. Ferric chloride was dissolved in 0.004 M HCl at 100 ^{o}C and the final Fe^{3+} concentration is 0.02 M. After mixing, the container was immediately placed in an oven (100 ^{o}C) for 24 hours. The prepared sol was centrifuged at 14000 rpm for 10 min and the supernatant was discarded and the sediment was rinse using 0.004 M HCl. Centrifugation and rinse was repeated 6 times and no free ion was detected.

Batches of larger size hematite particles were prepared by using the 53 nm hematite as seed to grow. 10 mM $FeCl_3$ and 4 mM HCl was heated to boiling and then seed sol was injected. The mixture was stirred by a magnetic stirrer to prevent settling of the sol. Every enlargement was achieved by using the grown sol as a seed sol in a subsequent growth cycle.

NPs The median particle sizes for these NPs were characterized by dynamic light scattering (DLS), hematite NPs and silver is very stable and their size was found to be 53, 98 and 205 nm for different size hematite NPs and 4.7 nm for silver NPs. SiO_2 NPs were aggregate in water the size was found to be 740 nm which is much larger than that of the reported original size.

2.2 Remove of NPs by natural sedimentation

Settling experiments were conducted in a 1000 mL graduated cylinder using DI water. At the start of the settling experiment, 10 mL of 1000 mg/L NPs suspension was added to 990 mL DI water. At 0, 1, 3, 6, 12, 24 and 48 h, NP suspensions were sampled from 10 cm below the water surface using a pipette.

2.3 Remove of NPs by coagulation/flocculation/sedimentation

Hematite NPs concentration was prepared using DI water. Removal of NPs using conventional coagulation-flocculation and sedimentation was evaluated using standard jar test with rapid mixing for 1min at 100 rpm, slow mixing for 30 min at 30 rpm and settling for 24 h. alum sulfate with a concentration of 20 and 60 mg/L were used and pH of the water was adjusted into 8.0. At 1, 3, 6, 12 and 24 h, NP suspensions were sampled from 10 cm below the water surface using a pipette.

2.4 Filtration of NPs using UF membrane

A PVC UF membrane was employed to evaluate the removal efficiency of NPs by membrane process. Molecular weight cut off (MWCO) of the UF membrane is 50000 Dalton and the filtration area of the membrane is 0.125 m^2. Dead end operation was used and the transmembrane pressure was maintained at 34.5 kPa.

2.5 Nanoparticles analysis

Analysis of NPs was based on the element analysis after digestion of these NPs. 50 mL NPs suspensions were dried and digested by 5 mL trace metal grade concentrated nitric acid. After that the sample was transferred to a PTEE tube and the final volume is 5 mL. GF-AAS (Varian SpectrAA 400) was used to analyze the metal concentration. Triplicate analyses were performed for each sample and the average value was reported.

3 Result and discussion

3.1 NPs removal using natural sedimentation

Fig. 1 shows NPs concentrations during natural sedimentation process. The concentrations of all NPs decreased gradually, while the fastest decrease was observed for SiO_2 NPs. There are still more than 72%, 90% and 97% of SiO_2, hematite and silver NPs remaining in the water column after 24 hours' settling. Settling processes is found to be not efficient in removal of these NPs.
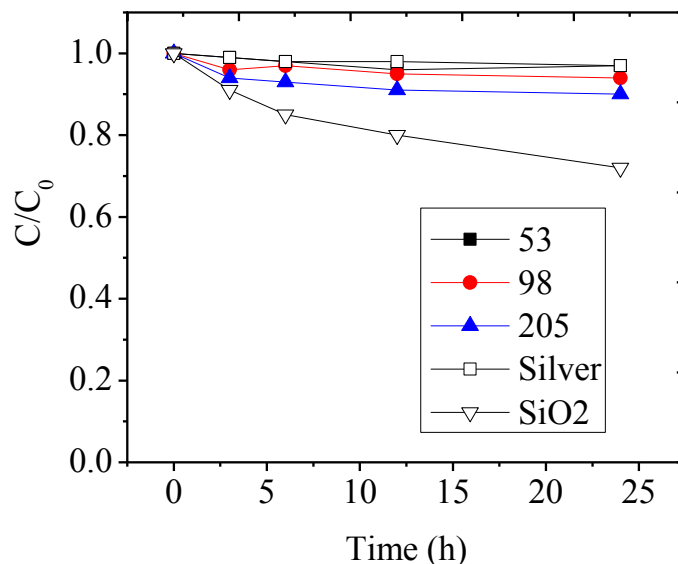

Fig. 1 Natural sedimentation of NPs

NPs have much smaller size than natural suspended particles in river. It is reported that predominantly suspended particles in Rhone River and Liu River are 34.3 μm to 58.8 μm and 9 to 11 μm respectively[13, 14]. Particles settle down due to the gravitional force while the thermal (Brownian) fluctuations resist the particle settlement. For the NPs, the Brownian motion of a 1 μm particle due to thermal fluctuation in water is offen greater thant the settling velocity. Hence, the c settling of NPs is much slower than that of natural particles. Chen found that about 70% of 100 μm silt particles in water settled in less than 2.5 h [15]. The slower settling of NPs in water indicates coagulant is needed to destabilize NPs for their removal.

3.2 Evaluation of hematite NPs removal using coagulation/flocculation/ sedimentation

Removal of NPs using simulated conventional treatment process is shown in Fig. 2. When alum was used, fast sedimentation was observed for all NPs. Removal rate decreased with the decreasing of particle size. The removal rate for SiO_2, hematite at 53, 98, 205 nm, and silver after 6 hours' sedimentation was 57%, 39%, 54%, 69%, and 15% respectively. It takes 12 hours to remove 58%~80% of the NPs. When aluminum sulfate concentration increased to 60 mg/L (Fig. 3), concentrations of all the NPs decreased sharply. For all the NPs, about 90% of removal was got after 3 hour's sedimentation. However, there are still 3%~ 5% NPs in water even after 24 hours sedimentation.
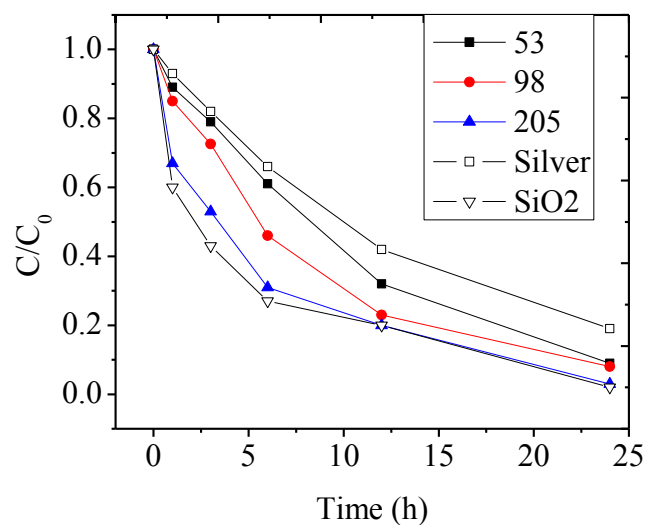
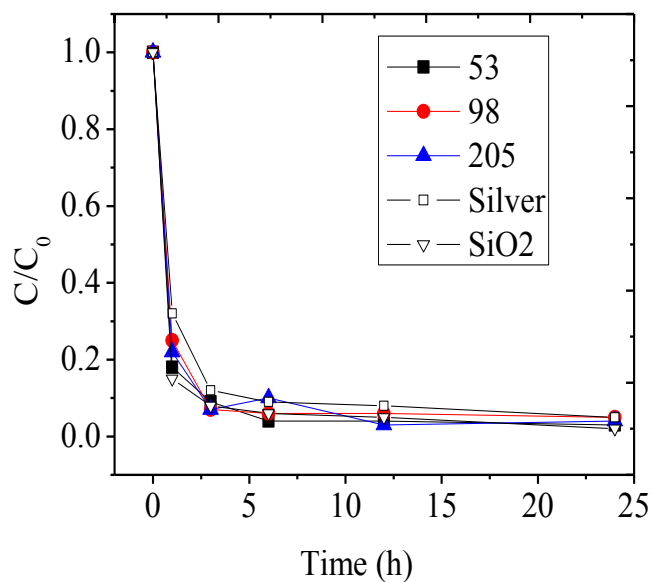Fig. 2 Sedimentation of NPs after coagulation using 20 mg/L alum

Fig. 3 Sedimentation of NPs after coagulation using 60 mg/L alum

Derjaguin – Landau – Verwey – Overbeek (DLVO) theory has been extensively applied to understand aggregation behavior of larger colloids. DLVO theory accounts for two forces between the particles, The sum of van der Waals attraction and electrical double layer (EDL) repulsion determines whether the net interaction between particles is either repulsive or attractive[16]. Fig. 4 shows the DLVO calculations for hematite, SiO_2

6

and silver NPs both in DI water with and without alum (20 mg/L). In DI water without alum, the EDL repulsive energy is dominant for hematite and silver NPs, which prevents them aggregate. SiO_2 NPs have a relatively lower energy barrier, which makes them aggregate to about 740 nm, and thus results their faster sedimentation in DI water. Smaller particles are more probable to coagulate than larger particles as the net repulsive energy barriers between NPs decrease with the decrease of primary particle size except for silver NPs. Although silver NPs have smaller size of 4.7 nm, it has a relative higher energy barrier which makes them stable. This is because their high absolute zeta potential (-56 mV) due to the surface modification of by carboxyl functionalized group.
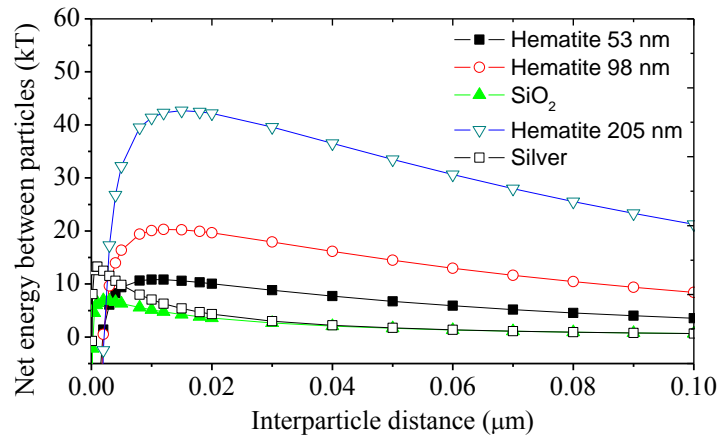
(a)
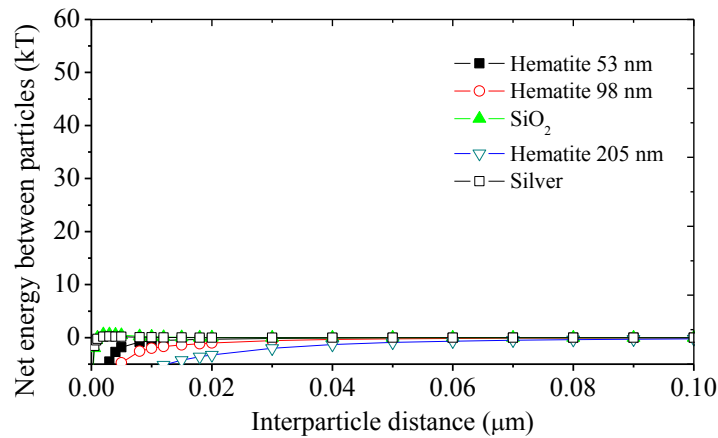
(b)

Fig. 4 Interaction energy with the separate distance between NPs

(a) DI water (b) 20 mg/L Alum

Alum induces rapid aggregation by depressing electrostatic repulsion and thereby minimizing the energy barrier to aggregation. When 20 mg/L alum was added, the energy barrier of all the NPs disappears thus makes them unstable and has the potential to settle down. Although smaller particles are prone to be easily destabilized by alum, at a concentration of 20 mg/L Alum, the settling of the smaller particles is slower than the larger one. Possible reason for this is as the same mass concentration, there are more surface area for smaller particles, and thus more Alum is needed for them to be coagulated. Hsu et al studied the effect of particle size on the critical coagulation concentration (CCC), and found the smaller the particle, the higher CCC [17]. When alum concentration increased to 60 mg/L, all the NPs settled down quickly.

The removal efficiency of NPs using alum coagulation/flocculation/sedimentation is about 90% after three hours' sedimentation and 95% after 24 hours's sedimentation. Chang and Lee studied the removal of NPs from wastewater by polyaluminum chloride (PACl) coagulation and sedimentation using coagulation, they found only 94% of turbidity was removed (from 6.4 to 0.39 NTU) at PACl dose of 10 mg/L and setting for 2 hours. Employing thermal treatment by increasing the temperature up to 65 ^{o}C, helps to remove 98.5% of turbidity *[11]*. Limbach et al. investigates the use of a model biological wastewater treatment plant for removal of CeO_2 NPs. They found that most of the CeO_2 NPs could be captured through adhesion to clearing sludge, while up to 6 wt% of the CeO_2 NPs was found in the exit stream of the model plant[18].

3.3 Evaluation of NPs removal using UF membrane

Remove of NPs by UF process was evaluated. Table 1 shows the removal of NPs using UF membrane. Hematite NPs in permeate was less than 0.005 mg/L and their removal rate is more than 99.95%. Removal rate for silver and SiO_2 are 99.9% and 99.7% respectively.

Table 1 NPs Removal by UF

	Hematite 53 nm	Hematite 98 nm	Hematite 205 nm	Silver 4.7 nm	SiO$_2$ 740 nm
Initial (mg/L)	10	10	10	10	10
Final (mg/L)	0.005	0.004	0.005	0.01	0.03
Removal (%)	99.95	99.96	99.95	99.9	99.7

The influence of initial concentration and pH on hematite NPs (53 nm) was also studied and the results are shown in Table 2. At higher initial concentrations of hematite NPs, hematite concentration in permeate is slightly higher and the value is 0.008 and 0.02 mg/L for the initial concentration of 99.6 mg/L and 492.0 mg/L respectively. The hematite NPs removals are higher than 99.99%. Removal efficiency of hematite NPs by UF is independent of the initial pH, and their removal was more than 99.95%.

Table 2 Influence of initial concentration and pH on the removal of Hematite by UF

	100 mg/L	500 mg/L	pH 5.0	pH 7.0	pH 8.0	pH 10.0
Initial (mg/L)	99.6	492.0	10.1	10.1	10.1	10.1
Final (mg/L)	0.008	0.02	0.005	0.003	0.004	0.003
Removal (%)	99.99	100.00	99.95	99.97	99.96	99.97

The absence of silver particle in permeate was also checked by spectrometer and the results were shown in Fig. 5. There is a peak at 440 nm and the absorbance is 0.305 for 10 mg/L silver NPs. Silver NPs at a concentration of 0.1 mg/L can be clearly detected. No peak was observed around 440 nm and the signal is smaller than that of 0.1 mg/L, indicating silver concentration in permeate was less than 0.1 mg/L and thus the removal efficiency was higher than 99 %.
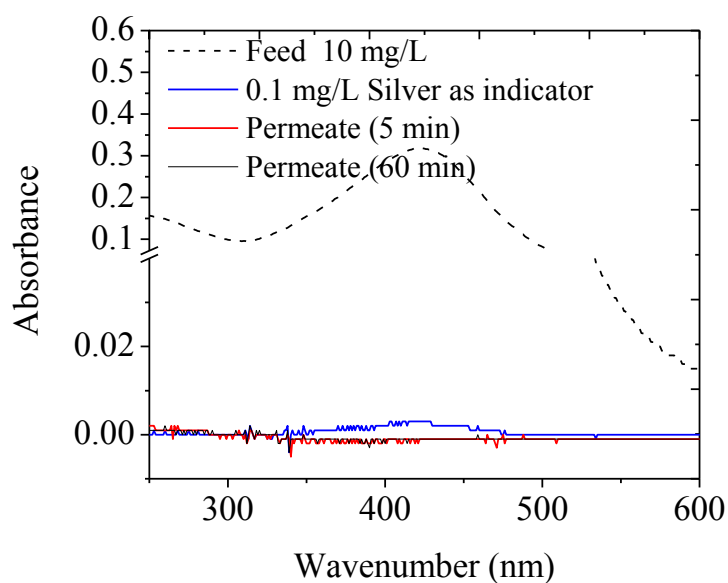
Fig. 5 UV-Vis spectrum of Silver NPs

Fig. 6 shows the EDX mapping images of membrane fiber after filtration of hematite NPs. Iron deposited on the filter layer of the hollow fiber and there is no iron in the inside pores of the membrane, indicating that no hematite NPs penetrate the separation layer.
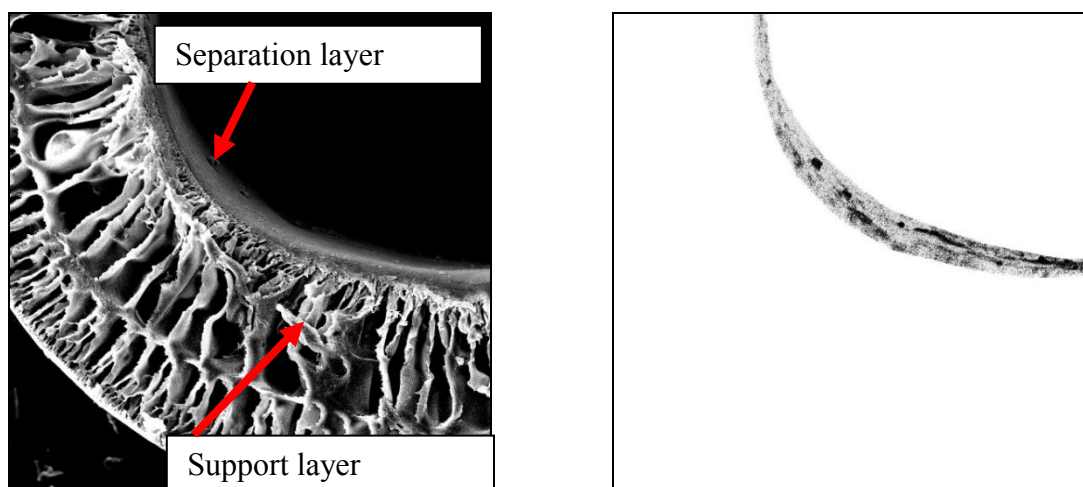

Fig. 6 EDX mapping image of iron in membrane surface. (a) SEM image of the cross section of one hollow fiber (b) EDX mapping of iron.
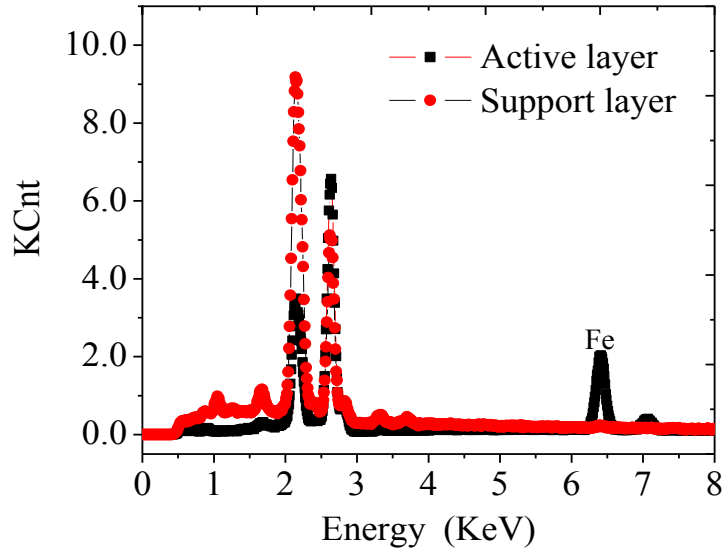
10

Fig. 7 EDX spectrum of the active layer and support layer of the membrane

The primary mechanism for removing particles from solution in membrane filtration is straining (also called sieving or size exclusion), but also removal is affected by adsorption and cake formation[19]. The removal of hematite and SiO_2 NPs should mainly due to straining in the initial stage. The increase of the removal efficiency of hematite fron 99.95 to 99.99 is considered to be approve of cake filtration

For the removal of particles smaller than the effective pore diameter (the diameter of the smallest particle that is completely rejected) by sieving, Ferry developed a model (Eq. 1)[20]. In the model, in laminar flow conditions, water follows parallel streamlines through cylindrical pores. Particles following a streamline near the edge of the pore opening impact the membrane surface and are retained, whereas particles following a streamline near the center of the pore are not retained.

$$R = 1 - 2(1 - \frac{dp}{d_{EP}})^2 + (1 - \frac{dp}{d_{EP}})^4 \qquad \text{Eq. 1}$$

where: d_P is particle diameter (m) and d_{EP} is effective pore diameter.

11

The calculated removal rate by sieving for 4.7 nm silver NPs was 51.71%. However, in this study, more than 99.9% of silver NPs were removed, indicating there are other mechanisms for silver NPs rejection. Attachment happened during the early stages of filtration as can be seen from Fig. 5 concentration of silver in permeate did not increase after 60 mins' filtration. Cake filtration maybe also happen as some pores were blocked by the silver NPs. cake of silver NPs was quickly accumulated on the membrane surface and thus cake filtration begins. This surface cake acts as a filtration medium, providing another mechanism for rejection. The illustration of the filtration process is presented in Fig. 8.
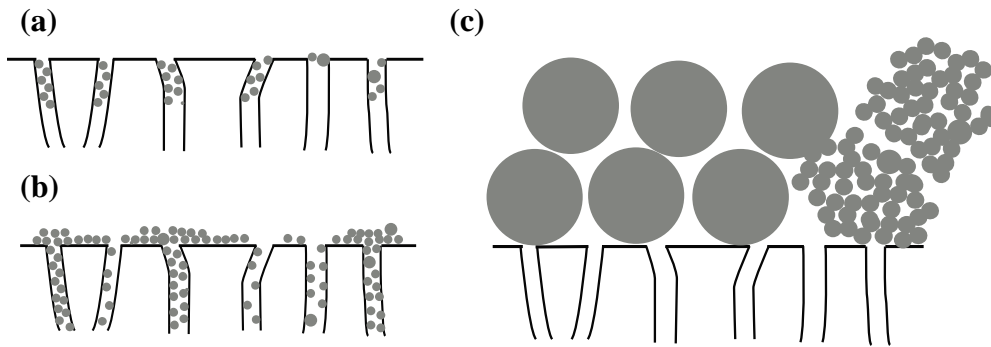

Fig. 8 Illustrations showing NPs removal, (a) smaller NPs remove by attachment, (b) smaller NPs removal by cake filtration, (c) Hematite and SiO_2 NPs remove

Yang and Li studied the electrofiltration of wastewater containing 1333 mg/L SiO_2 NPs using lab-prepared TiO_2/Al_2O_3 ceramic composite membranes with a MWCO of 95 KDa. They found that 90% of total suspended solids and silica respectively were removed and the final turbidity was lower than 0.75 NTU [9]. Much higher removal rate was achieved in this study because using of a lower MWCO UF membrane.

3.4 Suitability of NPs removal using UF

Fouling is a big challenge for membrane operation. Flux decline was recorded during the filtration of 10 mg/L and 99.6 mg/L hematite NPs with a size of 53 nm and the results are shown in Fig. 9. Flux is very stable in the filtration of 10 mg/L hematite NPs. When higher concentration of NPs was used, at first 50 mins, the flux is also relatively stable and the value is around 108 L/m^{2}h. After that, gradually flux decline was observed and finally flux at 152 mins' filtration decreased to 4.78 L/m^{2}h.
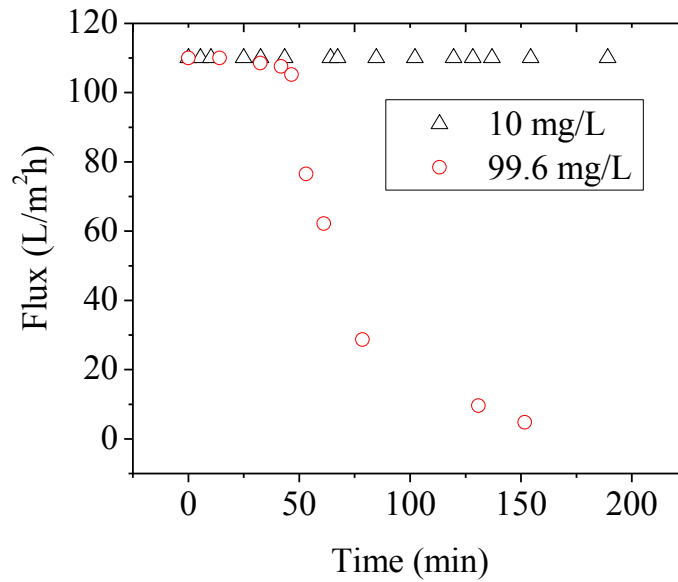

Fig. 9 Flux change during the filtration of hematite NPs

During the filtration process, the total membrane resistance is the sum of the intrinsic membrane resistance, cake resistance, and irreversible fouling resistance. A typical form of the resistance-in-series model is shown in Eq 2:

$$Q = \frac{A\Delta P}{\mu(R_m + R_c + R_{ir})} \qquad \text{Eq (2)}$$

where:

where Q (m^3/s) is the permeation flow rate,

ΔP is the transmembrane pressure,

μ is the viscosity of permeate,

R_m is the inherent membrane resistance,

R_c is the cake resistance

R_{ir} is the irreversible fouling resistance due to fouling that cannot be removed by backwash (m^{-1}).

Fig. 10 shows the fraction of resistances at the beginning and the end of the filtration process. After 15 mins of filtration, intrinsic membrane resistance (R_m) consist 99.13% of the total membrane resistance (R_t). As hematite NPs deposited on the membrane, cake resistance increased, and at the end of the filtration cake resistance increase to 95.61% of the total membrane resistance. Irreversible resistance only increased to 0.04% of the total resistance.
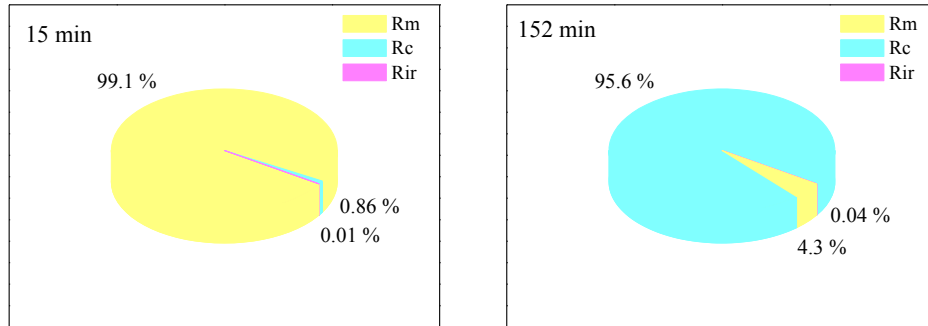

Fig 10 Fouling fraction in the initial (15 min) and final stage (152 min) of filtration.

Fouled membrane was backwashed and the permeability was tested and compared with that of the initial permeability. It was found 99.13% of the initial flux was resorted, which means the removal of NPs by UF is practicable. The fouling of colloids has been widely studied. Particle properties (such as size, concentration, surface charge), membrane properties (MWCO, hydrophobicity or hydropholicity, surface roughness,), water chemistry (ion strength, pH, presence of other contaminants) as well as operation conditions (TMP, backwash interval and pressure, etc) will play an important role for the fouling of membrane [21-24]. Nonetheless, results of this study indicating the fouling of UF membrane by hematite NPs is not a limiting factor for applying UF to remove NPs,

4 Conclusions

Natural sedimentation of NPs is very slowly due to their small particle size. In the simulated conventional treatment process, faster settlements were observed. Removal efficiency of NPs depends on alum concentration. At lower alum concentration (20 mg/L), it takes 12 hours to remove 58%~80% of the hematite, silver and SiO_2 NPs. Higher alum concentration (60 mg/L) makes removal of NPs easier and about 90% of the total NPs were removed after three hours' sedimentation. However, there are still 3%~5% NPs in water even after 24 hours' sedimentation.

UF is very effective for NPs removal. At an initial concentration of 10 mg/L, only trace amount of NPs in permeate are detected (0.005~0.03 mg/L) and their removal efficiency is more than 99.7%. Removal rate for 53 nm hematite NPs was pH independent. When filtrate 99.6 and 492.0 mg/L 53 nm hematite NPs, more than 99.99% of removal rate was achieved. SEM mapping shows that all hematite NPs were retained on the separation filter layer of the hollow fiber membrane and no hematite presents in the inside pores of the membrane. The primary mechanism for removing particles from solution in membrane filtration is sieving. Cake filtration and attachment also helps the rejection of NPs. Fouling of the membrane by hematite NPs is mainly due to the cake formation, the irreversible fouling is only 0.04% of the total resistance. After backwash, 99.13% of the initial flux can be resorted.

Reference:

1. Oberdorster, E., *Manufactured nanomaterials (Fullerenes, C-60) induce oxidative stress in the brain of juvenile largemouth bass.* . Environ. Health Perspect., 2004. **112**: p. 1058-1062.
2. Kamat, J.P., et al., *Reactive oxygen species mediated membrane damage induced by fullerene derivatives and its possible biological implications.* Toxicology, 2000. **155**: p. 55-61.
3. Ueng, T.H., et al., *Suppression of microsomal cytochrome P450-dependent monooxygenases and mitochondrial oxidative phosphorylation by fullerenol, a polyhydroxylated fullerene C-60.* Toxicol. Lett., 1997. **93**: p. 29-37.
4. Nakajima, N., et al., *Photo-induced cytotoxicity of water-soluble fullerene.* Fullerene Sci. Technol., 1996. **4**: p. 1-19.
5. Cheng, M.D., *Effects of nanophase materials (<) 20 nm) on biological responses.* . J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng., 2004. **39**: p. 2691-2705.

6.   Rahman, Q., et al., *Evidence that ultrafine titanium dioxide induces micronuclei and apoptosis in syrian hamster embryo fibroblasts.* Environ. Health Persp., 2002. **110** p. 797–800.

7.   Nakagawa, Y., et al., *The photogenotoxity of titanium dioxide particles.* Mutat. Res. , 1997. **394**: p. 125-132.

8.   Zhang, Y., et al., *Stability of commercial metal oxide nanoparticles in water.* Water Research, 2008. **42**(8-9): p. 2204-2212.

9.   Yang, G.C.C. and C.-J. Li, *Electrofiltration of silica nanoparticle-containing wastewater using tubular ceramic membranes.* Separation and Purification Technology, 2007. **58**(1): p. 159-165.

10.   Chang, M.R., D.J. Lee, and J.Y. Lai, *Nanoparticles in wastewater from a science-based industrial park--Coagulation using polyaluminum chloride.* Journal of Environmental Management, 2007. **85**(4): p. 1009-1014.

11.   Chang, M.R., D.J. Lee, and J.Y. Lai, *Coagulation and filtration of nanoparticles in wastewater from Hsinchu Science-based Industrial Park (HSIP).* Separation Science and Technology, 2006. **41**(7): p. 1303-1311.

12.   Penners, N.H.G. and L.K. Koopal, *Preparation and Optical-Properties of Homodisperse Hematite Hydrosols.* Colloids and Surfaces, 1986. **19**(4): p. 337-349.

13.   Fan, H., et al., *Temporal and spatial dynamics of different particle size of suspended sediment in the Liu River catchment, China.* International Journal of Sediment Research, 2006. **21**(3): p. 209-219.

14.   Santiago, S., et al., *PARTICLE-SIZE CHARACTERISTICS OF SUSPENDED AND BED SEDIMENTS IN THE RHONE RIVER.* Hydrological Processes, 1992. **6**(2): p. 227-240.

15.   Chen, H.S. and M.A. Shao. *Effects of NaCl on fine sediment flocculation and settling in still water.* in *Proceedings of 99 International Conference on Agricultural Engineering.* 1999. Beijing: China: Agricultural University Press,.

16.   *Hiemenz, P.C., Rajagopalan, R., 1997. Principles of Colloid and Surface Chemistry. Marcel Dekker, New York.*

17.   Hsu, J.P. and B.T. Liu, *Effect of particle size on critical coagulation concentration.* Journal of Colloid and Interface Science, 1998. **198**(1): p. 186-189.

18.   Limbach, L.K., et al., *Removal of Oxide Nanoparticles in a Model Wastewater Treatment Plant: Influence of Agglomeration and Surfactants on Clearing Efficiency.* Environmental Science & Technology, 2008. **42**(15): p. 5828-5833.

19.   *Crittenden J.C., Trussell R.R., Hand, D.W., Howe K.J., Tchobanoglous G., Water Treatment: Principles and Design, second ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 2005.*

20.   *Ferry, J.D. Statistical Evaluation of Sieve Constants in Ultrafiltration Journal of General Physiology 1936(20)95-104.*

21.   Singh, G. and L.F. Song, *Experimental correlations of pH and ionic strength effects on the colloidal fouling potential of silica nanoparticles in crossflow ultrafiltration.* Journal of Membrane Science, 2007. **303**: p. 112-118.

22.   Zularisam, A.W., A.F. Ismail, and R. Salim, *Behaviours of natural organic matter in membrane filtration for surface water treatment -- a review.* Desalination, 2006. **194**(1-3): p. 211-231.

23.   Kim, S., et al., *Crossflow membrane filtration of interacting nanoparticle suspensions.* Journal of Membrane Science, 2006. **284**(1-2): p. 361-372.

24.   Bourgeous, K.N., J.L. Darby, and G. Tchobanoglous, *Ultrafiltration of wastewater: Effects of particles, mode of operation, and backwash effectiveness.* Water Research, 2001. **35**(1): p. 77-90.

AFA
WORKSHOP
Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Membrane technology ultra-filtration as a pretreatment system and desalination process.

Dr. Abdel Aziz Konsowa~ Chairman – Environmental Engineering Consultants - Egypt

Evaluation of an innovative polyvinyl chloride (PVC) ultrafiltration membrane for wastewater treatment

Xuezhi Zhang, Yongsheng Chen*, A.H. Konsowa, Xiaoshan Zhu, John C. Crittenden

Department of Civil, Environmental and Sustainable Engineering, Arizona State University, Tempe, AZ 85287, USA

ABSTRACT

The use of ultrafiltration (UF) employing a polyvinyl chloride (PVC) membrane (LH3-1060-V) as pretreatment for a reverse osmosis (RO) system treating secondary water effluent at the Scottsdale Water Campus was investigated. Membrane fouling tendency was evaluated, foulants were characterized, and chemical cleaning was optimized. Feed and permeate water qualities were indexed to address the effect of UF as a pretreatment on the RO process, in view of RO design and scale calculations. The results showed that the pilot plant operated stably for 102 days with a chemical cleaning interval of 69 days. The transmembrane pressure (TMP) ranged from 35.44 to 71.15 kPa, and the normalized flux was 72 L/(m^2 h) at 20 °C. The majority of the foulants were organic compounds (tannins, fulvic acids, humic acids, amino sugars, etc.) along with a few inorganic ones (iron, calcium, etc.). SEM–EDX mapping showed that most of the foulants deposited on the inner surface of the fiber. The best cleaning sequence for the fouled membrane was found to be 2% sodium hydroxide–0.5% citric acid, as 97% of the initial membrane flux was restored. The PVC-UF membrane efficiently removed turbidity, suspended solids and color, with removal efficiencies of 96.41%, 88.33%, and 50.00%, respectively. The UF pretreatment was found to enhance the RO average permeate flux and recovery by 34% and 21%, respectively, compared to the simulated conventional pretreatment system.

1. Introduction

Membrane processes can be used successfully to obtain reusable quality water. A dual membrane UF-reverse osmosis (RO) process has become increasingly attractive for the reclamation of municipal wastewater [1–6]. UF is an excellent pretreatment for RO because it can consistently deliver filtrate with a very low turbidity and silt density index (SDI) regardless of feed water quality. However, the high levels of particulates, dissolved organic matter (DOM) and microorganisms in wastewater can easily foul UF membranes. Many efforts have been made to understand and alleviate fouling, including characterization of fouling [7–12], water pretreatment [13,14], development of backwashing and cleaning strategies [15,16], and membrane surface modification and new membrane material development [17,18]. UF processes predominantly use organic membranes, with cellulose acetate (CA), polysulfone (PS), polyethylene (PE), polyethersulfone (PES), and polyvinylidene difluoride (PVDF) in use in water treatment [3]. Polyvinyl chloride (PVC) is an outstanding material because of its robust mechanical strength, low cost, and excellent chemical prop-

erties (e.g., acid, alkali, and solvent resistance). In a lab scale study, a membrane made of PVC exhibited higher permeate fluxes and lower rejections [19]. To the best of our knowledge, no data has previously been available regarding the fouling of this PVC membrane during wastewater treatment. In this paper, the fouling tendency and performance of the PVC membrane in wastewater treatment is evaluated.

2. Experimental

2.1. Pilot UF system

A UF pilot plant with a single hollow fiber PVC membrane module was evaluated at the Scottsdale Water Campus (Scottsdale, AZ). The PVC module was provided by Litree Co. (Hainan, China). Table 1 lists the properties of the PVC membrane.

Secondary effluent from media filtration at the Scottsdale Water Campus served as feed water. This feed water was pumped through a 100 μm pre-filter before it entered the UF unit. Dead end filtration was used. A programmable logic controller (PLC) drove all the operational processes of the UF system. The pilot plant was equipped with instruments for on-line monitoring of flow rate, operating pressure, turbidity, and number of particles. The instruments were connected to a data logging system for data keeping,

* Corresponding author. Tel.: +1 404 894 3089.
 E-mail address: yongsheng.chen@ce.gatech.edu (Y. Chen).

Table 1
Characteristics of PVC membrane[a].

Parameter	Value
Membrane material	PVC
Configuration	Inside-out hollow fiber
Cartridge dimension (mm)	∅277
Molecular weight cut-off (kDa)	50
Membrane area (m^2)	33
Fiber inner/outer diameter (mm)	1.0/1.66
Operating pH range	2–13
Maximum operating temperature (°C)	5–40

[a] Data provided by membrane manufacturer.

analysis and normalization. Operation parameters were optimized with a flux of 72 L/(m^2 h) and a 25 min backwash interval. An air assisted backwash process coupled with a pulsated flushing process was used every 25 min to backwash and flush the fouled membrane. In the air assisted backwash, compressed air (0.1 m^3/min) was used instead of the backwash pump to push water in the housing out of the module through the membrane. At the same time, compressed air scoured foulants from the membrane surface inside the hollow fiber. After that, a pulsated flushing process that employed a mixture of compressed air and water began. At 5th, 15th and 25th second the water flow rate was doubled rapidly for 5 s to improve the flushing efficiency. The membrane was soaked with 100 mg/L NaClO every 3.5 days. The overall water recovery was 94%.

Transmembrane pressure (TMP) and membrane resistance were used to evaluate the different backwash processes. TMP, resistance and flux were recorded and calculated according to the EPA membrane guideline normalized equations with reference to temperature 20 °C, since water temperature can have a significant impact on TMP and flux [5].

2.2. Characterization of foulants

During one of the optimization tests, TMP increased to 80 kPa after 30 days' operation. After an air assisted backwash, stronger air (0.15 m^3/min) was used to scour the membrane for 10 min. Then the membrane was backwashed, and the discharge was collected and dried at 80 °C. Between 2 and 5 mg of foulants was mixed into KBr pellets, and a PerkinElmer System 2000 FTIR spectrometer was used to collect the spectrum. The instrument scanned from 4000 to 400 cm^{-1}, averaging 10 scans at 1.0 cm^{-1} interval with a resolution of 4.0 cm^{-1}. After acquisition the spectrum was normalized to a maximum absorbance of 1.0 for comparative purposes.

To obtain information about the foulants remaining on the membrane, the module was autopsied, and the fibers were removed from the module and dried. To acquire images of both the inner side and the cross section, at the end of the fiber some of the top was further removed. After coating the samples with gold, a scanning electron microscope (SEM) (Philips XL30, FEI Company, USA) equipped with an energy dispersive X-ray analysis (EDX) system was used to determine the morphology and chemical composition of the foulants on the membrane.

2.3. Chemical cleaning

Fouled membranes were cleaned in place after the TMP reached the cleaning limit value. Chemicals including 2% NaOH and 0.5% citric acid were used to soak the membrane. The measured average pH values of the 0.5% NaOH and 2% citric acid were 12.6 and 2.8, respectively. Two cleaning sequences (citric acid–NaOH and NaOH–citric acid) were evaluated by measuring the recovered flux after each cleaning. Three different flow rates that covered the range of anticipated flux rates were tested. Then the normalized specific flux was calculated and plotted against TMP.

After the membrane soaked in NaOH, FTIR was used to characterize changes in functional groups on the membrane surface, and a contact angle meter (EasyDrop, Kruss, Germany) was used to characterize the hydrophobicity of the membrane surface. The average of five measurements was reported.

2.4. Permeate quality

Permeate turbidity was detected online. Other parameters, such as color, total organic carbon (TOC), iron, aluminum, calcium, and SDI were analyzed using standard procedures described in ASTM [10] or Standard Methods [6].
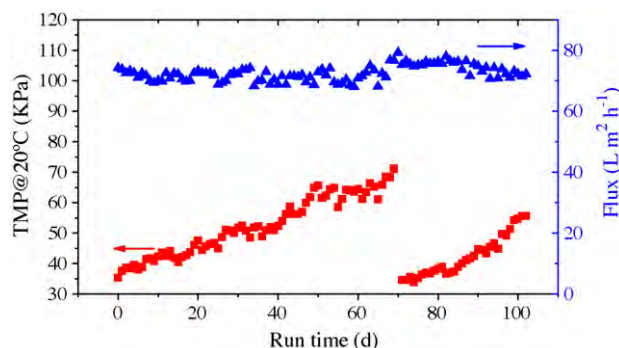
Because no RO system is connected to the UF pilot system, three sets of full design calculations for RO were completed. These considered different types of feed: UF permeate water, secondary effluent with no treatment, and simulated conventionally treated secondary effluent. The effects of these different feeds were evaluated by comparing the average permeate flux and recovery for the RO system. The software used for the calculation was Reverse Osmosis System Analysis, July 2000 Version 4.30 for Windows (FilmTec Co.). A commercially available RO membrane, TWLE-4040, which has a filtration area of 7.6 m^2 and a rejection of 99.5%, was selected in the calculation. RO feed SDI ranges from <3, 3–5 and >5 for UF membrane pretreatment, conventional pretreatment and no pretreatment was used in the calculation. The design calculations were carried on element to element basis and single stage one stream was used.

3. Results and discussion

3.1. Changes in TMP, flux and resistance

The UF pilot plant was operated using the air assisted backwash in pulsated flushing mode for 3.5 days run time intervals between each NaClO soaking. Fig. 1 shows TMP and flux changes. The initial TMP was 35.44 kPa, but as irreversible foulants accumulated, the TMP increased to 71.15 kPa after 69 days of operation (filtration and backwash). The chemical cleaning interval for the pilot test was 69 days, which is in the range of the typical membrane cleaning interval (1–6 months) [20]. After chemical cleaning with NaOH and citric acid, the TMP dropped to 34.56 kPa, and then increased slowly with operation until it reached 55.71 kPa at day 102. The normalized flux ranged from 68.1 to 79.2 L/(m^2 h), and the normalized average flux was 72 L/(m^2 h).

Yamamura et al. studied the fouling tendency of PE (0.1 μm), PVDF (0.1 μm), and PAN (100 kDa) membranes in drinking water treatment, and the results showed that the extent of fouling differed significantly depending on the membrane type. During 30 days of operation, the TMP increased from 24 to 125 kPa for the PAN membrane, from 5 to 160 for PVDF, and the smallest increase
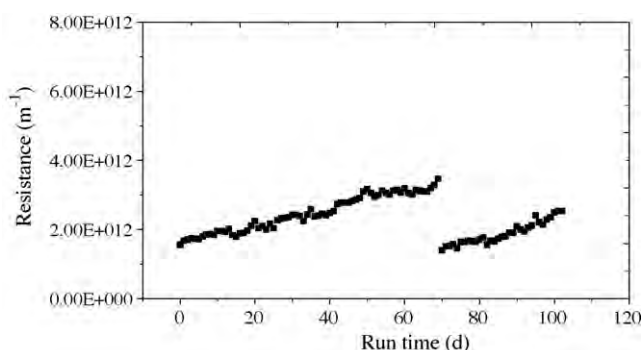

Fig. 1. TMP change profile.

Fig. 2. Resistance change profile.

where R_t is the total membrane resistance (m^{-1}); R_m the is intrinsic membrane resistance in the feed water (m^{-1}); R_i is the irreversible fouling resistance due to fouling that cannot be removed by backwashing (m^{-1}); R_r is the reversible fouling resistance due to fouling that can be removed by backwashing (m^{-1}).

At the start of filtration, the total membrane resistance (R_t) can be considered to be equal to the intrinsic membrane resistance (R_m) because almost no fouling has occurred. Irreversible fouling resistance (R_i) can be calculated from the difference between the total resistance (R_t) after backwashing and the intrinsic resistance (R_m). Reversible fouling can be calculated from the difference between the total resistance before and after backwashing.

Fig. 3 shows the resistance fractions at days 0, 34 and 68. At the beginning of the filtration, the irreversible resistance is negligible, and the reversible resistance is only 5% of the total membrane resistance; the rest is intrinsic resistance. As irreversible fouling accumulates, the irreversible resistance increases; at day 34 it reached 25% of the total resistance, while the reversible fouling was 8%. This may be ascribed to pore blocking and buildup of the caked-on layer. At day 68 the percentages of irreversible and reversible fouling were higher still, 44% and 13%, respectively. After chemical cleaning at day 69, the hydraulic irreversible fouling was removed, and the total resistance dropped to the low value of 1.55×10^{12}, which is very close to the initial value. The total membrane resistance was due to reversible fouling and intrinsic membrane resistance, which account for 4% and 96% of the total resistance, respectively.

3.2. Characterization of Foulants

The organic foulants were identified using FTIR; Fig. 4 presents the spectrum. The foulants include tannins (1504 (C=C), 1244 (φ-O)), fulvic and humic acids (1660–1630 (φ-C=O)), hydrocarbons (2960 (CH_3), 2940 (CH_2), 1460 (CH_2), 1380 (CH_3)), amino sugars (1660 (amide I band, N–C=O)), and aromatic sulfonic acids (1040 (φ-SO_3H)) [26,27].

(less than 10 kPa) was observed for the PE membrane [21]. However, in another study, Nobuhiro et al. found that PVDF is superior to PE in terms of prevention of fouling in MBRs used for the treatment of municipal wastewater [22]. The membrane properties (permeability, hydrophobicity, surface charge, roughness and rejection efficiency) and water characteristics (type and concentration of inorganics, NOM fraction) may also influence the fouling of the membrane [23–25].

Fig. 2 shows the change in resistance during the filtration process. Its trend is the same as that of TMP. The initial resistance was 1.56×10^{12} m^{-1}, which gradually increased to 3.47×10^{12} m^{-1} at day 69. After chemical cleaning the resistance dropped to 1.40×10^{12} m^{-1}, then increased slowly to 2.54×10^{12} m^{-1} at day 102. During the filtration process, the total membrane resistance is the sum of the intrinsic membrane resistance, irreversible fouling resistance, and reversible fouling resistance. A typical form of the resistance-in-series model is shown in Eq (1):

$$R_t = R_m + R_i + R_r \tag{1}$$

Fig. 3. Fouling fraction at days 0, 34, 68 and 69.

Fig. 4. FTIR spectrum of the foulants.

Fig. 6. EDX spectrum of the virgin membrane and fouled membrane.

Table 2
Atomic composition (%) of the element.

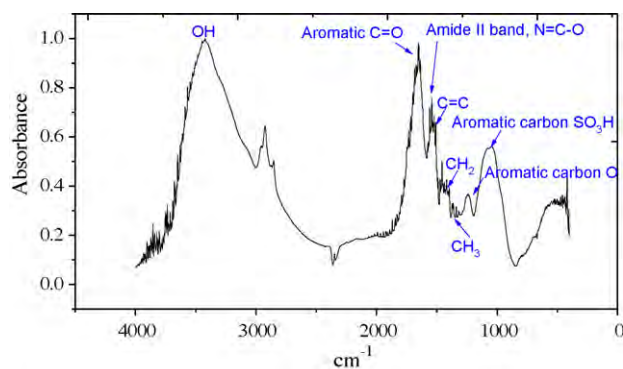| Element	Virgin membrane	Fouled membrane
C	74.87	79.41
O	10.39	15.13
Cl	14.74	02.45
Na	–	00.81
Mg	–	00.24
Ca	–	00.70
Fe	–	01.26

The organic fractions in the secondary effluent can be categorized into three groups: hydrophobic (fulvic and humic acids, etc.), transphilic, and hydrophilic (amino sugars, etc.). In particular, the hydrophilic fraction is the most abundant one in the majority of biologically treated sewage effluent (BTSE), constituting 32–74% of the total organic carbon (TOC); hydrophobic acids are the second most abundant portion, accounting for 17–28% [28]. The hydrophilic fraction was thought to be a minor contributor to organic matter fouling compared to the hydrophobic fraction, but studies by Fan et al. [29] and Lee et al. [30] have revealed that the hydrophilic fraction, which is primarily composed of polysaccharide-like substances (amino sugars), polysaccharide groups, and proteins, plays a significant role. The bulky macromolecular shape and neutral character of polysaccharides likely make them prone to foul and adsorb on membrane surfaces.

Fig. 5 presents SEM images of virgin and fouled membranes. The inside of the virgin membrane is very smooth. In the fouled membrane, however, the geometry of the pores has changed slightly. Also, a caked-on layer was observed on the inner surface of the hollow fiber. Cracks appear in the cake material of the fouled membrane surface because of dryness, as the membrane is out of operation. Residual foulant material, particularly iron, calcium, and organic substances, was observed by energy dispersive X-ray analysis (EDX); the results are shown in Fig. 6 and Table 2. Several researchers have reported that Ca, Mg and Fe play an important role in fouling development in the presence of NOM, as a formed metal-NOM complex will deposit on the membrane surface and foul the membrane [31–33].

Table 2 presents the atomic compositions (%) of the virgin and fouled membranes. Compared with the virgin membrane, the fouled membrane contains more O and less Cl. Also, Na, Ca, Mg and
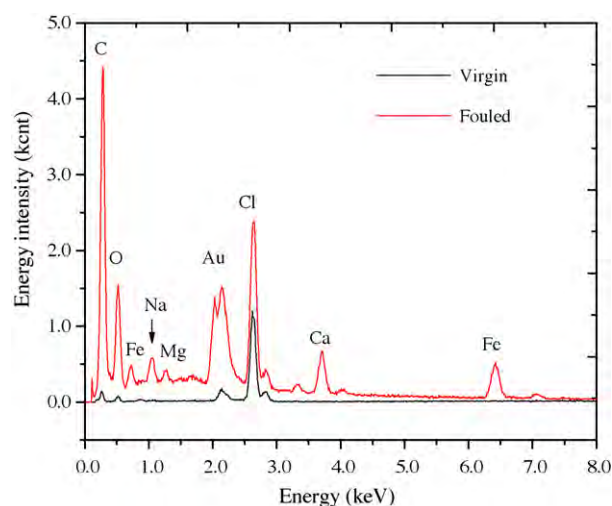
Fe were found in the fouled membrane.

Fig. 7 shows the distribution of the membrane elements (Cl), organic foulants (C and O), and inorganic (Ca and Fe) foulants on the fouled membrane. Based on these images, Cl is mainly located in the cross section of the membrane; much less Cl is present in the foulants layer, which contains both organic (C, O) and inorganic (Ca and Fe) elements. Small amounts of Ca and Fe are also deposited in the inner pores of the membrane.

3.3. Chemical cleaning of the membrane

Adsorptive fouling and the formation of a caked-on layer by inorganic and organic matter in water impair the efficiency of purely hydraulic membrane cleaning methods, such as flushing and backwash. As a consequence, the reagents used for chemical clean-
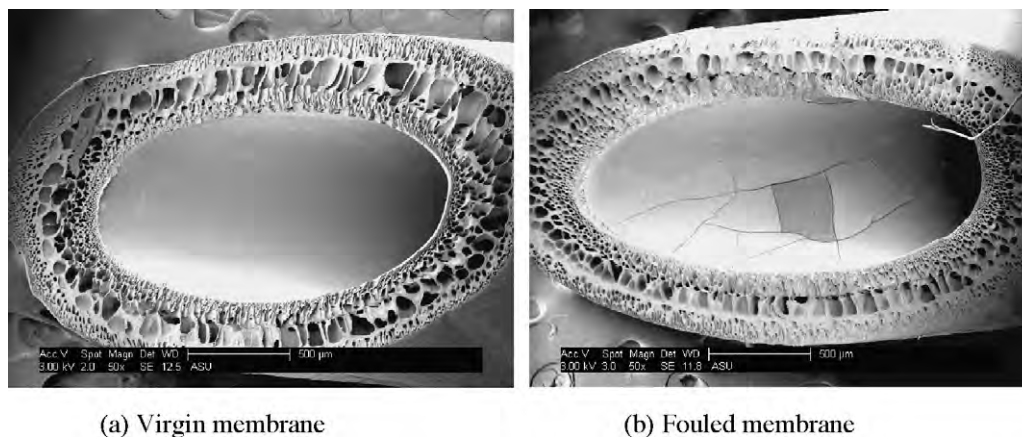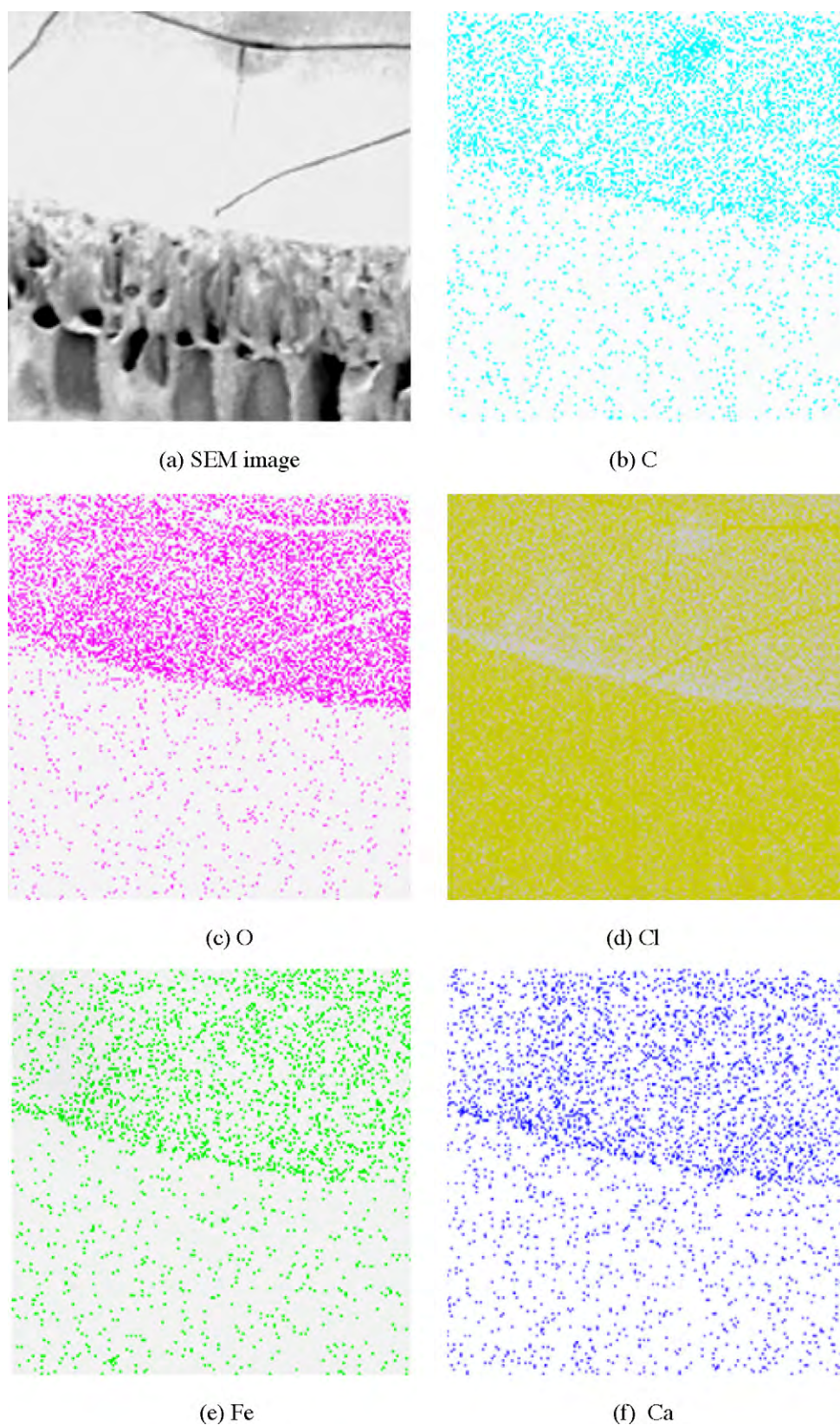

(a) Virgin membrane (b) Fouled membrane

Fig. 5. SEM images of the virgin membrane (a) and fouled membrane (b).

Fig. 7. Mapping of C, O, Cl, Ca and Fe in the fouled membrane.

ing of the membrane must efficiently deteriorate or re-dissolve these foulants. Based on the above analysis, the foulants in this system are mainly organic (NOM), although a few inorganic (Ca, Fe) ones are present as well. NaOH and citric acid were thus chosen to clean the fouled membrane. Acidic cleaners are most effective in removing calcium salts and metal oxides, while NaOH effectively removes organic material. Two cleaning sequences (NaOH–citric acid and citric acid–NaOH) were compared. Fig. 8 shows the flux
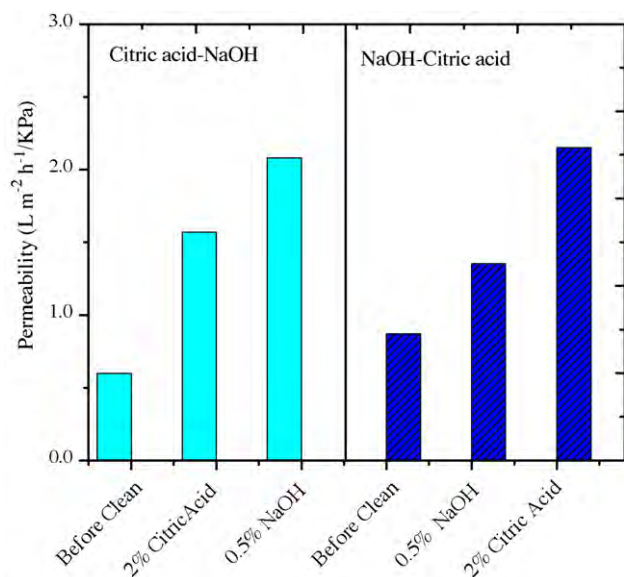
Fig. 8. Flux recovery after chemical cleaning.

Fig. 10. FTIR spectrum of the membrane before, during and after cleaning with NaOH.

restoration of the membrane. Both of the cleaning sequences work well; the final specific permeabilities were about 2.08 and 2.15 L/(m² h kPa), respectively, which are about 94% and 97% of the membrane's initial value (2.21 L/(m² h kPa)).

Fig. 9 shows the TMP profile after using different cleaning sequences. TMP was very stable when the membrane was cleaned using NaOH–citric acid, as the TMP increased only by 2.76 kPa. However, a fast TMP increase was observed when using the sequence of 2% citric acid–0.5% NaOH, and overall TMP increased to 79.63 kPa after 42 h filtration. The same trend was observed when NaOH alone was used to clean the membrane.

Characterization by FTIR and contact angle analysis suggests that the rapid TMP changes after chemical cleaning may be attributed to the hydrophilicity change caused by the reaction with NaOH of the functional groups on the membrane. The contact angle of the modified PVC membrane is $67 \pm 2°$, but it is $85 \pm 3°$ for the membrane soaked with 0.5% NaOH for 30 min. Thus, after soaking with NaOH the membrane surface is more hydrophobic, making it more susceptible to fouling [14]; this may explain the rapid TMP increase.
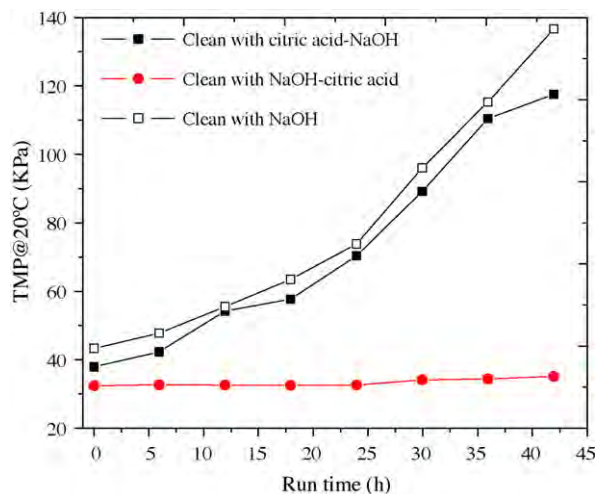
Another potential reason for the rapid TMP increase is the deposition of iron and calcium hydroxides in the pores of the membrane due to the presence of residual NaOH. Fig. 10 shows FTIR spectra of the virgin membrane, NaOH soaked membrane, and rinsed membrane after NaOH soaking. From Fig. 10 it is clear that the membrane contains residual NaOH (peaks appear at 1450 and 810 cm⁻¹). Rinsing with deionized water removes the residual NaOH, so the spectrum is almost identical to that of the virgin membrane. In our pilot operation the membrane was not rinsed after cleaning with NaOH. Thus, residual NaOH on the membrane pores and surface could lead to the formation and deposition of calcium and iron hydroxides when feed water is pumped into the module. The reduction in the concentrations of calcium and iron in the permeate after cleaning with NaOH reinforce this conclusion; in the first 5 min of filtration after soaking, the removal rates for Ca and Fe were about 20% and 30% higher, respectively, than those in the normal filtration process.

Fig. 11 shows the change in flux with different chemical cleaning sequences. The use of 0.5% NaOH–2% citric acid was found to be the best in view of the recovered flux of 2.15 L/(m² h kPa), which represents 97% of the initial specific flux.

3.4. Permeate quality

3.4.1. Permeate quality

Table 3 presents other water quality parameters, such as color, as well as concentrations of TOC, aluminum, iron, calcium, man-
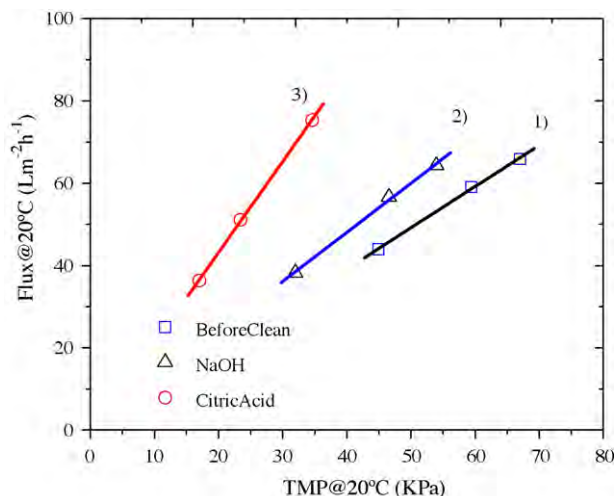

Fig. 9. TMP profile after using different chemical cleaning sequences.

Fig. 11. Results of chemical cleaning.

Table 3
Average permeate quality for the PVC-UF membrane.

Parameter	Unit	Feed	Permeate	Removal (%)
Nitrogen, ammonia, N	mg/L	6.10 ± 0.31	4.80 ± 0.24	21.31
Alkalinity, total	mg/L	158.00 ± 7.09	142.00 ± 7.10	10.13
Barium, Ba	mg/L	0.05 ± 0.01	0.05 ± 0.01	0.00
Calcium, Ca^{2+}	mg/L	86.73 ± 4.34	72.31 ± 3.62	16.63
COD	mg/L	18.00 ± 0.90	17 ± 0.85	5.56
Color	Pt–Co	2.00 ± 0.10	1 ± 0.05	50.00
Fluoride	mg/L	0.55 ± 0.03	0.476 ± 0.02	13.45
Iron, Fe	mg/L	0.03 ± 0.01	0.021 ± 0.01	30.00
Magnesium, Mg	mg/L	30.24 ± 1.51	27.06 ± 1.35	10.52
Nitrogen, nitrate (as N)	mg/L	7.28 ± 0.36	6.63 ± 0.33	8.93
Silica, as SiO_2	mg/L	14.55 ± 0.73	11.1 ± 0.56	23.71
Strontium, Sr	mg/L	1.08 ± 0.05	0.88 ± 0.04	18.52
Sulfate, $SO_4{}^{2-}$	mg/L	239.68 ± 11.98	213.18 ± 10.66	11.06
TOC	mg/L	4.77 ± 0.24	4.36 ± 0.22	8.60
Phosphorus, $PO_4{}^{3-}$	mg/L	6.20 ± 0.31	5.54 ± 0.28	10.65
Residue, total dissolved	mg/L	1076.00 ± 53.80	967 ± 48.35	10.13
Residue, total suspended	mg/L	6.00 ± 0.30	0.7 ± 0.04	88.33
Turbidity	NTU	0.92 ± 0.05	0.023 ± 0.01	97.50

ganese, etc., and their removals during UF treatment. The PVC-UF membrane efficiently removed suspended solids (SS) and color, with removal efficiencies of 88.33% and 50.00%, respectively. Removals of iron, silica, strontium, sulfate, and TOC were fair, with efficiencies of 30.00%, 23.71%, 18.52%, 11.06%, and 8.60%, respectively. Although these removal efficiencies are low, they are significant and considerable when the RO process limitations are considered.

Although the feed turbidity fluctuated somewhat (from 0.65 to 1.20), the UF system was very successful in removing turbidity, with a typical permeate value of less than 0.03 NTU. This is one of the most important advantages of UF over conventional pretreatment processes, as the turbidity of conventional pretreatment effluent generally follows the turbidity of the influent, rising when plant influent turbidity rises and falling when it falls.

SDI is the standard method to evaluate the suitability of influent water for undergoing RO. The SDI_{15} of the UF permeates were less than 1, between 0.38 and 0.82. Experience has shown that conventional pretreatment systems are often inadequate in reducing the turbidity and SDI of feed water streams. For example, a full-scale conventional pretreatment was compared to a full-scale microfiltration pretreatment (approximately 0.2 μm) for RO at a water recycling plant in EI Segundo, California. The results yielded an SDI for the conventional pretreatment effluent of 4.5~6.5, while the SDI of the microfiltration pretreatment effluent was considerably lower, ranging from 0.9 to 2.2 [34]. Kumar et al. [35] studied the pretreatment of seawater for RO using 1 μm filtration (representing conventional filtration), 0.1 μm microfiltration, and 100 and 20 kDa UF; as expected, the RO flux decline decreased as the membrane pore size decreased. The MWCO of the PVC membrane used in this test is 50 kDa, and thus a lower SDI value was obtained.

3.4.2. Enhancement of RO flux and recovery

Table 4 presents the calculated RO flux and recovery based on the quality of secondary effluent (no treatment, after conventional pretreatment, and after UF membrane pretreatment). A simulated RO system based on UF pretreatment leads to flux enhancement of 131% and 34%, and recovery improvement by 129% and 21%, when

compared to results obtained for simulated RO with untreated or conventionally treated secondary effluent as feeds.

The PVC-UF membrane was an excellent pretreatment for secondary water effluent to be used as feed for the RO process at the Scottsdale Water Campus. In particular, the high quality of the UF permeate feed water is likely to increase the efficiency and life of RO systems by minimizing fouling, scaling, and membrane degradation while optimizing permeate flux, permeate quality, and recovery.

4. Conclusions

(1) The pilot plant operated stably for 102 days with a chemical cleaning interval of 69 days. The TMP ranged from 35.44 to 71.15 kPa, and the normalized flux was 72 L/(m^2 h) at 20 °C.
(2) Foulants deposited on the PVC membrane were both organic (tannins, fulvic acids, humic acids, amino sugars, etc.) and inorganic (iron, calcium, etc.), and most of the foulants deposited on the inner surface of the fiber. The fouled membrane was chemically cleaned with two sequences: 2% sodium hydroxide–0.5% citric acid, and 0.5% citric acid–2% sodium hydroxide. Both of the sequences worked well, and the final specific permeabilities were about 94% and 97%, respectively, of the initial value (2.21 L/(m^2 h kPa)). The first sequence is preferred because when NaOH was used as the last step, a rapid TMP rise was observed due to the increase membrane hydrophobicity and the precipitation of iron and calcium hydroxide on the membrane due to reaction with residual NaOH.
(3) According to the RO design calculation, pretreatment with the PVC-UF membrane was found to enhance the RO system average permeate flux and recovery by 131% and 129%, respectively, over non-treated secondary effluent as a direct feed to the RO, and by 34% and 21%, respectively, over simulated conventionally treated secondary effluent as the feed.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.seppur.2009.08.019.

References

[1] A.-S.J. Abdel-Jawad, Non-conventional treatment of treated municipal wastewater for reverse osmosis, Desalination 142 (1) (2002) 11–18.
[2] J.P. Chen, S.L. Kim, Y.P. Ting, Study on feed pretreatment for membrane filtration of secondary effluent, Sep. Purif. Technol. 29 (2) (2002) 171–179.

Table 4
Effect of pretreatments on the simulated RO flux and recovery.

Treatment	Flux (L/(m^2 h))	Recovery (%)
Secondary effluent (no pretreatment)	10.36	35.0
After conventional pretreatment	17.82	66.0
After UF membrane pretreatment	23.94	80.0

[3] M.P. del Pino, B. Durham, Wastewater reuse through dual-membrane processes: opportunities for sustainable water resources, Desalination 124 (1–3) (1999) 271–277.
[4] J.A. Lopez-Ramirez, S. Sahuquillo, D. Sales, J.M. Quiroga, Pre-treatment optimisation studies for secondary effluent reclamation with reverse osmosis, Water Res. 37 (5) (2003) 1177–1184.
[5] C. Reith, B. Birkenhead, Membranes enabling the affordable and cost effective reuse of wastewater as an alternative water source, Water Sci. Technol.: Water Supply 17 (1) (1999) 75–81.
[6] M. Wilf, S. Alt, Application of low fouling RO membrane elements for reclamation of municipal wastewater, Desalination 132 (1–3) (2000) 11–19.
[7] D. Abdessemed, G. Nezzal, R.B. Aim, Coagulation-adsorption-ultrafiltration for wastewater treatment and reuse, Desalination 131 (1–3) (2000) 307–314.
[8] R.B. Aim, H. Chapman, S. Vigneswaran, H.H. Ngo, S. Dyer, Pre-flocculation of secondary treated wastewater in enhancing the performance of microfiltration, Desalination 146 (1–3) (2002) 367–372.
[9] M.H. Al-Malack, G.K. Anderson, Coagulation-crossflow microfiltration of domestic wastewater, J. Membr. Sci. 121 (1) (1996) 59–70.
[10] C. Jarusutthirak, G. Amy, Membrane filtration of wastewater effluents for reuse: effluent organic matter rejection and fouling, Water Sci. Technol. 43 (10) (2001) 225–232.
[11] T.F. Speth, R.S. Summers, A.M. Gusses, Nanofiltration foulants from a treated surface water, Environ. Sci. Technol. 32 (22) (1998) 3612–3617.
[12] M. Zhang, C. Li, M.M. Benjamin, Y. Chang, Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment, Environ. Sci. Technol. 37 (8) (2003) 1663–1669.
[13] T. Leiknes, The effect of coupling coagulation and flocculation with membrane filtration in water treatment: a review, J. Environ. Sci. 21 (1) (2009) 8–12.
[14] H.-f. Zhang, B.-s. Sun, X.-h. Zhao, Z.-h. Gao, Effect of ferric chloride on fouling in membrane bioreactor, Sep. Purif. Technol. 63 (2) (2008) 341–347.
[15] K. Katsoufidou, S.G. Yiantsios, A.J. Karabelas, A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: experiments and modeling, J. Membr. Sci. 266 (1–2) (2005) 40–50.
[16] K. Kimura, Y. Watanabe, N. Ohkuma, Filtration resistance and efficient cleaning methods of the membrane with fixed nitrifiers, Water Res. 34 (11) (2000) 2895–2904.
[17] F. Meng, S.-R. Chae, A. Drews, M. Kraume, H.-S. Shin, F. Yang, Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material, Water Res. 43 (6) (2009) 1489–1512.
[18] C.-H. Zhang, F.-l. Yang, W.-J. Wang, B. Chen, Preparation and characterization of hydrophilic modification of polypropylene non-woven fabric by dip-coating PVA (polyvinyl alcohol), Sep. Purif. Technol. 61 (3) (2008) 276–286.
[19] J. Xu, Z.-L. Xu, Poly(vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC/additives/solvent, J. Membr. Sci. 208 (1–2) (2002) 203–212.
[20] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, Water Treatment: Principles and Design, 2nd ed., John Wiley & Sons, Inc., Hoboken, NJ, 2005.
[21] H. Yamamura, K. Kimura, Y. Watanabe, Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment, Environ. Sci. Technol. 41 (19) (2007) 6789–6794.
[22] N. Yamato, K. Kimura, T. Miyoshi, Y. Watanabe, Difference in membrane fouling in membrane bioreactors (MBRs) caused by membrane polymer materials, J. Membr. Sci. 280 (1–2) (2006) 911–919.
[23] K. Boussu, A. Belpaire, A. Volodin, C. Van Haesendonck, P. Van der Meeren, C. Vandecasteele, B. Van der Bruggen, Influence of membrane and colloid characteristics on fouling of nanofiltration membranes, J. Membr. Sci. 289 (1–2) (2007) 220–230.
[24] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, Environ. Sci. Technol. 36 (16) (2002) 3571–3576.
[25] A.G. Fane, C.J.D. Fell, A review of fouling and fouling control in ultrafiltration, Desalination 62 (1987) 117–136.
[26] D4189-95R02 Test Method for Silt Density Index (SDI) of Water, Annual Book of ASTM Standards, vol. 11.01, American Society for Testing and Materials, 2007.
[27] American Public Health Association, American Water Works Association, Water Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.
[28] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: a detailed effluent organic matter (EfOM) characterization, Water Res. 38 (7) (2004) 1933–1939.
[29] L. Fan, J.L. Harris, F.A. Roddick, N.A. Booker, Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes, Water Res. 35 (18) (2001) 4455–4463.
[30] N. Lee, G. Amy, J.-P. Croue, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res. 38 (20) (2004) 4511–4523.
[31] Q. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms, Environ. Sci. Technol. 38 (17) (2004) 4683–4693.
[32] W. Yuan, A.L. Zydney, Humic acid fouling during microfiltration, J. Membr. Sci. 157 (1) (1999) 1–12.
[33] W. Yuan, A.L. Zydney, Effects of solution environment on humic acid fouling during microfiltration, Desalination 122 (1) (1999) 63–76.
[34] M.J. Chipps, M.J. Bauer, R.G. Bayley, Achieving enhanced filter backwashing with combined air scour and sub-fluidising water at pilot and operational scale, Filtr. Sep. 1 (1995) 55–62.
[35] M. Kumar, S.S. Adham, W.R. Pearce, Investigation of seawater reverse osmosis fouling and its relationship to pretreatment type, Environ. Sci. Technol. 40 (6) (2006) 2037–2044.

Membrane Technology for Water Production from Surface water

Eng. Wissam El Mahgoub

Eng. Alaa Ali

Pall Corporation - France

"Membrane Technology for Water Production from Surface water"

ABSTRACT

Key Words: surface water, membrane systems, High Crystalline PVDF

****

Recently, Membrane Treatment Systems have been used to reliably produce high quality water from surface water ie Nile River .These systems have been applied in various applications, from small, medium and large capacities.

The purpose of this presentation is to show; via case study the positive experience of membranes versus conventional treatment in North-Africa and Middle-East. The paper shows the enhanced removal of bacteria and algae using membrane filtration.

The raw / source water is characterized by high organic load, variable particulate loading mainly fine colloidal matter.

Apart from the production of high quality water, the use of membranes also allows for reduced operational costs by less chemical usage.

Typical water quality requirements will be summarized with respect to membrane treatment.

****

I   Introduction

Historically, conventional treatment technologies were used in surface water filtration; but as regulations tighten, they become unreliable and expensive to operate. They also often require high doses of water-treating chemicals.

In the last 10 years conventional treatments (Chemical dosing, Clarifier, Sand Filters) are rapidly being replaced by Advanced Membrane Technologies hence improving the downstream operations, reducing the foot print and the running cost.

State of the art Membrane Technologies are well suited for treatment of alternative and more difficult water sources with a single stage treatment (Figure 1)

Figure 1. Single stage Pall Membrane systems over conventional treatment
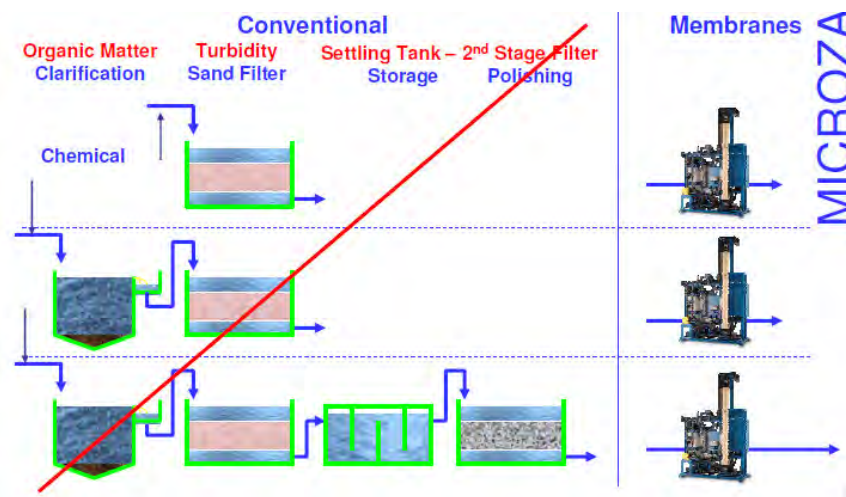
Pall Membranes are less sensitive to variations in feed water quality and can handle peak flows without deterioration in filtrate quality. Moreover, Membrane solutions are offered in pre-engineered, packaged and mobile designs. They can be designed as full automatic systems or semi-manual units, as per customer requirement.

The "plug and play" designs allow rapid deployment and site assembly. Regardless of capacity, these membrane systems continue to provide a product quality that surpasses stringent filtered water purity specifications.

A Reverse Osmosis Membrane System, when installed removes dissolved solids / Bacteria from feed water. These membranes are mostly available in a spiral wound configuration which is susceptible to plugging by suspended solids, colloids causing the requirement for more efficient pre-treatment. Conventional pre-treatment technologies used on variable feed waters can be expensive, operator intensive and may not produce the consistent and high quality filtrate desired. To overcome these problems, a Membrane system is often a choice of pre-treatment.

1.1   Membrane Technology

Pall Hollow Fiber Membrane is made from a High Crystalline Poly-Vinylidene Fluoride (PVDF) polymer and has a uniform construction throughout its thickness.

The Thermal Induced Phase Separation production process makes this High Crystalline PVDF membrane unique in the market.

Because of its unique symmetrical configuration, there is no skin or coating which can delaminate or separate from the substrate under operating stress. The membrane does not have a skin that is susceptible to surface defects, pinholes, ruptures and fiber breakage.

This and the production process, gives fiber a unique strength, were there are practically no breakages during the warranted life time of the fibre.

In the Figure 2 below, is seen the SEM photographs of the Pall Hollow Fiber Membrane at various sections.

Figure 2. SEM Photos of Pall Hollow Fiber Membrane

Cross Section

Inner Surface
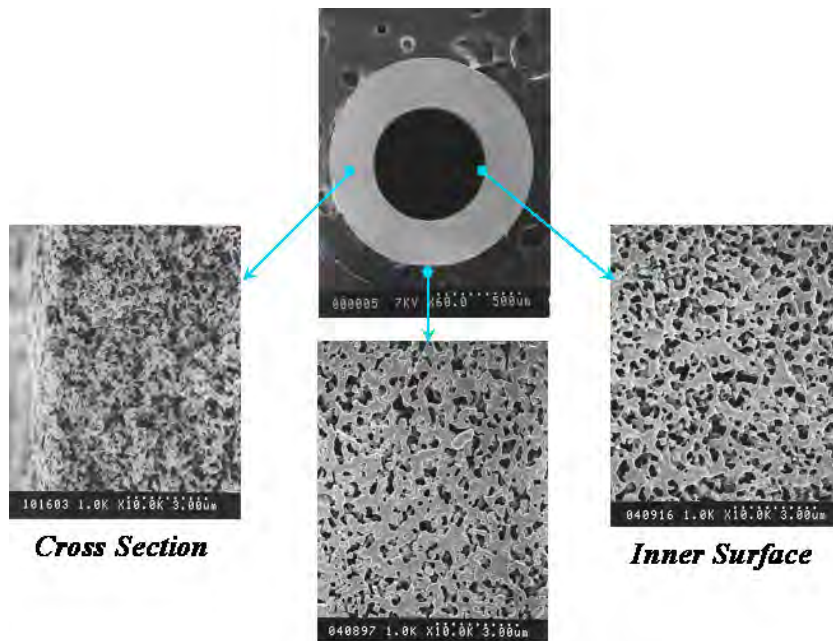
Unlike the conventional pre-treatment the Hollow Fiber Membranes are operating in the submicron range hence allowing the removal of bacteria, Algae, and other contaminants such as Iron and Mn with suitable oxidation.

The tight pore structure of the Pall Aria^{TM} Hollow-Fiber Membrane allows for the production of safe drinking and process water from nearly any source of water.

For potable water treatment and wastewater treatment, the Pall Aria^{TM} membrane has received major approvals, eg:

- Egyptian Ministry of Health – High Counsel of Drinking Water
- National Food Standard "NSF"
- DWI (United Kingdom),
- California Department of Health Services (CDHS) – USA
- Australian Water Authorities
- Dubai Electricity and Water Authority (DEWA) - UAE.

1.2 System Technology

The Pall Aria^{TM} MF systems are engineered in pre-packaged models with treatment sizes from 5.0 m^3/hr to 820 m^3/hr per single train / unit. The single units can be custom designed to treat 350,000 m^3/day of water or 15,000 m^3/hr

Below is a Pall Aria^{TM} system, engineered in pre-packaged models with each line having treatment size of 800 m³/h (Figure 3)

Figure 3: Custom-Designed System for 25 ML/d Capacity with 4 trains

The modules and racks designs have typically lower installation costs and faster delivery schedule than conventional systems as indeed less civil constructions are required and the overall building requirements are smaller.

Comparisons over conventional plants have shown 60% space savings when using a Pall Membrane System. This clearly reduces the overall plant installation or capital expenditure to build a water treatment facility.

For remote areas Pall Corporation developed self-sufficient containerized units (fig 4a and 4b) including all automation and remote access. The same units are available in semi-automatic mode and are covering both small and large flow applications.

1.3   Water Sources

Pall Corporation integrated membrane systems are designed to operate on highly variable feed waters. In applications where conventional treatment has its limitations; a correctly sized membrane system including sufficient flexibility in the design may treat any water source without the need for extensive pre-treatment such as Clarifier, Sand Filters or chemical assistance.

The following specific water sources are discussed:

   1.3.1 Surface Water: - River Nile and Side Canals   – low TDS water, high organic load

1.3.1 Surface Water: - River Nile and Side Canals   – low TDS water, high organic load

The water from Mahmoudia Canal; Manshya near Alexandria (River Nile) is characterized by a rather high temperature of around 25 °C and high organic contamination. Total dissolved solids (TDS) of the water are low and stable below 400 ppm. The physical parameters such as TSS vary from 10 to 50 ppm but can show high peaks.

Figure 5. Intake on Mahmoudia canal
showing algal bloom and organic contamination

Figure 6. Visual results from
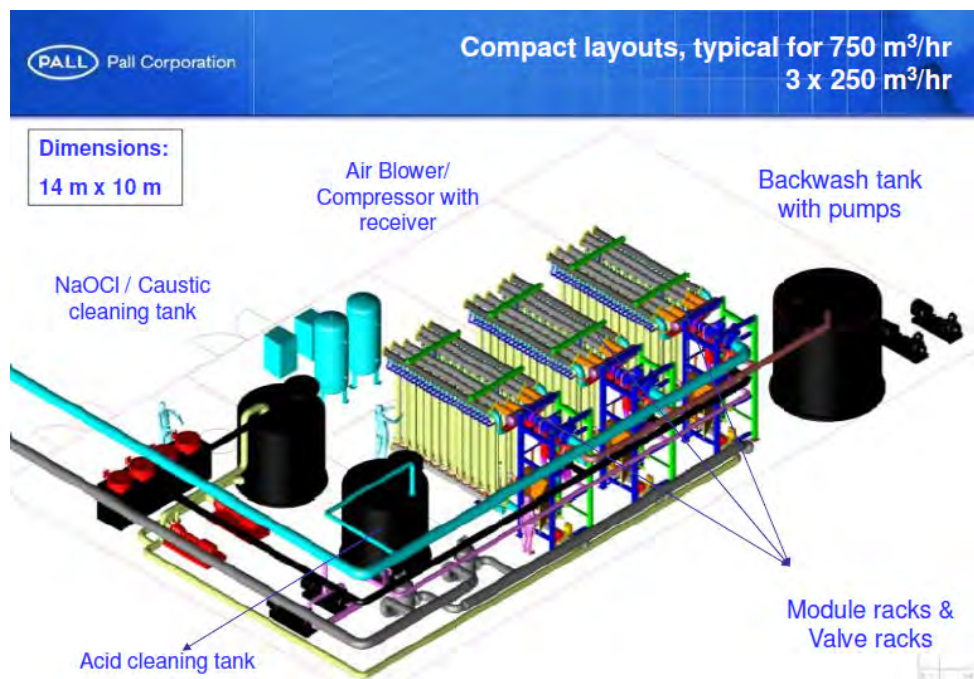**Pall membrane filtration system**

A Pall Membrane System was operated on direct intake (Figure 5) from Mahmoudia Canal, Manshya near Alexandria and was showing long term stable operation with consistent filtered water results as compared to other treatment technology with the use of any coagulant.

Algal bloom and high turbidity events have been successfully countered with membrane system. There was no need for pre-treatment, hence chemical consumption and operating costs have been greatly reduced under all conditions. Also, high purity water specifications are achieved as seen in Figure 6.

1.4 Membrane technology and Foot Print

From the extensive piloting and studies, Pall has calculated that the foot print size is reduced from 40% to 60% comparing with the conventional filtration systems.
This is in addition to the civil work reduction as the membrane technology replaces the big clarifiers and settling tanks by one filtration step.

Fig7: 18000 m3/day compact design

Furthermore it is possible to accommodate up to 7000 m3/day in a mobile water treatment system mounted in a 40 feet container and completely automated and packaged with PALL ARIA membrane filtration system. With appropriate site preparation and minimal labor, the system can be operational within hours.

All client needs to do is to supply the source water, connect the effluent pipe, provide waste disposal, and add power.

Fig8: Membranes containerized mobile systems
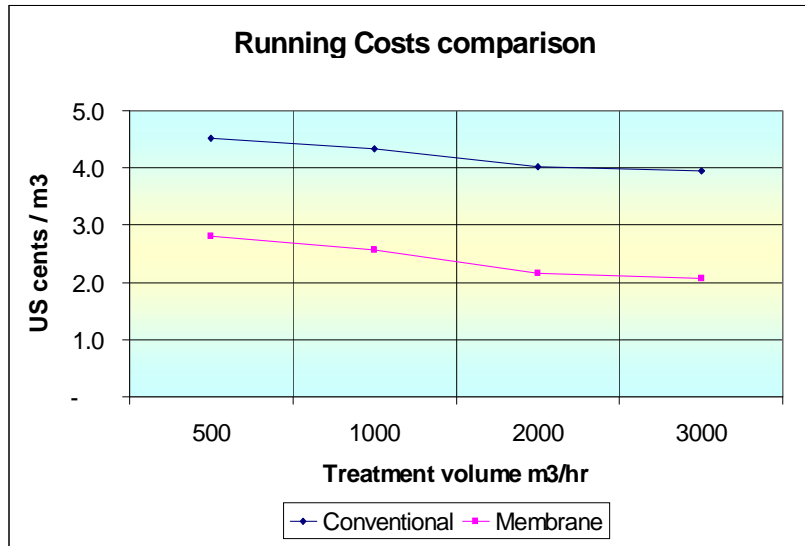
1.5 Cost of Membrane systems.

This section provides some quick guidelines with respect to cost of treated water as a function of treatment capacity and required quality.

The cost of the treatment units vary significantly with the complexity of the design specifications, the level of controls and safety integrity level, design codes, etc. Capital costs are function of various inputs such as design flexibility, design standards, and function. However if considering the cost of civil works, building costs, land costs, Membrane systems if not cheaper may be equal to the cost of the conventional plants.

The cost of the treated water includes the capital cost depreciation and also membrane replacement costs.

A 20-yr plant life has been assumed with the pre-treatment membranes being replaced every 10 years.

Comparisons of operational costs of Membranes over conventional plants are found to be less. Typical values are as low as approximately US$ 0.02 to 0.03 / m^3 for a Membrane plant in Graph 1

Graph 1. Running cost comparison of Membrane systems over conventional treatment

Conclusion

Pall Membrane technologies increase the value of poor quality water by enabling the production of a high quality supply for potable water and water reuses. Pre-engineered, packaged designs have driven down the costs. The units are designed to operate safely and reliably in all operating conditions; at start-up, shutdown and in emergency situations.

The systems can handle all type of water and operate in a large range of different environments while maintaining the overall production, reliability and availability.

For larger-sized plants, savings can still be realized with increasing economy of scale as custom-designed plants become increasingly more common.

Different multipurpose water treatment units have been discussed and compared. It can be concluded that the incorporation of a flexible pre-treatment step is key to reliable success. The use of correctly designed systems results in stable operating units which do not suffer from loss of product quality.

Pall Corporation has more than 700 units installed world-wide, were in Western Hemisphere Pall has more than 450 units, some of them operating for more than 10 years without any major modifications or membrane replacements.

AFA WORKSHOP

Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Membrane Technology for Waste Water Recycle

Eng. Wissam El Mahgoub

Eng. Alaa Ali

Pall Corporation - France

"Membrane Technology for Waste Water Recycle"

ABSTRACT

<u>Key Words:</u> waste water, case study

****

1. Waste water treatment (TSE) :- (Ajman – UAE)

As fresh water sources are becoming more and scarcer, various municipalities and government institutions are looking at using the treated sewage coming from conventional waste treatment plants by recycling the water.

State of the art membrane technologies are particularly well suited for use in recycling water and providing a new source of water for many applications. Membranes are less sensitive to variations in feed water and can handle peak flows without deterioration in effluent quality and hence safe for use for irrigation and other applications close to human activities and at the same time meet the tight regulations.

In Middle-East one of the most popular applications for waste water re-use is irrigation hence requiring high quality water from bacteriological point of view. Only membranes can give this safety and guarantee.

Pall Corporation supplied large residential and industrial areas with advanced membrane treatment for final wastewater polishing prior to irrigation.

Table 4. Waste water treatment Middle-East

	Feed to membranes	Filtrate
BOD (ppm)	30	5
COD (ppm)	60	10
TSS (ppm)	> 30	0
NTU	> 40	< 0,1
Micro-organism	Too many to count	> 6 log reduction

Figure 11. This shows the TSE water Feed, and the filtrate water from Pall Membrane syste

1.4 Membrane technology and Foot Print

From the extensive piloting and studies, Pall has calculated that the foot print size is reduced from 40% to 60% comparing with the conventional filtration systems.

This is in addition to the civil work reduction as the membrane technology replaces the big clarifiers and settling tanks by one filtration step.
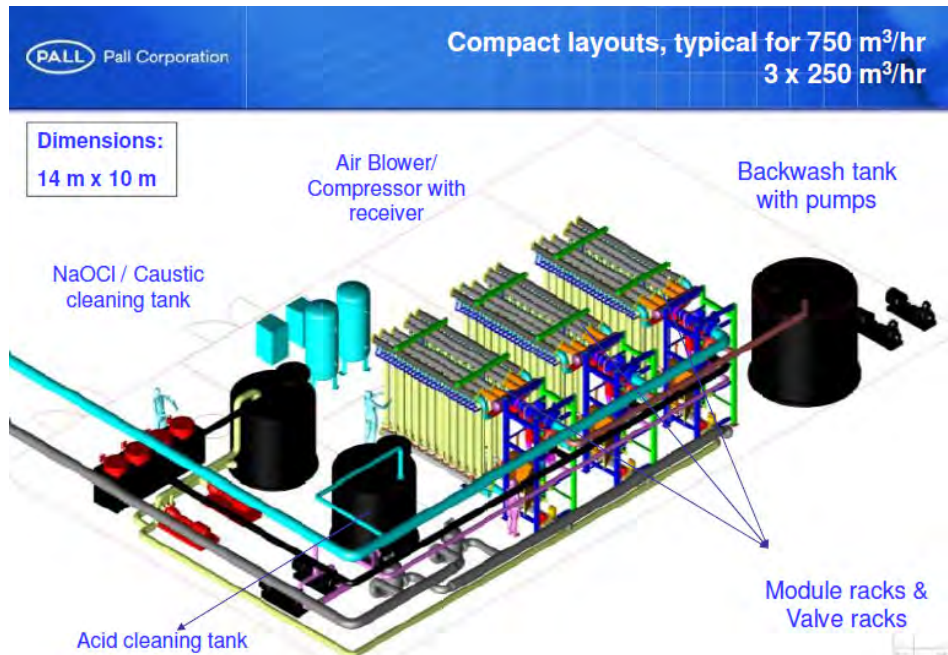

Fig14: 18000 m3/day compact design

Furthermore it is possible to accommodate up to 7000 m3/day in a mobile water treatment system mounted in a 40 feet container and completely automated and packaged with PALL ARIA membrane filtration system. With appropriate site preparation and minimal labor, the system can be operational within hours.

All client needs to do is to supply the source water, connect the effluent pipe, provide waste disposal, and add power.

Fig15: Membranes containerized mobile systems
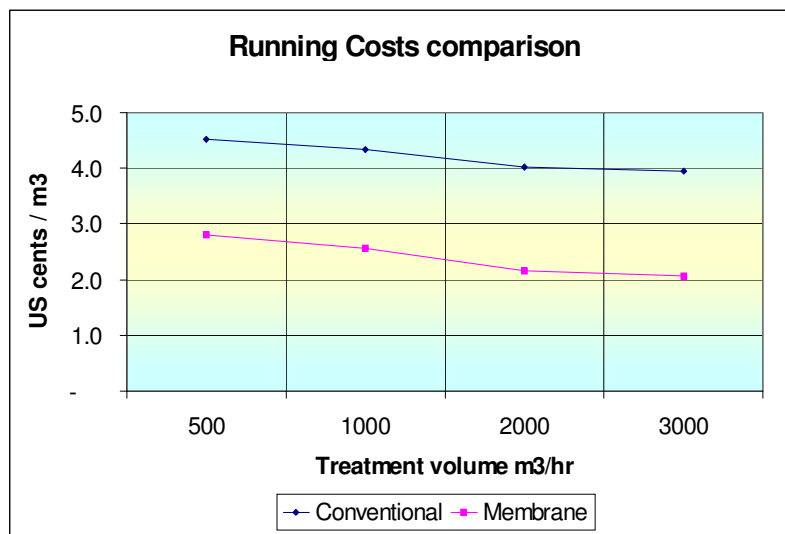
1.5   Cost of Membrane systems.

This section provides some quick guidelines with respect to cost of treated water as a function of treatment capacity and required quality.

The cost of the treatment units vary significantly with the complexity of the design specifications, the level of controls and safety integrity level, design codes, etc. Capital costs are function of various inputs such as design flexibility, design standards, and function. However if considering the cost of civil works, building costs, land costs, Membrane systems if not cheaper may be equal to the cost of the conventional plants.

The cost of the treated water includes the capital cost depreciation and also membrane replacement costs.

A 20-yr plant life has been assumed with the pre-treatment membranes being replaced every 10 years.

Comparisons of operational costs of Membranes over conventional plants are found to be less. Typical values are as low as approximately US\$ 0.02 to 0.03 / m^3 for a Membrane plant in Graph 1

Graph 1. Running cost comparison of Membrane systems over conventional treatment

Conclusion

Pall Membrane technologies increase the value of poor quality water by enabling the production of a high quality supply for potable water and water reuses. Pre-engineered, packaged designs have driven down the costs. The units are designed to operate safely and reliably in all operating conditions; at start-up, shutdown and in emergency situations.

3

The systems can handle all type of water and operate in a large range of different environments while maintaining the overall production, reliability and availability.

For larger-sized plants, savings can still be realized with increasing economy of scale as custom-designed plants become increasingly more common.

Different multipurpose water treatment units have been discussed and compared. It can be concluded that the incorporation of a flexible pre-treatment step is key to reliable success. The use of correctly designed systems results in stable operating units which do not suffer from loss of product quality.

Pall Corporation has more than 700 units installed world-wide, were in Western Hemisphere Pall has more than 450 units, some of them operating for more than 10 years without any major modifications or membrane replacements.

Day 3: Wednesday: December 24th, 2013

Session IV

afa
الإتحاد العربي للأسمدة
Arab Int'l Organization هيئة عربية دولية
Arab Fertilizer Association
Since 1975

**AFA
WORKSHOP**
**Water Treatment and Water Quality in
Fertilizer and Petrochemical Industries**

Role of Electrochemical Technologies in the Treatment of Wastewater Generated From Fertilizer

Dr. Ahmed Elshazly

Chairman of the Chemical and Petrochemical Department, School of Energy,Environmental and Chemical Engineering, E-JUST - Egypt

Role of Electrochemical Techniques in the Treatment of Wastewater Generated From Fertilizer

By
Prof. Ahmed H. Elshazly
Chairman of the Chemical Engineering Department
Egypt-Japan University of Science and Technology
Alexandria-Egypt.

Introduction

- Using electricity to treat water was first proposed in UK in 1889.
- Electrocoagulation (EC) with aluminum and iron electrodes was patented in the US in 1909.
- The electrocoagulation of drinking water was first applied on a large scale in the US in 1946.

Introduction (continued)

▸ Because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies did not find wide application worldwide

Introduction (continued)

▸ With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades.

Introduction (continued)

▸ In the last decade, this technology has been increasingly used in North and South America and in Europe for treatment of industrial wastewater containing

❖ Metal processing and mining industry

❖ pulp and paper industries,

❖ oil wastes, dyes, suspended particles,

❖ organic matterials, etc.

When to use electrocoagulation

1. when biological treatment is difficult, such as the case of refractory organic (phenols, halogenated organics) or for the cases where biological treatment is very sensitive to process variation.

2. In the cases where to replace more expensive processes such as ion exchange and membrane separation processes.

Theoretical background on EC process

Definition of electrocoagulation (EC)

▸ Electrocoagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium.

Theoretical background continued

In another words

▸ Electrocoagulation is the electrochemical production of destabilizing agents (such as Al, Fe) that brings about neutralization of electric charge for removing pollutant. Once charged, the particles bond together like small magnets to form a mass which can be removed easily.

Theoretical background continued
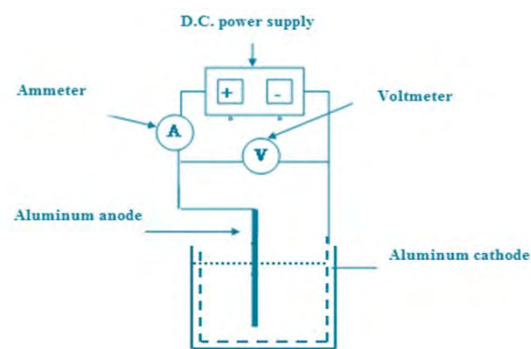
‣ **How Electrocoagulation Works**

As wastewater contaminants e.g. Suspended solids, heavy metals, and emulsified oil or grease pass by the electrochemical cell, which is energized by a D.C. electrical current; they accept a positive and negative charge causing the tiny particles to bond together like miniature magnets where it can be removed easily.
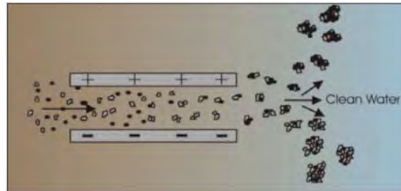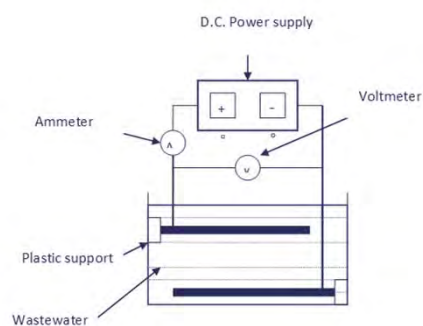

Electrocoagulation unit (cell)

‣ In its simplest form, an electrocoagulation reactor may be made up of an electrolytic cell with one anode and one cathode.

‣ The conductive metal plates are commonly known as sacrificial electrodes (anode)

‣ they may be made of the same or different materials (anode and cathode)
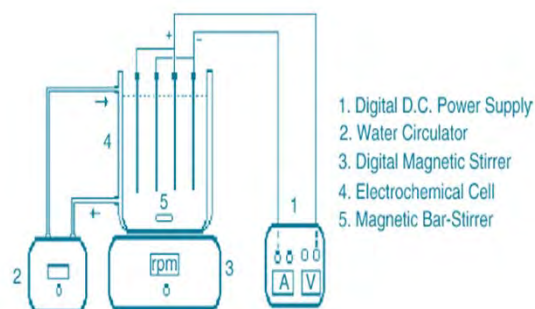
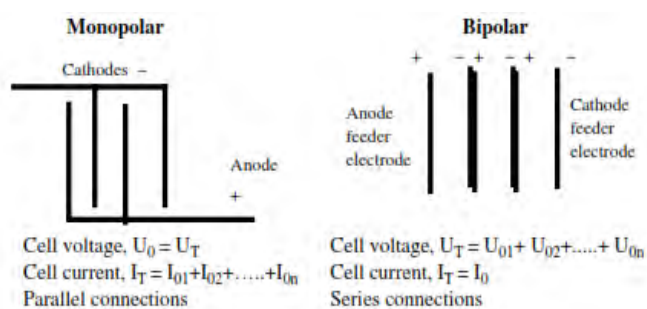# Schematic diagram of the EC cell (Vertical electrode arrangement)


(Horizontal electrode arrangement)

Cell with agitation and/or circulation

1. Digital D.C. Power Supply
2. Water Circulator
3. Digital Magnetic Stirrer
4. Electrochemical Cell
5. Magnetic Bar-Stirrer

Types of electrode arrangement

Monopolar

Cathodes –

Anode +

Cell voltage, $U_0 = U_T$
Cell current, $I_T = I_{01} + I_{02} + \ldots + I_{0n}$
Parallel connections

Bipolar

Anode feeder electrode

Cathode feeder electrode

Cell voltage, $U_T = U_{01} + U_{02} + \ldots + U_{0n}$
Cell current, $I_T = I_0$
Series connections

Monopolar and bipolar electrode connections in the EC reactor

(a) Bipolar electrodes (b) Monopolar electrodes
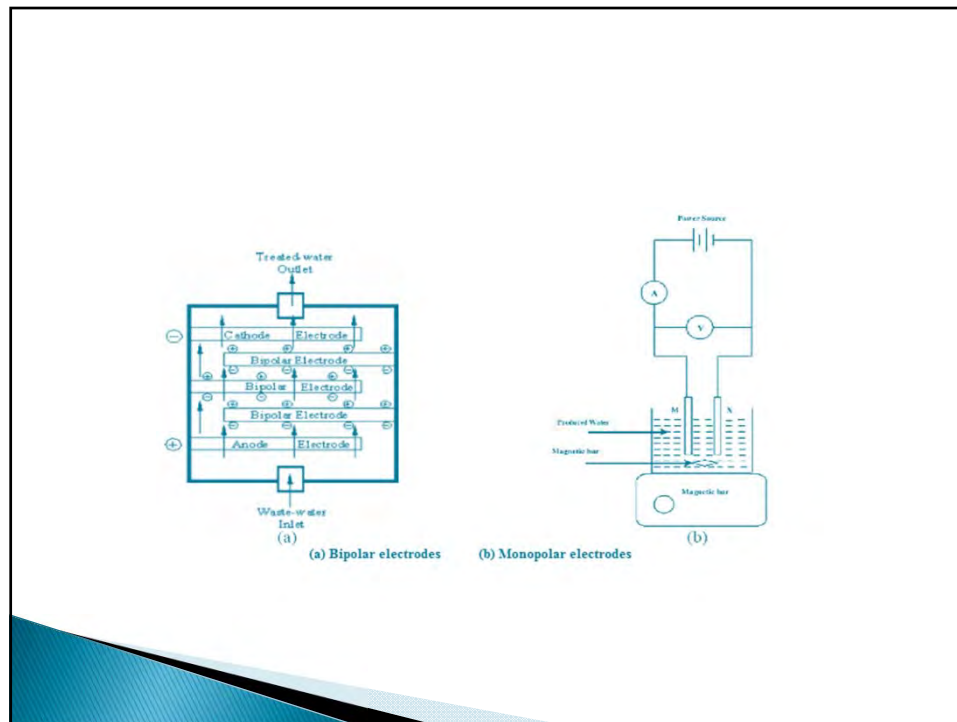
Electrocoagulation Reactions

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from respectively aluminum or iron electrodes.

‣ The metal ions generation takes place at the anode.

‣ hydrogen gas is released from the cathode.

EC Reactions continued

‣ The hydrogen gas would also help to float the flocculated particles out of the water.

‣ This process sometimes is called electrofloculation.

EC Reactions continued

The chemical reactions taking place are
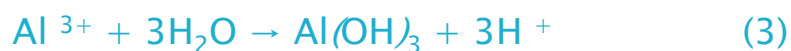
At the anode (Oxidation):

For aluminum anode

$$Al - 3e \rightarrow Al^{3+} \tag{1}$$

‣ at alkaline conditions

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \tag{2}$$

‣ at acidic conditions

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{3}$$

EC Reactions continued

For iron anode:

$$Fe - 2e \rightarrow Fe^{2+} \quad\quad\quad (4)$$

▸ at alkaline conditions

$$Fe^{2+} + 3OH^- \rightarrow Fe(OH)_2 \quad\quad\quad (5)$$

▸ at acidic conditions

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \quad (6)$$

In addition, there is oxygen evolution reaction

$$2H_2O - 4e \rightarrow O_2 + 4H^+ \quad\quad\quad (7)$$

EC Reactions continued

Meanwhile, if anode potential is sufficiently high, secondary reactions may occur also, such as:

▸ direct oxidation of organic compounds to $(CO_2 + H_2O)$

▸ direct oxidation Cl^- ions present in wastewater

$$2Cl^- \rightarrow Cl_2 + 2e \quad\quad\quad (8)$$

The chlorine produced is a strong oxidant that can oxidize some organic compounds and promote electrode reactions.

EC Reactions continued

at the cathode (Reduction):

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad (9)$$

In addition,

the cathode, may be chemically attacked by OH^- ions generated during H_2 evolution at high pH values:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \quad (10)$$

EC Reactions continued

Al^{3+} (aq) and OH^- ions generated by electrode reactions (1) and (9) react to form various **Monomeric species such as:**

- $Al(OH)_2^+$,
- $Al(OH)^{2+}$,
- $Al_2(OH)_2^{4+}$,
- $Al(OH)_4^-$, and

EC Reactions continued

polymeric species such as

▸ $Al_6(OH)_{15}^{3+}$

▸ $Al_7(OH)_{17}^{4+}$

▸ $Al_8(OH)_{20}^{4+}$

▸ $Al_{13}O_4(OH)_{24}^{7+}$

▸ $Al_{13}(OH)_{34}^{5+}$

which transform finally into $Al(OH)_3$ according to complex precipitation kinetics.

EC Reactions continued

▸ The same for iron, electrogenerated ferric ions may form monomeric ions, ferric hydroxocomplexes with hydroxide ions and polymeric species, depending on the pH range. These are:

▸ $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_4^-$, $Fe(H_2O)^{2+}$, $Fe(H_2O)_5OH^{2+}$,$Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$, which transform finally into $Fe(OH)_3$.

EC Reactions continued

Finally:

▸ The nascent Al^{3+} or Fe^{2+} ions are very efficient coagulants for particulates flocculation.

▸ The hydrolyzed aluminum ions can form large networks of Al–O–Al–OH that can chemically adsorb pollutants such as F^-.

Mechanism of electrocoagulation

Generally, three main processes occur serially during electrocoagulation:

1. Electrolytic reactions at electrode surfaces
2. Formation of coagulants in aqueous phase
3. Adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or floatation.

Factors affecting the performance of the EC unit

1- Current density or charge loading

▸ The supply of current to the EC system determines the amount of Al^{3+} or Fe^{2+} ions released from the respective electrodes.

▸ For aluminum, the electrochemical equivalent mass is 335.6 mg/(Ah).

▸ For iron, the value is 1041 mg/(Ah).

Effect of current continued

▸ A large current means a small EC unit.

▸ However, when too large current is used, there is a high chance of wasting electrical energy in heating up the water.

▸ More importantly, a too large current density would result in a significant decrease in current efficiency.

Effect of current continued

▸ In order for the electrocoagulation system to operate for a long period of time without maintenance, its current density is suggested to be 20–25 A/m^2 .

▸ The current density selection should be made with other operating parameters such as pH, temperature as well as flow rate to ensure a high current efficiency.

Effect of current continued

▸ The current efficiency for aluminum electrode can be 120–140% while that for iron is around 100%.

▸ The over 100% current efficiency for aluminum is attributed to the pitting corrosion effect especially when there are chloride ions present.

▸ The current efficiency depends on the current density as well as the types of the anions.

Effect of current continued

- Significantly enhanced current efficiency, up to 160%, was obtained when low frequency sound was applied to iron electrodes.

- Table 1 gives the values of the required Al^{3+} and power consumption for treating some typical pollutants in water treatment.

Effect of current continued

Table 1
The aluminum demand and power consumption for removing pollutants from water

| Pollutant	Unit quantity	Preliminary purification		Purification	
		Al^{3+} (mg)	E (W h/m^3)	Al^{3+} (mg)	E (W h/m^3)
Turbidity	1 mg	0.04–0.06	5–10	0.15–0.2	20–40
Color	1 unit	0.04–0.1	10–40	0.1–0.2	40–80
Silicates	1 mg/SiO$_2$	0.2–0.3	20–60	1–2	100–200
Irons	1 mg Fe	0.3–0.4	30–80	1–1.5	100–200
Oxygen	1 mg O$_2$	0.5–1	40–200	2–5	80–800
Algae	1000	0.006–0.025	5–10	0.02–0.03	10–20
Bacteria	1000	0.01–0.04	5–20	0.15–0.2	40–80

Effect of current continued

▸ There is a critical charge loading required. Once the charge loading reaches the critical value, the effluent quality does not show significant improvement for further current increase

Effect of current continued

The findings of El-Shazly et al. confirm the above rule.
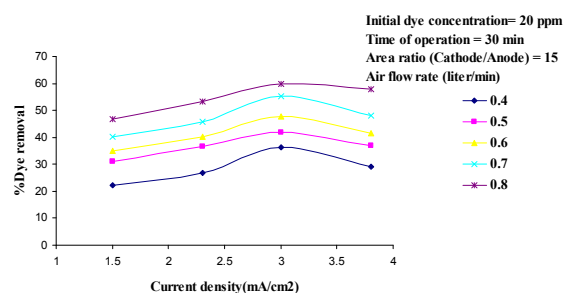
Factors affecting the performance of the EC unit continued

2- Effect of the presence of NaCl

▸ NaCl is usually employed to increase the conductivity of the water or wastewater to be treated.

▸ It was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO_3^-, SO_4^{2-}.
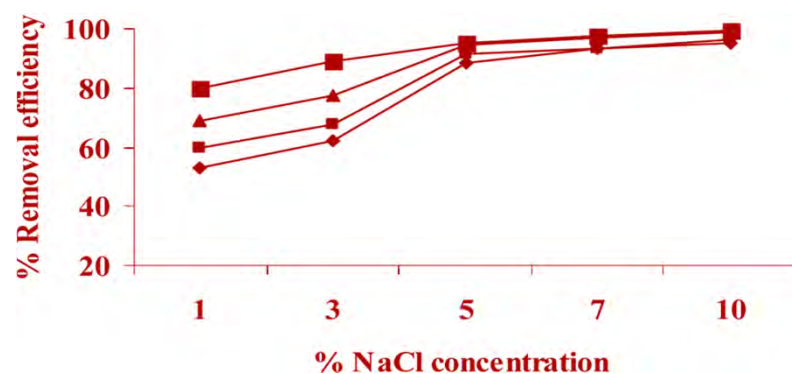
Effect of NaCl continued

▸ The existence of the carbonate or sulfate ions would lead to the precipitation of Ca^{2+} or Mg^{2+} ions that forms an insulating layer on the surface of the electrodes.

▸ This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency.

Effect of NaCl continued

- It is therefore recommended that among the anions present, there should be 20% Cl^- to ensure a normal operation of EC in water treatment.
- The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity.
- Moreover, the electrochemically generated chlorine was found to be effective in water disinfections

Effect of NaCl continued
The finding of El-Shazly et al. confirm the above results

Factors affecting the performance of the EC unit continued

3- Effect of solution pH

▸ The effects of pH of water or wastewater on electrocoagulation are reflected by the current efficiency as well as the solubility of metal hydroxides.

Effect of solution pH continued

▸ It is generally found that the aluminum current efficiencies are higher at either acidic or alkaline condition than at neutral.

▸ The treatment performance depends on the nature of the pollutants with the best pollutant removal found near pH of 7.

Effect of solution pH continued

▸ The power consumption is, however, higher at neutral pH due to the variation of conductivity.

▸ When conductivity is high, pH effect is not significant.

Effect of solution pH continued

▸ The effluent pH after EC treatment would increase for acidic influent but decrease for alkaline influent.

▸ This is one of the advantages of this process.

Effect of solution pH continued

The **increase of pH at acidic** condition can be attributed to:

- hydrogen evolution at cathodes.
- due to CO_2 release from hydrogen bubbling.
- due to the formation of precipitates of other anions with Al^{3+}

Effect of solution pH continued

- <u>On the other hand</u>, besides hydrogen evolution, the formation of $Al(OH)_3$ near the anode (see eqn. 3) would **release H^+** leading to **decrease of pH**.

- In addition, there is also **oxygen evolution** reaction leading to pH decrease.

- When there are **chlorine ions**, there are following chemical reactions taking place:
  - $2Cl^- - 2e \rightarrow Cl_2$
  - $Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$
  - $HOCl \rightarrow OCl^- + H^+$

Effect of solution pH continued

▸ Hence, the increase of pH due to hydrogen evolution is more or less compensated by the H$^+$ release reactions above.

Effect of solution pH continued

The decrease in pH at alkaline conditions can be attributed to:

▸ The formation of hydroxide precipitates with other cations.

▸ The formation of Al(OH)$_4^-$ by the reaction
Al(OH)$_3$ + OH$^-$ → Al(OH)$_4^-$

Effect of solution pH continued

▸ The pollutants removal efficiencies were found to be the best near neutral pH using aluminum electrode.

▸ When iron electrode was used in textile printing and dying wastewater treatment, alkaline influent was found to give better color as well as COD removals.

Factors affecting the performance of the EC unit continued
4- Effect of solution temperature

▸ The literature shows that current efficiency of aluminum increases initially with temperature until about 60°C where a maximum CE was found.

▸ Further increase in temperature results in a decrease in CE.

Effect of temperature continued

▸ The increase of CE with temperature was attributed to the increased activity of destruction of the aluminum oxide film on the electrode surface.

▸ When the temperature is too high, there is a shrink of the large pores of the $Al(OH)_3$ gel resulting in more compact flocs that are more likely to deposit on the surface of the electrode.

Effect of temperature continued

▸ Similar to the current efficiency, the power consumption also gives a maximum at slightly lower value of temperature, 35°C, for treating oil–containing wastewater.

▸ This was explained by the opposite effects of temperature on current efficiency and the conductivity

Power supply

When current passes through an EC reactor, it must overcome the following resistances:

▸ Equilibrium potential difference,
▸ Anode overpotential,
▸ Cathode overpotential and
▸ Ohmic potential drop of the solution.

Power supply continued

▸ The anode overpotential includes the
  ❖Activation overpotential ,
  ❖Concentration overpotential, as well as the
  ❖ Possible passive overpotential resulted from the passive film at the anode surface,

▸ The cathode overpotential includes
  ❖Activation overpotential and
  ❖Concentration overpotential.

Power supply continued

Calculation of the total cell voltage

$$E = E_o + (\eta_a + \eta_c)_{anode} + (\eta_a + \eta_c)_{cathode} + R$$

Where E is the required cell voltage, E_o is the equilibrium potential difference, η_a and η_c are activation and concentration polarization respectively, R is cell resistance due to solution and wire connections
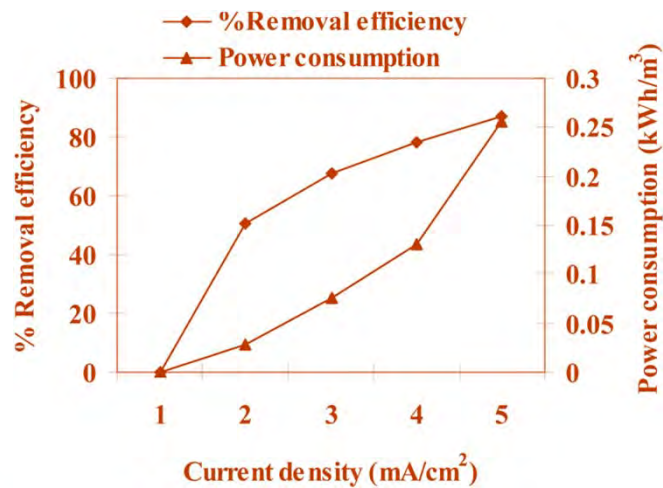
Power consumption evaluation

P = EIt/1000V
Where
‣ P is the specific power consumed (kWh/m^3).
‣ E is the cell voltage in volt (V),
‣ I is the current in ampere (A),
‣ t is the time of EC in hour (h) and
‣ V is the solution volume in cubic meter (m^3).

Both % removal efficiency and power consumption increase by increasing the current density
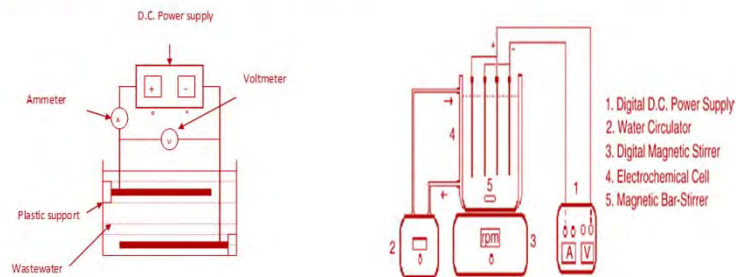

The figure below indicates that the ratio (%R/E) decreases with increasing the current density
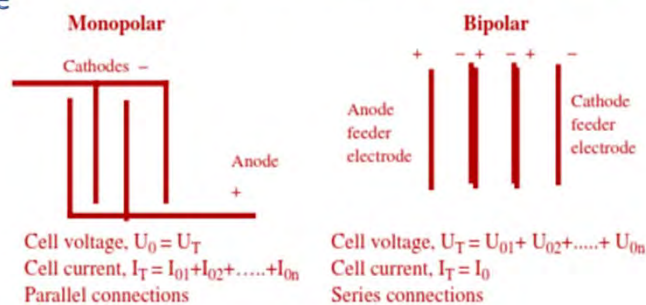
28
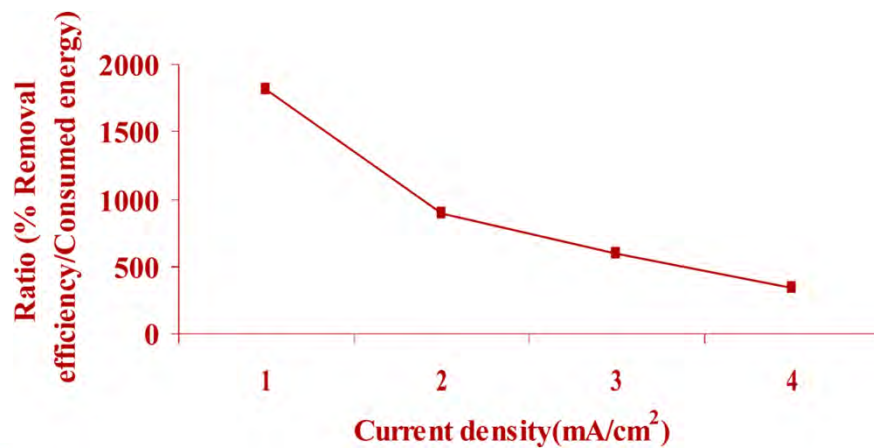
Typical design of EC unit

Depending on the orientation of the electrode plates, the electrocoagulation cell can be horizontal or vertical,
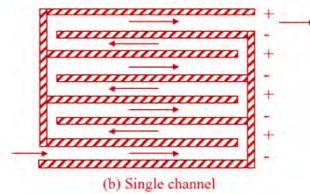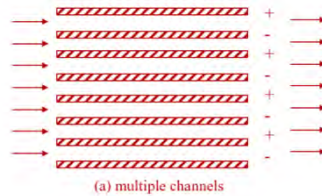

Typical design of EC unit continued

To keep the electrocoagulation system simple, the electrode plates are usually connected in bi-polar mode

Monopolar

Cathodes –

Anode
+

Cell voltage, $U_0 = U_T$
Cell current, $I_T = I_{01}+I_{02}+.....+I_{0n}$
Parallel connections

Bipolar

Anode feeder electrode

Cathode feeder electrode

Cell voltage, $U_T = U_{01}+ U_{02}+.....+ U_{0n}$
Cell current, $I_T = I_0$
Series connections

Monopolar and bipolar electrode connections in the EC reactor

Typical design of EC unit continued

The water flow through the space between the plates can be multiple channels or a single channel.

(a) multiple channels

(b) Single channel

Typical design of EC unit continued

▸ Multiple channels are simple in the flow arrangement but the flow rate in each channel is also small.

▸ When the electrode surface passivation cannot be minimized otherwise, increasing the flow rate by using a single channel flow is recommended.

Typical design of EC unit continued

▸ The electrocoagulation reactor can be operating in continuous as well as in batch operation.
▸ For batch operation such as the cases for treating small amount of laundry wastewater or for the water supply of construction site, the automation is an important issue.

Typical design of EC unit continued

▸ The electrocoagulation has to be followed by a sludge removal process. It is either a sedimentation unit or a flotation unit.

Benefits of EC System

▸ **Treats Multiple Types of Contaminants Simultaneously**
 ✓Removes heavy metals

 ✓Removes suspended and colloidal solids

 ✓Breaks oil emulsions in water

 ✓Removes fats and grease

 ✓Removes complex organics

 ✓Destroys & removes bacteria and viruses

Benefits of EC (continued)

▸ **Sludge Minimization**
 the only chemicals required is for pH adjustment.

▸ **Meet Discharge Requirements**
 Removal efficiency of contaminant can reach very high levels by controlling the process.

Benefits of EC (continued)

‣ **Totally Automated**

it is very easy to automatically controlling the treatment process.

‣ **More Economic**

compared to other techniques such as ion exchange, membrane separation, etc., the treatment costs, including utilities and consumables,(averages 1/3$ per gallon) is considered low.

Disadvantages of EC

1. The sacrificial electrodes are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.

2. The use of electricity may be expensive.

3. In some EC systems an impermeable oxide film can form on the cathode, leading to loss of efficiency of the EC unit.

Where to use electrocoagulation

It has been proven to be effective in water treatment such as drinking water supply for

▸ small or medium sized community,

▸ for marine operation

Where to use EC continued

For industrial water as:

▸ for boiler water supply for industrial processes where a large water treatment plant is not economical or necessary.

▸ For wastewater treatment such as for textile, petroleum, carpet wastewater, municipal sewage, chemical fiber wastewater, oil–water emulsion, oily wastewater, clay suspension, nitrite, and dye stuff, etc.

Recent development in EC processes

▸ The state of the art in this area is use solar energy for the supply of energy required instead of using electricity generated from petroleum oil. This can be done by using an assembly of photovoltaic cells and storage batteries.

▸ Second is to use low frequency sound waves with iron electrodes

▸ The third development is to use ozonation or ion exchange assisted EC in purpose of the production of high quality water.

Thank you

An Online Cleaning System to Reduce Demister Fouling in MSF Sidi Krir Desalination Plant

Chemist Mohamed A. Ismail

Senior Chemist - Sidi Krir - Egypt

An online Cleaning System to reduce demister fouling
in MSF Sidi Krir Desalination Plant, 2 x 5000 m^3/Day.
By

Hassan E. S. Fath* and Mohamed A. Ismail**
*Energy Association (EWE), Alexandria, Egypt. Mobile +20105142218
Fax: 03 5469378 , E-mail < h_elbanna_f@hotmail.com>
**Egyptian Electricity Holding Co. (EEHC), West El Delta Zone, Alexandria. Egypt.
Mobile: +201228374398 , E-mail< ismaileea@yahoo.com>

ABSTRACT

This paper discusses the demister scaling issue in (MSF) 2 x 5000 m^3/day Sidi Krir Desalination Unit`s site , and how like this issue affects directly in the performance of this system and in production rate too, which decreases gradually till 50%, in addition the unscheduled outage costs for acid cleaning or replacement of these demister sheets by new ones.
A fixing an online cleaning system during operation was proposed using the flow of condensate brine heater discharge pumps through two headers are fixed at the both lateral side of those stages in which the scaled demisters were recorded. The proposed system will maintain the performance and saves the costs of Chemical Cleaning and the un scheduled outage of the system. The technical and economical advantages of this proposal are highlighted.

INTRODUCTION

Sidi Krir power plant (2 x 325 MWe. Gas/oil Fired Steam Generators), Located at the Mediterranean Sea (West coast of Alexandria, Egypt) has a 2 x 5000 m^3/day MSF distillation units of brine recirculation type. More plant specifications are given in Table (2). Scale formation occurrence at demister sheets in evaporator flashing chamber during operation is highlighted in this paper, such phenomenon occurs due to disturbances in some parameters (such as; brine level, Anti-foam injection rate and concentration factor, ..etc), causing drop in all targets values of operation parameters and consequently in performance of the system as a whole .. see Table No.(1). The demister fouling was observed in stages (1-8), where the density scale gradually decreases toward stage (8). In stage (1), the inlet jet of condensate brine heater return line, has intensive flashing due to its high temperature causing a continuously flushing to the facing demister plates near this jet maintaining those plates much cleaner than the ones far from the jet, which are heavily scaled. Due to previous observation, a flushing system for demister sheets was proposed using the discharge flow of condensate return

brine heater through two headers fixed at the two lateral sides of the eight stages as show in Figure (8), (9). A periodical flushing term with a frequency three times per day with duration time not exceeding 30 mints hour is enough to maintain and save the performance of the demister plates. The expected costs and economical advantages are highlighted in Table No.(4).

The Cleaning System

The Demister is made of a metal mesh made of thin wires (Stainless Steel) installed inside evaporator flash chamber to reduce the salty saturated mist passing to distillate trays. According to its location, where it is usually facing the brine water level, it is usually exposed to the flashing activity ,and also due to the disturbances in brine water level inside flashing chambers, these demisters plates receive high salinity water drops leading to formation of scale in the demister. This was detected in stages 1,2,3,4,5,6,7,8 of the Sidi Krir Desalination Plant .

Table (2) shows specifications of Sidi Krir Desal. Plant 2 x 5000m^3/day.

The scale at demister plates gradually build up forming a considerable thick layer and becomes impermeable for vapor . In this case, the production efficiency at such stage decreases and the bottom brine temperature rises in the last stage because, little heat was transferred from the brine into the recovery cycle in the stages with scaled demisters. Consequently the efficiency of such cycle decreases as a coolant for steam flashing leading to deterioration in vacuum pressure and production rate (due to decreasing in flashing range).

Disturbances of brine seawater level inside flashing chambers and orifices disadjustment of their gates are not the only cause. Stages pressure also plays an important role. A good vacuum will reduce the impact of salty saturated brine mist droplets on demisters tissues. Thus, due to the variation of vacuum along flashing chambers, the density of scale will be vary too.
Stage temperature is an another important factor in demister scaling.

By inspection we detected the scaled demisters in stages (1-8)where the density of scale decreases as temperature decreases. Figure (1) shows the behavior of flashing steam in both cases (scaled and clean demister). Figures (3),(4),(5) show the scaled demisters in stage (5,6,and 8) respectively.

Density Scaling has a direct effect in all parameters operation control system, consequently in distillate production rate.
Figure (2) shows a comparison of production rate between a system with clean demister and that of a scaled one.

Chemical analysis tests of the collected samples of demister scale show that it was composed of 80% carbonates (Soft Scale) and 20% MgOH (hard scale).

Demister Cleaning Process
This cleaning process requires a plant shutdown of four days, where it is achieved by citric acid 5% .

Some times in the case of large desalination plants, e.g. El Rowees 15000T/day -(Abu Dhabi,U.A.E), and in cases with sever demister scaling plates are replaced by new ones. This will increase the maintenance cost.

As mentioned earlier, during demisters inspection, it was noted that in stage (1), 60% of its demister plates were clean specially the area which was near the inlet jet of brine heater condensate . This is due to the intensity of flashing action of this condensate due to its high temperature, demister plates were usually sprayed and flushed. This reduces the concentration of brine droplets in the demister and thus their scaling potential.

Figure (7). Shows the brine heater condensate system and its discharge .

This condensate system has two discharge paths. The first is transferred to the first stage flash chamber and the other one is into the main condensate circuit. This system is controlled by online conductivity analyzer which directs the discharge according to the conductivity value of this condensate.

Proposal Description:
It is proposed that the B/H condensate is discharged through two headers at both lateral sides of the eight stages to spray the demisters in order to reduce scaling. The proposed system is shown in figures (8),(9).

The proposed online cleaning system could be applied three times per day with duration time for each washing period not exceeding 30 minutes. Further, this schedule of washing should be maintained independent of the quality of the condensate.

The occurrence of demisters scaling is matured after one year through continuous operating system by load 100%.

This proposed modification to the original system is not expensive compared To the costs of production losses during shutdown for cleaning , restoration and chemicals, especially if the demisters are replaced. Table (4) shows a comparison between the costs of the present and modified system.

<u>The proposed system will have the following advantages:</u>

1-Maintains the performance of demisters during operation
2-Maintains the performance of the system and the target values of
     operation parameters
3-Saves the costs of outage for cleaning.
4-Saves the costs of chemical cleaning.
5-Saves the costs of demisters replacement in the case of sever fouling.

REFERENCES
  1-Babcock- Hitachi K.K, 1997, " Operation, Maintenance & Safety Manual
   0f 2x5000 m^3/day Desalination Plant " .
  2-Hassan E. S. Fath, 1999, " Improving the Performance Of MSF
   Desalination Plants " Proceedings of IDA Int.Conf., San diego,USA .
  3-EEHC Records, 2000-2004.
  4-C. W. L. Badger, 1959, "Conventional Methods of Scale Prevention"
   Office of Saline Water Report, US-Washington .

Items / Case	Steam Flow T/h	Heating Steam Temp.	B/H inlet Temp.	B/H outlet Temp.	Bottom Brine Temp.	Distilled Flow T/h	Make up Flow T/h	Vent Condenser Pressure (Vacuum)
Clean Demister	26	117	100.4	107.5	30.2	209	547	-1.0
Scaled Demister	29	114	100	108	55.0	133	338	-0.78

Table (1). Operation readings recorded in Sidi Krir Desal. system before and after the issue :-

Parameter	Valur (Remark)
No. of Units	2
Unit Capacity	5000 m3/day
No. of Stages	20 (17 + 3)
Designed PR	8 kg (PW) / kg (steam)
TBT	110 C
Seawater Temp.	27 C
Heating Steam Temp.	117 C
Cooling Water Flow Rate	1570 m3/hr
Brine Recirculation Flow Rate	1850 m3/hr
Seawater Concentration	43900 ppm
Brine Concentration	63000 ppm
PW Quality	25 ppm
Method of Scale Control	High Temp. Additives (Belgard EV 2000)
Tube Sheet Material (BH + Condensers)	90 / 10 Cooper Nickel
Condensers Tubes	90 / 10 Cooper Nickel
Brine Heater Tubes	70 / 30 Cooper Nickel
Water Box (BH + Condensers)	90 / 10 Cooper Nickel

Table (2) Technical Specifications of Sidi Krir

2 x 5000 m3/day MSF Desalination Plant

Item	Remark
Transfer Pump	**2**
Pump Type	**Centrifugal**
Pressure	**6.0 Bar**
Flow	**26 Tons/h**
Condensate Temperature	**110 C`**

Table (3) demonstrates the specification of B/H conden sate system.

Item	Present	Modified
The modification which is required to the original system will costs Outage Time (Days)	4	----------
Costs of PW loss with scaled demisters (USD)	**818181.80**	----------
Costs of PW loss during cleaning (USD)	36363	----------
Chemical Costs (USD)	2000	----------
Modification Costs (USD)	-----------	2000
Total Costs (USD)	**856544.80**	**2000**

Table (4) Estimating and comparison between present and modified system.
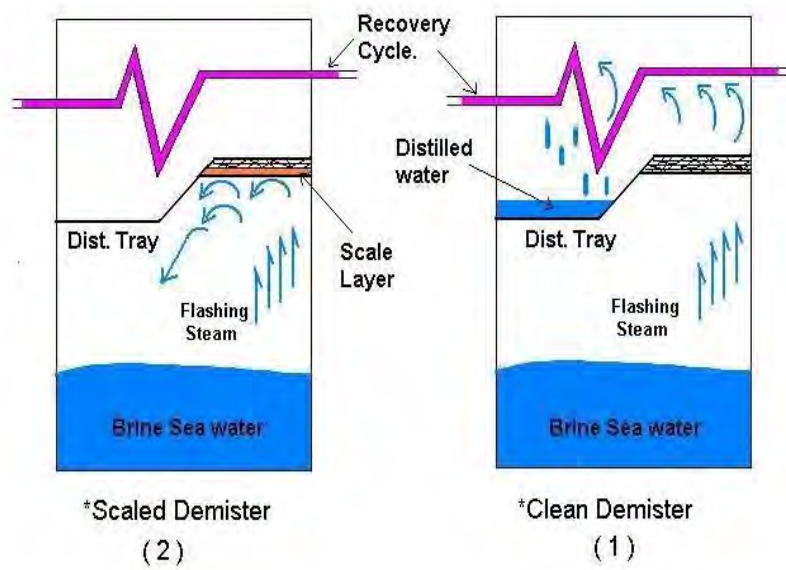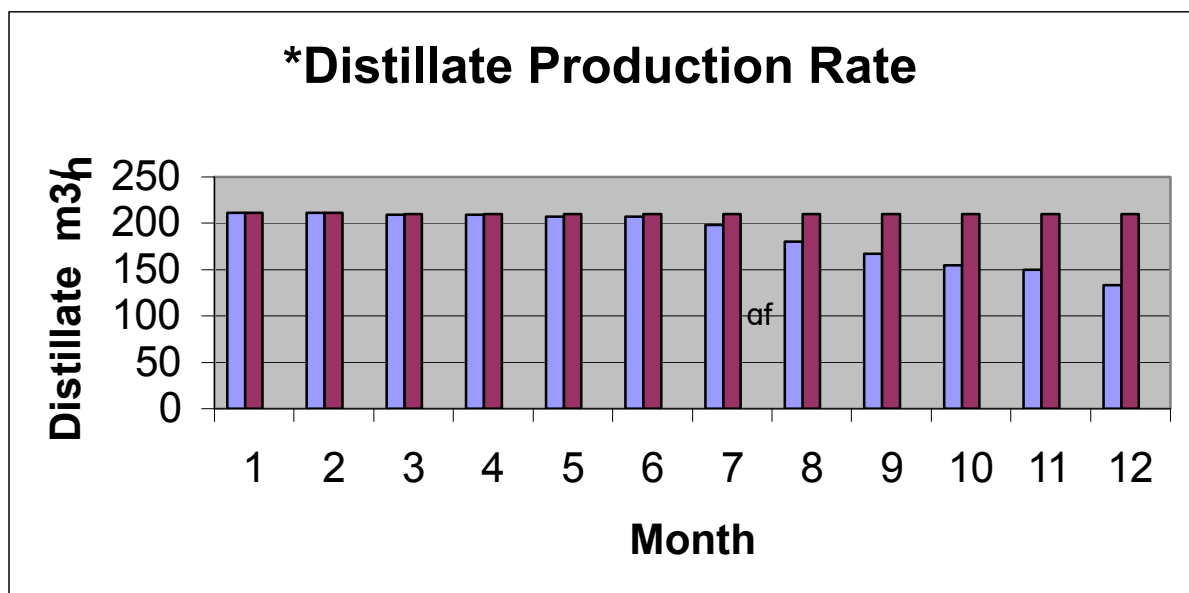
Figure (1). Behavior of Flashing Steam.

Figure (2). Comparison 0f PW. Between Ideal system and Scaled one.

Figure (3). Demister of stage No: 5
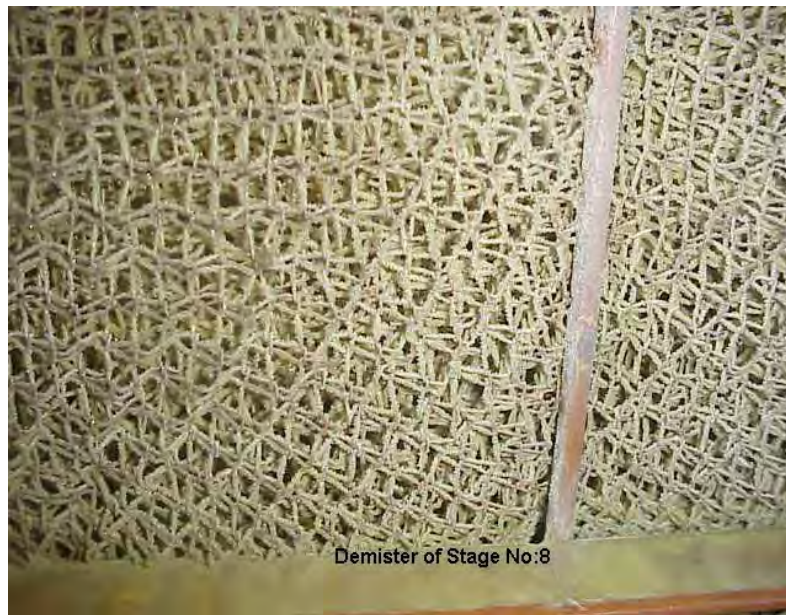

Figure (4). Demister of stage No: 6

Figure (5). Demister of stage No: 8

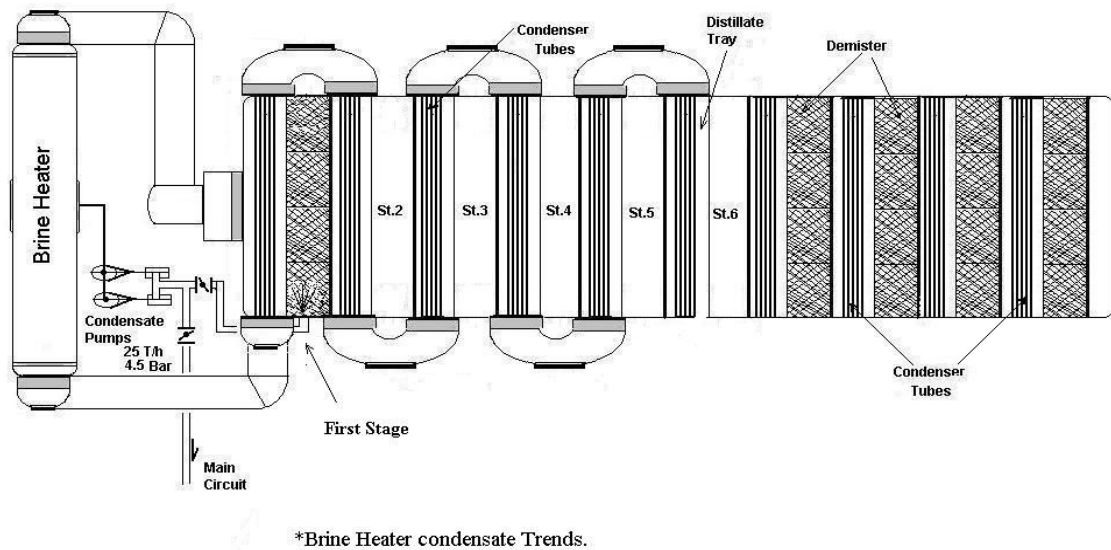Figure (6).Clean demister. (After Acid Clean).
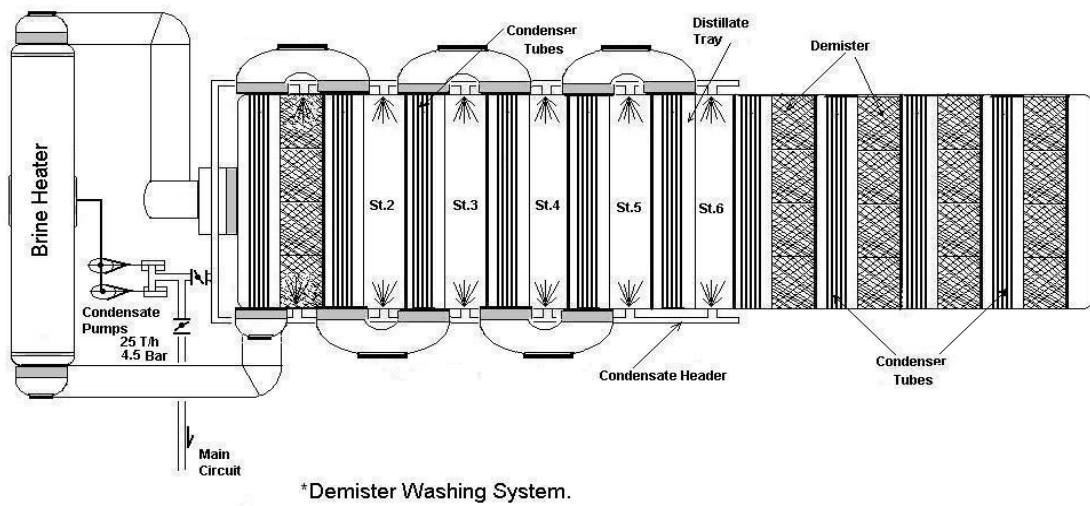
Figure (7). Brine Heater Condensate System.

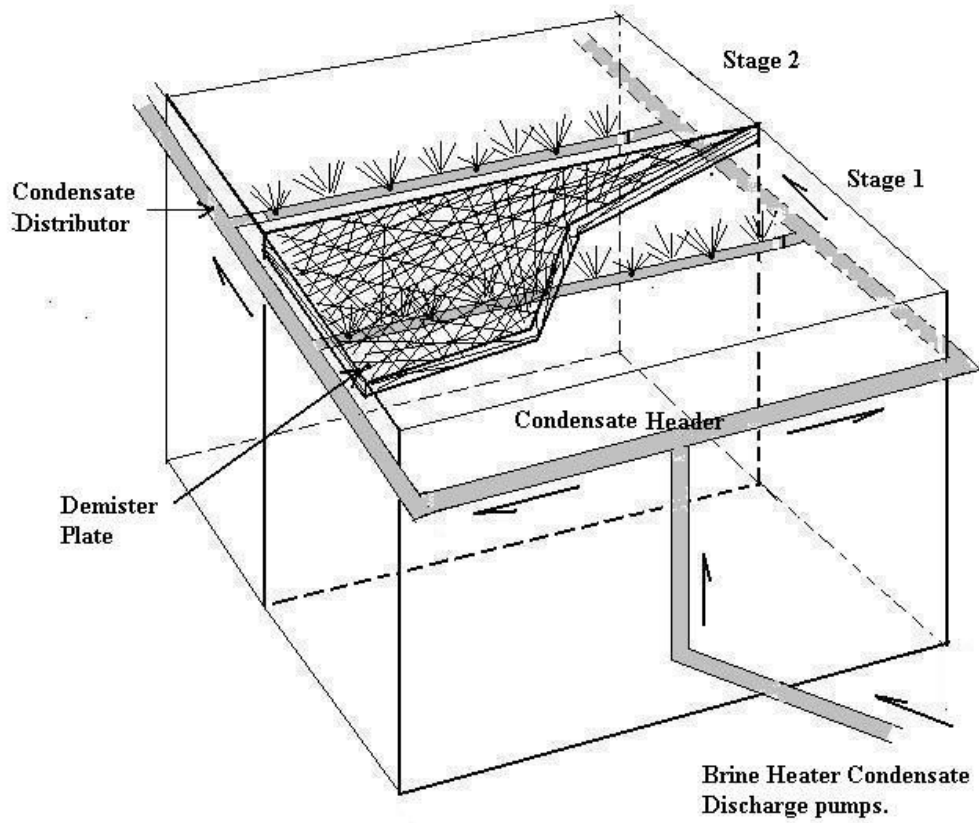Figure (8).Demister Washing System.

Figure (9) Demister Washing System.

AFA
WORKSHOP
Water Treatment and Water Quality in
Fertilizer and Petrochemical Industries

Oxygen Control in Steam Boilers

Eng. Osama Khalil

Power Plant Chemical Supervisor

Eng. Fouad Alzoubi

Power & Energy Manager
APC, Jordan

Arab Potash Company

Oxygen Control
In
Steam Boilers

Prepared by Eng. Osama Khalil

Power Plant Chemical Supervisor

Reviewed by

Eng. Fouad Alzoubi

Power & Energy Manager

Contents

1. Oxygen Corrosion Basics
- O2 attach results in pitting type corrosion
- Rapid localized metal loss

General Description

One of the most frequently encountered corrosion problems results from exposure of boiler metal to dissolved oxygen. Since the oxides of iron are iron's natural, stable state, steels will spontaneously revert to this form if conditions are thermodynamically favorable. Generally, conditions are favorable if steel that is not covered by the protective form of iron oxide (magnetite) is exposed to water containing oxygen. The following reactions occur:

$$2Fe + H_2O + O_2 \rightarrow Fe_2O_3 + 2H \uparrow \quad \text{-----------------------(1)}$$
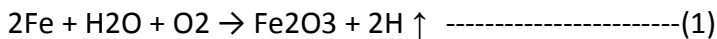
This reaction is the basis for the intensive mechanical and chemical deaeration practices that are typical of sound water-treatment programs. These practices are generally successful. In fact, occurrences of oxygen corrosion in boilers are generally confined to idle periods. For example, moisture condensing on the walls of an idle superheater tube will dissolve atmospheric oxygen. Fractures in the protective magnetite are caused by contraction stresses as the superheater is cooled to ambient temperatures. The fracture sites furnish anodic regions where oxygen-containing moisture can react with bare, unprotected metal. Figures 1 & 2 shows pitting corrosion of steam drum. In addition to tube-wall perforation, oxygen corrosion is troublesome from another perspective. Oxygen pits can act as stress-concentration sites, thereby fostering the development of corrosion-fatigue cracks, caustic cracks, and other stress-related failures.

Figure 1: pitting corrosion inside steam drum of an O-type Boiler

Figure 2: pitting corrosion inside steam drum of an O-type Boiler

Corrosivity of Oxygen

Temperature:

Higher temperatures reduce O2 solubility, but significantly increase corrosivity

Dissolved Oxygen Concentration

Higher O2 concentrations increases corrosivity

The three critical factors governing the onset and progress of oxygen corrosion include the presence of moisture or water, the presence of dissolved oxygen, and an unprotected metal surface. The corrosiveness of water increases as temperature and dissolved solids increase, and as pH decreases. Aggressiveness generally increases with an increase in oxygen.

An unprotected metal surface can be caused by three conditions:

- The metal surface is bare — for example, following an acid cleaning.
- The metal surface is covered with a marginally protective, or nonprotective, iron oxide, such as hematite, Fe2O3 (red).
- The metal surface is covered with a protective iron oxide, such as magnetite, Fe3O4 (black), but cracks exist in the coating.

Breakdown, or cracking of the magnetite, is due largely to mechanical and thermal stresses induced during normal boiler operation. These stresses are increased—and, therefore, are more damaging—during boiler start-up, during boiler shutdown, and during rapid load swings. During normal boiler operation, the environment favors rapid repair of breaches in the magnetite. However, if excessive levels of oxygen are present, either during operation or outages, the cracks in the magnetite cannot be adequately repaired and corrosion commences.

Identification

Simple visual examination is sufficient if affected surfaces are accessible. Nondestructive testing techniques, such as ultrasonic testing, may be required if affected surfaces are not accessible.

Elimination

The three critical factors that govern oxygen corrosion in a boiler are moisture or water, oxygen, and an inadequately protected metal surface. Since both water and corrosion sites are present, mitigation of oxygen corrosion is achieved by sufficiently diminishing dissolved oxygen levels.

Possible causes of excessive levels of dissolved oxygen are, for example, a malfunctioning deaerator, improper feed of oxygen-scavenging chemicals, or air in-leakage. Monitoring of oxygen levels at the economizer inlet, especially during start-up and low-load operation, is recommended.

2. Oxygen Corrosion Control

2.1. Mechanical Deaeration

- **Primary means of O2 Removal**
- **Cheaper to remove O2 with steam than to remove it chemically**

2.2. Chemical Oxygen Scavenging

- **Remove traces amounts remaining after deaeration**

2.1 Mechanical Deaeration

What Affects Mechanical Deaeration?

Most gases are removed

- **O2 is always a gas**
- **pH affects the amount of CO2 and NH3 removed**

Mechanical deaeration is the physical removal of dissolved gases from water. The primary goal is to remove oxygen from the boiler feed water, but carbon dioxide and ammonia (NH3) can also be reduced by deaeration.
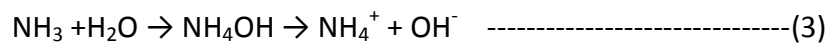
Gas	Ionic
O_2	-----
CO_2	HCO_3^- or CO_3^{--}
NH_3	NH_4^+

Mechanical deaeration influenced by the following physical-chemical considerations.

Ionization:

The degree to which gases can be deaerated depends on the ionization state of gases involved. Oxygen does not ionize; therefore, it is easily removed. Carbon dioxide and ammonia do ionize, as shown in the following equations:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \quad \text{--------------------------------(2)}$$

$$NH_3 + H_2O \rightarrow NH_4OH \rightarrow NH_4^+ + OH^- \quad \text{-----------------------------(3)}$$

Only that portion of these gases that remains in nonionized molecular form (CO_2 and NH_3) can be removed by mechanical deaeration.

Figures 3 & 4 show the effect of pH on the portions of these two gases that are available for mechanical removal
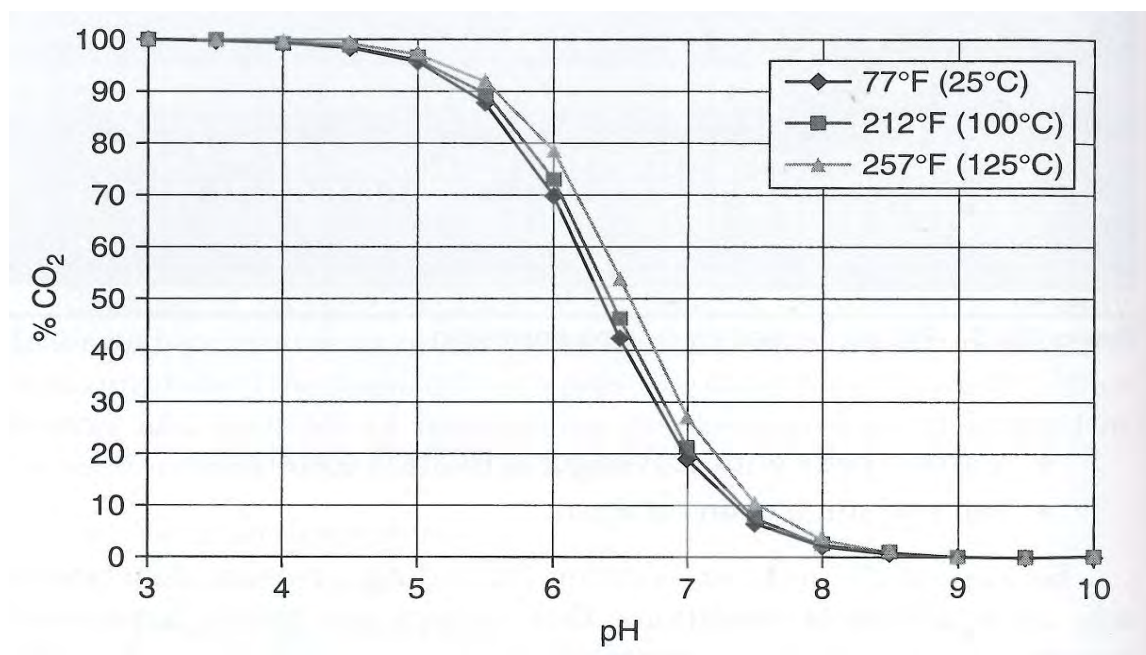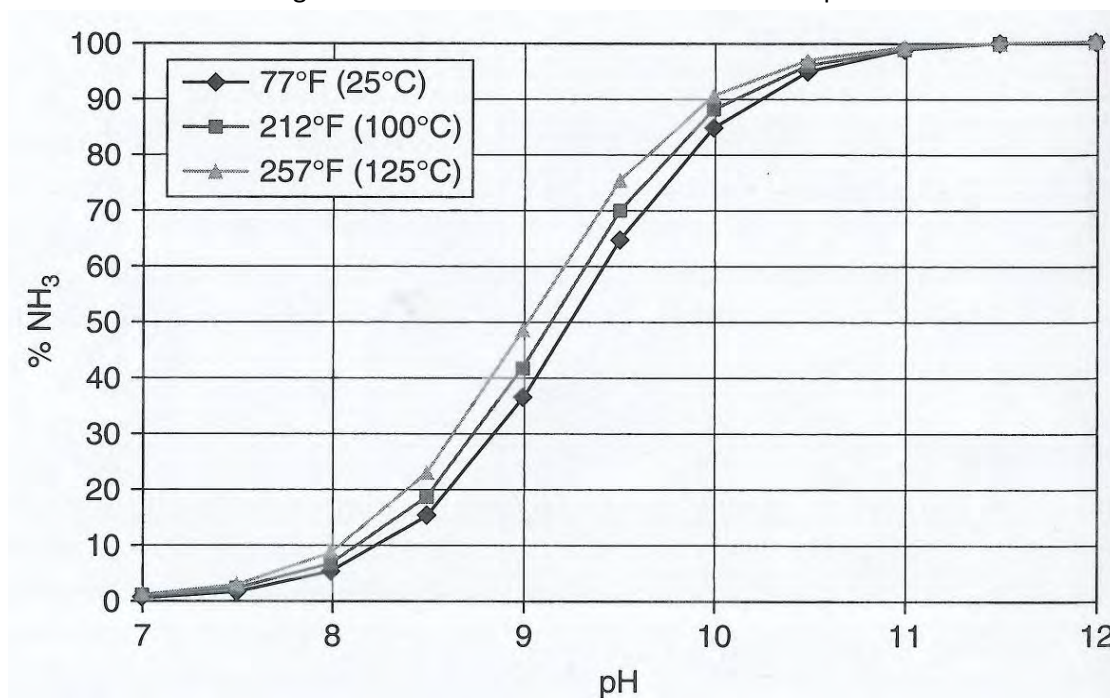

Figure 3: carbon dioxide concentration versus pH

Figure 4: Ammonia concentration versus pH

Relative partial Pressure

Henry's Law

Water will dissolve a free (nonionized) gas only to the point at which equilibrium is reached between the partial pressure of the gas in the water and the partial pressure of gas in the atmosphere with which it is in contact. This is the Henry's Law.

Air contains approximately 20% oxygen (O2) and 79% nitrogen (N2). The partial pressure exerted by oxygen in air is 1/5 atmosphere. Water surrounded by air can, therefore can dissolve oxygen up to the point at which oxygen in the water exerted a partial of pressure1/5 atmosphere. See fig.5

At 77 °F (25 °C) and atmosphere pressure, this correlates to an approximate content of 8.4 mg/L oxygen in water. In traditional mechanical deaeration, the equilibrium between oxygen in the water and the atmosphere contacting it is deliberately upset. This is accomplished by blanketing the water with an atmosphere of steam that contains little oxygen.
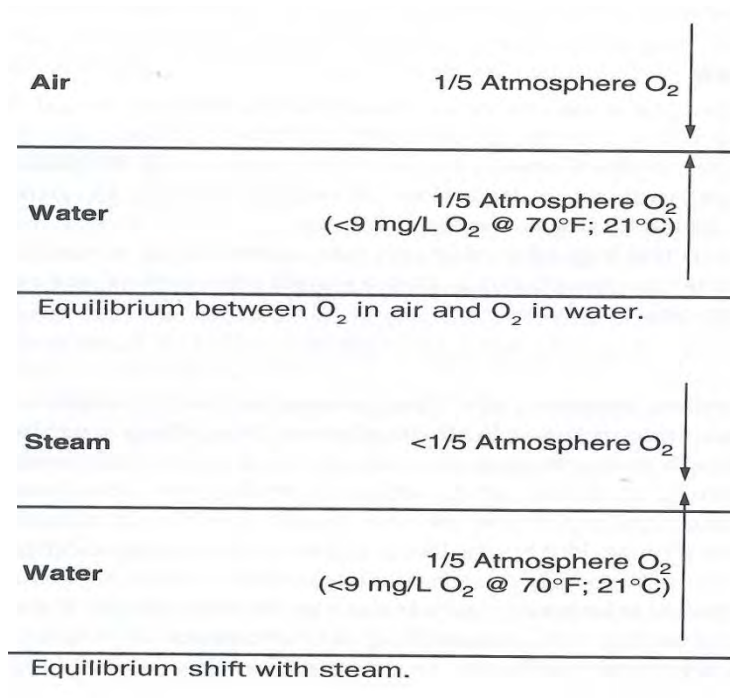

Figure 5   oxygen equilibrium

Temperature

Oxygen Solubility Decreases as Temperature Increases

As the temperature of water is raised to its boiling point (saturated temperature for a specific pressure), all free (nonionized) gases theoretically become insoluble. Fig-6 graphically illustrates the solubility of oxygen as a function of temperature. In practice, total removal of gases does not occur. Henry's law relates the steam oxygen contents to the liquid water oxygen content. As a result neither of these contents can reach zero. And a small amount of gases remain dissolved in the water phase.
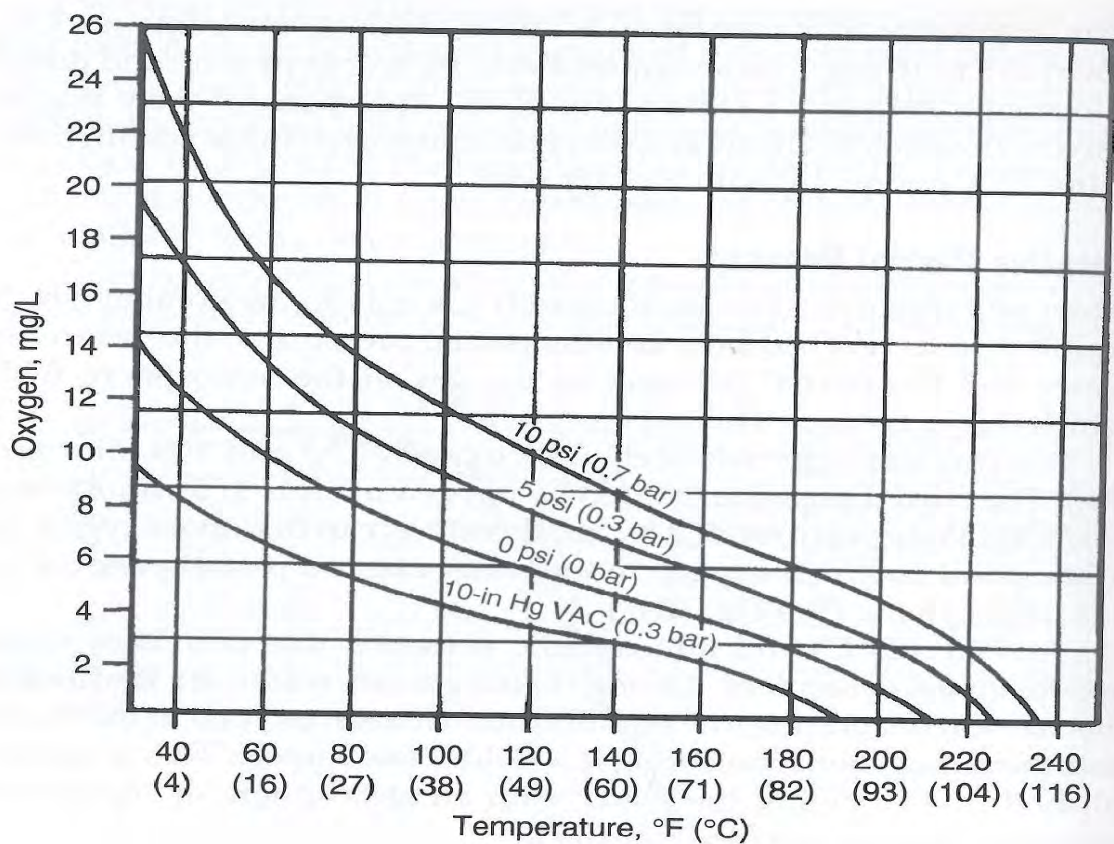
Figure 6   solubility of oxygen in pure water vs. temperature

Agitation:

Small droplets heat easier.

Small droplets provide greater surface area for removal of gases.

Agitation is the biggest differentiator of deaerator type

A more complete removal of entrapped gases can be obtained by breaking the water stream into small droplets or thin films and then preventing these droplets from agglomerating. Smaller droplet can be heated more efficiently, and the vapor/liquid interfaces will be repeatedly broken, reducing the tendency of the gases to remain dissolved in the in the cooler liquid phase.

Gas Removal

The gases released from the water must be physically removed, or they will redissolve. Removal is accomplished by maintaining a flow of fresh steam over the droplets, directing the oxygen contaminated steam away from the deaerated water. In mechanical deaeration, removal is accomplished by continuously venting the gases to atmosphere.

Pressure Deaerators

Deaerating equipment is designed to heat water to the temperature of saturated steam at the pressure nominated within the deaerator and to reduce oxygen in the feed water to about 0.007 to 0.04 mg/L (7 to 40 µg/L). If the unit is guaranteed to reduce the oxygen to 7 µg/L or less, it's commonly designated as deaerator. If the unit is guaranteed to reduce the oxygen to only 40 µg/L or less, it's commonly referred to as a deaerating heater.

Spray type deaerators

In spray-type deaerator, feed water enters the primary preheater section through spring-loaded spray valves (Figure-7). Steam supplied to the primary preheater section comes from the secondary stage deaerator.

Feedwater leaving the primary preheater section contains only traces of oxygen and other noncondensable gases. The water enters the second stage scrubber section, flowing through internal piping or channels. The hot water mixes with live fresh steam, which has entered the scrubber section through the steam inlet.

Both steam and water enter the bottom of scrubber pot or chamber, where the two forms an intimate mixture that is heated to the full saturation temperature. As the mixture flows upwards, it may first pass through a distribution orifice or port that imposes a negligible pressure drop. At the outlet or throat of the scrubber, the mixture must pass through a final fixed area orifice, which imparts a significant pressure drop on the mixture. The drop in the pressure creates a superheated mixture that immediately boils as it leaves the scrubber.

This action scrubs the final remnants of oxygen from the mixture. The deaerated water falls to the storage area, while the steam and noncondensable gases are drawn into the preheater section.

The scrubber is a fixed orifice device that is designed and sized relative to a certain steam volume and velocity. Any change in operating conditions that creates a substantial change in steam volume or velocity will have a negative impact on stripping and therefore the deaerator performance.
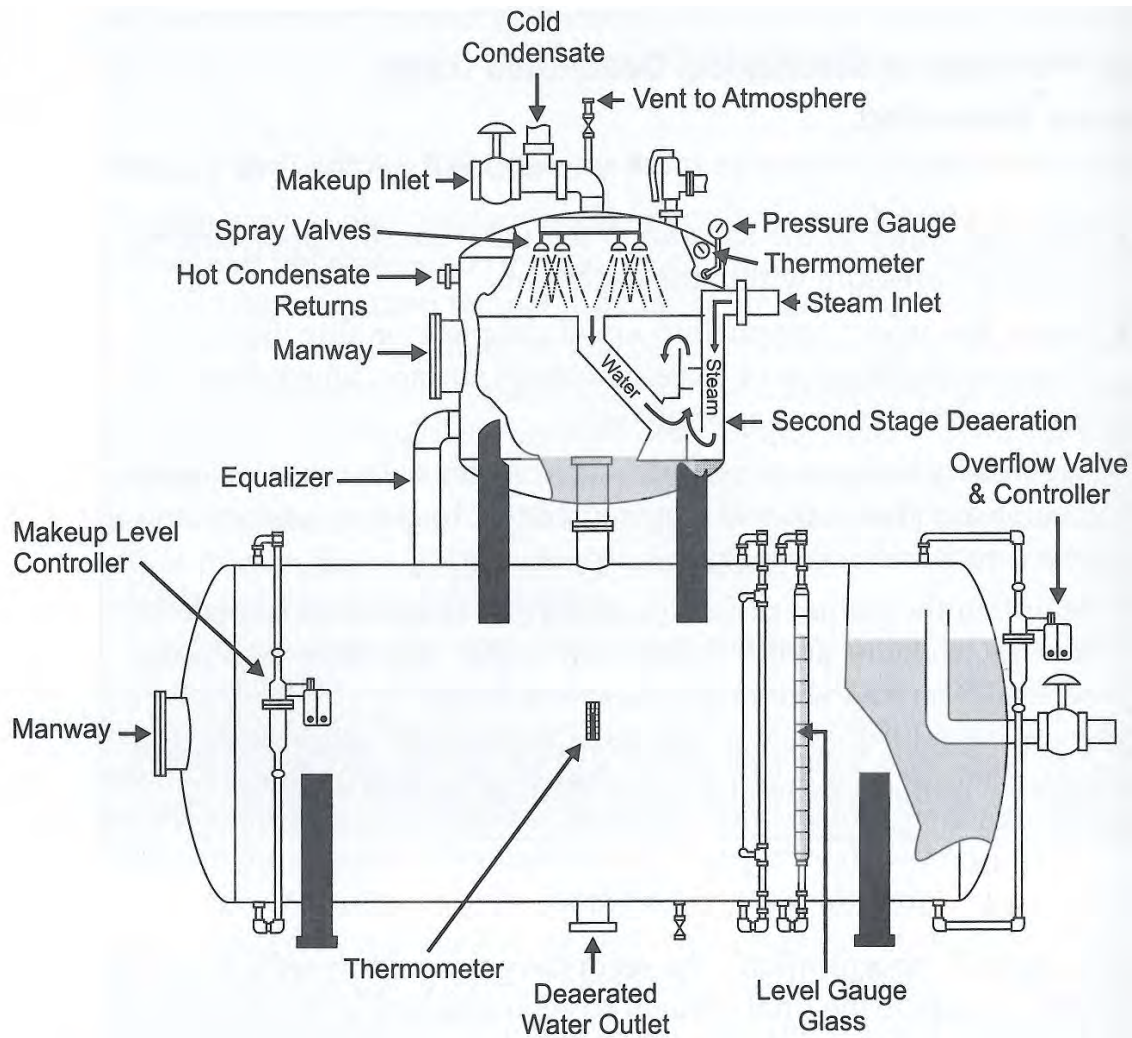
Fig-7: spray-type deaerator

Tray type deaerators

In tray-type deaerator, feed water enters the primary preheater section through spring-loaded spray valves (Figure-8). Steam supplied to the primary preheater section comes from the secondary stage deaerator.

Feedwater leaving the primary preheater section contains only traces of oxygen and other noncondensable gases (less than 5 to 10% of the original concentration), is then directed into the secondary deaerating section. This is typically an enclosed stack of distributing pans or trays of stainless steel construction.

The preheated water spills uniformly over the tray stacks or packing and cascades downward forming thin, uniform films. These thon films or curtains of water allow the

oxygen to diffuse rapidly to the surface, where the equilibrium allows it escape into the vapor phase or steam.

Steam flow in the tray section may take one of three configurations; co-flow, cross-flow, or counter-flow. In a coflow unit, the steam is introduced at the top of the tray bank and flows down through the trays with the water, in a crossflow unit, the steam passes from left to right as the water descends through it. In a counterflow unit, the steam is introduced at the bottom of the tray stack and passes up through the descending water. This is probably the best of three designs, since the cleanest steam mixes with the cleanest water at the bottom of the tray stack.

The tray deaerator is ideally suited for wide load swings or operation at partial loads, because of the capability of the tray stack to distribute and detain the falling water resulting in longer, more intimate steam-water contact. Thus the tray deaerator is more tolerant of variations in steam flow and velocity. Steam flow through the tray section, however, must be sufficient to maintain water contact with oxygen free steam and to maintain the desired equilibrium conditions necessary for full deaeration. Steam flows can only be maintained by condensation of steam in the preheater section as feedwater is heated to saturation temperature.
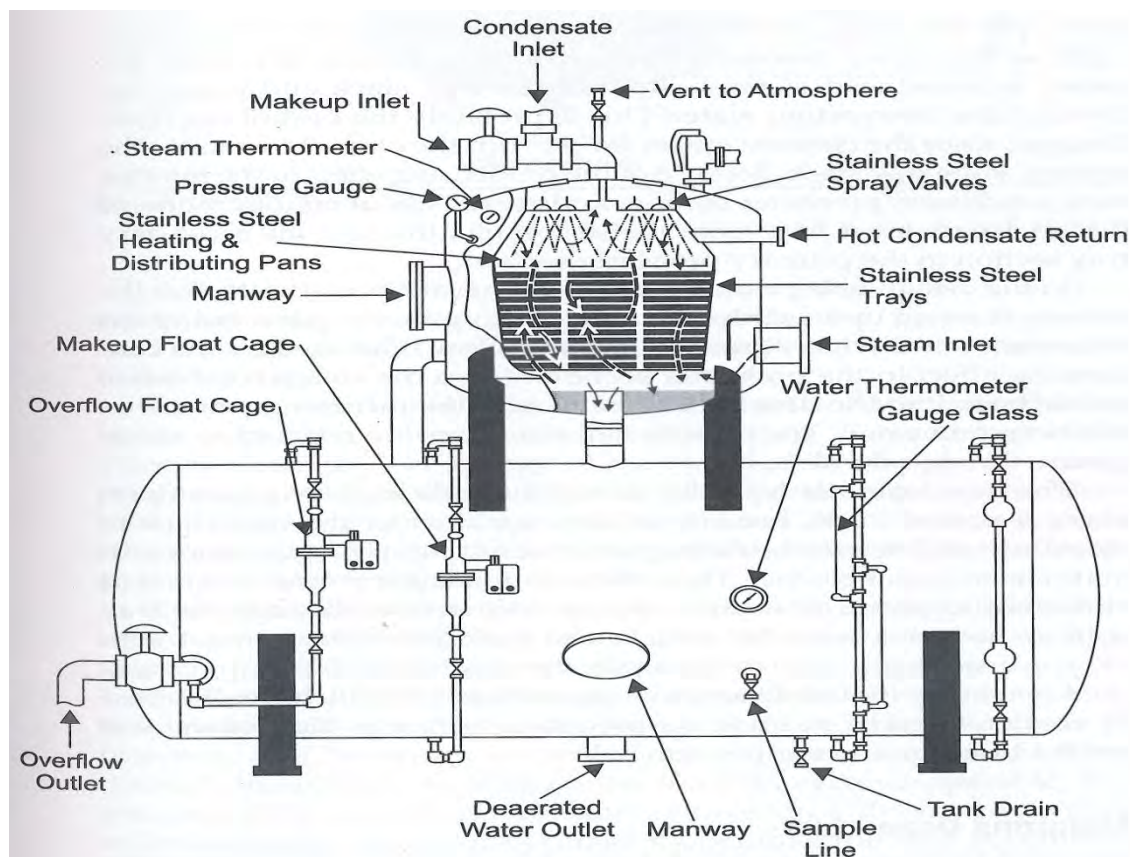

Fig-8: tray-type deaerator

Spray vs. Tray Type deaerators

Spray	Tray
More economical; Lower initial capital cost, lower cost of maintenance items	Better at accommodating rapid load fluctuations
Lower maintenance need	Trays must be inspected regularly - prone to damage /upset
Operates down to 20% of design	Operates down to 10% of design
- Dome Temp should be within $2°F$ ($1°C$) of saturation for operating pressure - Storage temp should be within $4°F$ ($2.2°C$) of dome temp - High inlet water temp results in an inadequate ΔT Spray DAs need ΔT of greater than 30-50$°F$ ($16.8-28°C$)	- Dome Temp should be within $2°F$ ($1°C$) of saturation for operating pressure - Storage temp should be within $4°F$ ($2.2°C$) of dome temp - High inlet water temp results in an inadequate ΔT Tray DAs need ΔT of greater than 10-20 $°F$ ($5.6-11.2C$)

Deaerator Venting

Knox has provided the following graphs for estimating the required vent steam from boiler feed water deaerators. Vent steam rate depends upon the type of deaerator (spray or tray type) and the percentage of makeup water (in contrast to returning condensate). Low makeup water rates require relatively lower steam vent rates, but there is a minimum rate required to remove CO2 from the returning condensate

Venting Requirements for Tray Deaerators: **Vent rate for Tray type deaerators is 0.05-0.1 %, (Fig-9)**
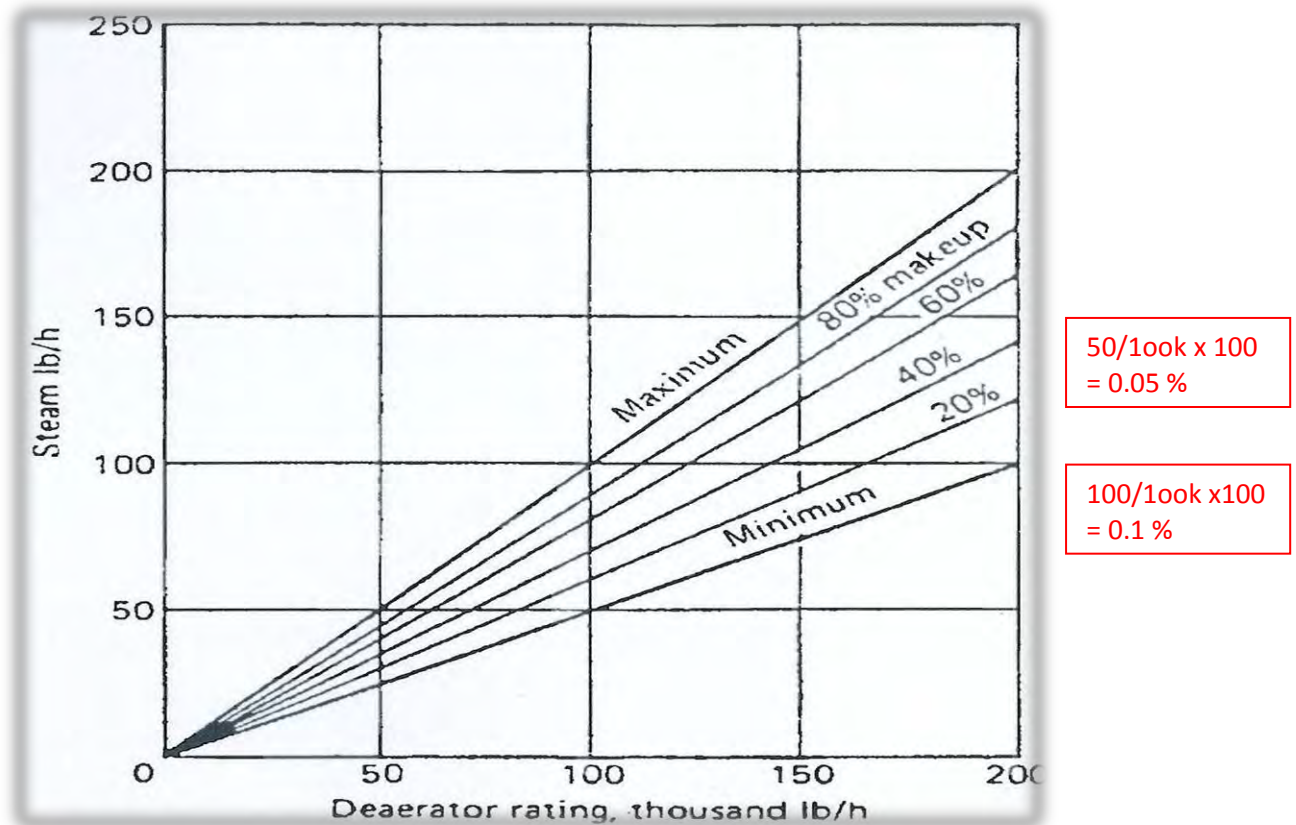

50/100k x 100 = 0.05 %

100/100k x100 = 0.1 %

Fig-9 Steam vent rate vs. deaerator rating for a tray-type deaerator

Venting Requirements for Spray Deaerators: **Vent rate for Spray type deaerators is 0.07-0.14 % (fig-10)**
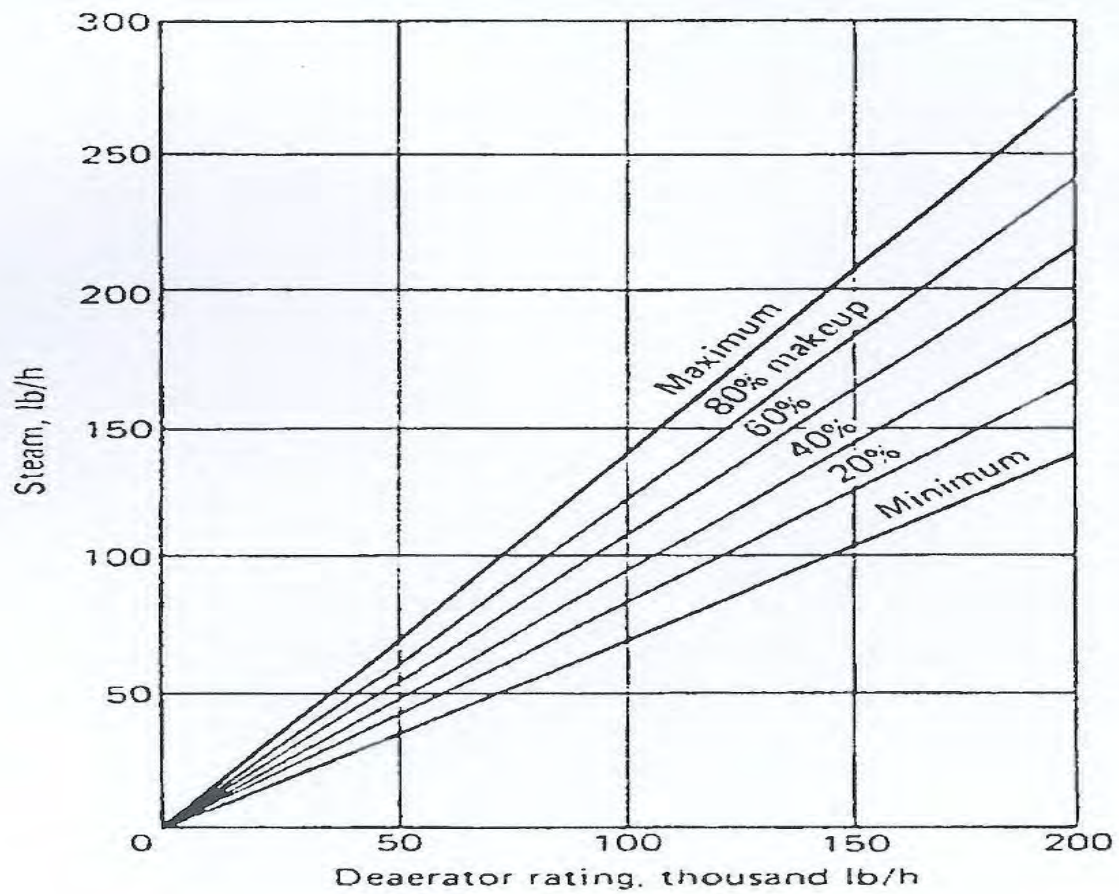

Fig-10 Steam vent rate vs. deaerator rating for a spray-type deaerator

2.2. Chemical Oxygen Scavenging

Purpose: To chemically remove the dissolved oxygen left in the feed water after the feed water has been mechanically deaerated.

Traditional Scavengers: Sulfite & Hydrazine

Sodium sulfite (Na_2SO_3)
The most widely used materials in this application are sodium sulfite (Na2SO3) and hydrazine (N2H4), both of which are usually sold as catalyzed systems to enhance reactivity with oxygen at lower temperatures and pressures. Quinones and cobalt salts are typically used as catalysts. Sulfite is the least expensive and most active (when catalyzed) for lower and medium pressure boilers [up to 600 psig (42 bar abs)]. In its reaction with oxygen, sodium sulfite produces sodium sulfate, which contributes solids to the circulating boiler system

$$2 \ Na_2SO_3 + O_2 \rightarrow 2 \ Na_2SO_4 \ \text{-----------------------(4)}$$

Thus, in high pressure and supercritical boilers, where any solids constitute a severe problem, sulfite cannot be used.

The theoretical dosage of sodium sulfite, or the number of parts of Na2SO3 required to consume 1 part of O2, can be calculated based on its reaction with oxygen described above:

$$\underline{2(126 \ g/mole \ Na2SO3)} = 7.88 \ theoretical$$
$$32 \ g/mole \ O2$$

Therefore, about 8 parts of Na2SO3 are fed to the boiler to consume each part of oxygen. Typically, residual concentrations of sulfite of up to 20 ppm are maintained in the boiler.

Sulfite also breaks down at pressures as low as 600 psig (41 bar abs) resulting in the formation of sulfur dioxide or hydrogen sulfide, by either of two routes:

$$Na2SO3 + H2O \rightarrow SO2 + 2 \ NaOH \ \text{-----------------------(5)}$$
$$4 \ Na2SO3 + 2 \ H2O \rightarrow H2S + 2 \ NaOH + 3 \ Na2SO4 \ \text{-----------------------(6)}$$

Both are corrosive gases which leave the boiler with steam, resulting in low pH steam and condensate and potential attack throughout the system.

Sulfite is an effective oxygen scavenger, but it is nonvolatile and does not leave the boiler with the steam, thus providing no protection in the condensate system. Sulfite also does not reduce hematite to magnetite and is ineffective in repassivating boilers with existing rust.

Hydrazine (N_2H_4)

The oxygen scavengers used in the higher pressure boilers, and the ones with which diethylhydroxylamine (DEHA) competes most directly are hydrazine and catalyzed hydrazine. Hydrazine does not produce corrosive gases at high temperatures and pressures, and in application, reacts with oxygen to form nitrogen and water:

$$N2H4 + O2 \rightarrow 2\ H2O + N2\ \text{------------------------(7)}$$

In calculating the theoretical requirement of hydrazine for scavenging oxygen, a value of 1 part per part oxygen is obtained:

$$\frac{\underline{32\ g/mole\ hydrazine}}{32\ g/mole\ O2} = 1$$

In operation, a 100% excess of hydrazine is used. Boiler residuals of 1 ppm hydrazine are typically maintained.

Hydrazine does not contribute solids to the system, so boiler blow down, or the mechanical removal of solids from the after-boiler section as sludge, is reduced. It also promotes the formation of the protective magnetite film on the boiler tubes and drum, and converts red iron dust (hematite) to magnetite. It is because of these passivation effects that an excess of scavenger to oxygen is required when changing a boiler system form a non-passivating scavenger to one which passivates.

Hydrazine is not without limitations. It is not considered "volatile", so it does not leave the boiler with the steam to scavenge oxygen and passivate metal throughout the system. In boilers operating above 400°F (205°C), it can degrade to ammonia and volatilize with steam, and, in the presence of oxygen, attack metals containing copper:

$$2\ N2H4 \rightarrow 2\ NH3 + N2 + H2\ \text{------------------------(8)}$$

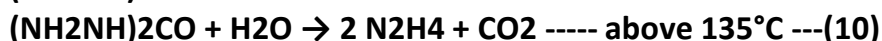Finally, and most importantly of late, is the inclusion of hydrazine on the OSHA and NIOSH lists as a suspect carcinogen. Papers and sales literature presenting laboratory and field data on "hydrazine alternatives" abound, and include those listed in Tables 1 and 2. Each claims to be a safe and effective material for boiler protection through oxygen scavenging, but the levels required and optimum conditions for use vary.

Second Generation Scavengers (Carbohydrazide, Erythorbate, hydroquinone, Diethylhydroxylamine, Methylethylketoxime)

Carbohydrazide [(NH$_2$NH)$_2$CO] is a volatile oxygen scavenger, contributes no solids to the system, reacts readily with oxygen at low temperatures and pressures, and passivates the metal of the boiler system. Carbohydrazide can (and does) break down to hydrazine above temperatures of 275°F (135°C) to scavenge oxygen, but this conversion is not necessary for oxygen scavenging activity because it reacts directly with oxygen:

$$(NH2NH)2CO + 2O2 \rightarrow CO2 + 2N2 + 3H2O \text{ -----below 135°C -----(9)}$$
$$(NH2NH)2CO + H2O \rightarrow 2 N2H4 + CO2 \text{ ----- above 135°C ---(10)}$$

The theoretical dosage required to scavenge one part O2 is 1.4 parts carbohydrazide. It should be noted that in its reaction with oxygen, carbohydrazide creates carbon dioxide, a gas that when dissolved in the condensate as carbonic acid, H2CO3, results in corrosion in the return line. Carbohydrazide cannot be used in applications where the steam comes into contact with food.

Erythorbate (RC6H6O6) where R is H+, Na+, or amine), however, is generally regarded as safe (GRAS) by the FDA and can be used in food processing applications. It, too, is a metal passivator and contributes no solids to the system. It has a theoretical dosage level of 11 parts per oxygen (as O2). Erythorbic acid is non-volatile. It will remain in the boiler, and will not travel with the stream to control oxygen corrosion in the condensate.

$$RC6H6O6 + ½ O2 \rightarrow RC6H4O6 + H2O \text{ ------------------------(11)}$$
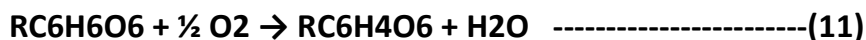
Methylethylketoxime (C4H8NOH) , or MEKO, is a volatile oxygen scavenger which displays metal passivating characteristics. It reacts with oxygen to form methyl ethyl ketone, nitrous oxide, and water:

$$2 CH3CH3CH2CNOH + O2 \rightarrow 2 CH3CH3CH2CO + N2O + H2O \text{ ------------(12)}$$

Its theoretical dosage is 5.4 parts per part of oxygen.

Hydroquinone (C6H4(OH)2), which has been used to catalyze the reaction with O2 of some of these oxygen scavengers, has been examined and proven to be effective itself in lowering O2 levels to the 1-2 ppb range, It reacts with oxygen to form benzoquinone:

$$C6H4(OH)2+ 1/2O2 \rightarrow H2O + C6H4O2 \text{ ------------------------(13)}$$

It has a theoretical dosage level of 6.9 parts per part O2. It is extremely reactive with oxygen at the lower boiler temperatures and pressures, and is volatile in higher pressure

systems. It does not degrade to ammonia, so it is safe for use with copper-containing alloys.

Diethylhydroxylamine (C2H5)2NOH), or DEHA is a volatile metal-passivating oxygen scavenger which reacts with oxygen to form acetate, nitrogen and water:

$$\textbf{4 (C2H5)2NOH + 9O2 →8 CH3COOH + 2 N2+ 6 H2O ------------(14)}$$

In theory, 1.24 parts of DEHA react with 1 part of oxygen, but in application, a dosage of 3: 1 DEHA to O2 is recommended.
It is generally true that all oxygen scavenger requirements in the field are larger (by up to a factor of 10) than projected by calculations.

DEHA has other advantages over each of the above-mentioned O2 scavengers. It has higher volatility and metal passivating characteristics than sulfite, hydrazine and erythorbate, and can be used more safely than hydrazine.
Less DEHA is required than erythorbate and methylethylketoxime in theoretical considerations. It offers toxicity advantages over carbohydrazide in that it does not yield hydrazine under use conditions.

3. Boiler Lay-up

Water is always present in an operating boiler. Also, the protective magnetite coating exists in a state of continuous breakdown and repair. At any given time, holidays and cracks in the magnetite will be present, although the percentage of the entire internal surface they represent will be very small. Therefore, since both water and corrosion sites are present, mitigation of oxygen corrosion is achieved by sufficiently diminishing dissolved oxygen levels. Possible causes of excessive levels of dissolved oxygen are, for example, a malfunctioning deaerator, improper feed of oxygen-scavenging chemicals, or air in-leakage. Monitoring of oxygen levels at the economizer inlet, especially during start-up and low-load operation, is recommended

Idle boiler- wet lay-up
An idle boiler during wet lay-up is subject to conditions similar to those in an operating boiler as far as oxygen corrosion is concerned. Therefore, the preventive method, reduction of oxygen content to very low levels, and continuous control that prevents these levels from rising, is the same. In general, this procedure requires complete filling of the boiler, use of sufficiently high levels of oxygen-scavenging chemicals, and maintenance of properly adjusted pH levels, as well as periodic water circulation.

Idle boiler - dry lay-up
Successful protection of an idle boiler during dry lay-up depends upon consistent elimination of moisture and/or oxygen. A procedure for boiler protection by dry lay-up can involve the use of desiccants and nitrogen blankets, or the continuous circulation of dry, dehumidified air (<30% relative humidity).

Boiler after chemical cleaning
Protection of a boiler following acid cleaning is achieved by developing a protective iron oxide coating on the metal surface. This is usually accomplished by a thorough rinsing followed with a "post boilout." A sodium carbonate solution or other alkaline substance can be used in the post boilout-passivation step

Alternative Wet Storage (Cascade)
Continuous blow down from an operating boiler is used to keep the idle boiler filled with treated water. If the unit has not been cooled and drained, connect the continuous blow down line from an operating unit to a convenient bottom location of the laid-up boiler. If refilling the idle boiler, first open a vent line and close it only after completely filling the unit. Then open the continuous blow down line of the stored boiler (Fig 11).
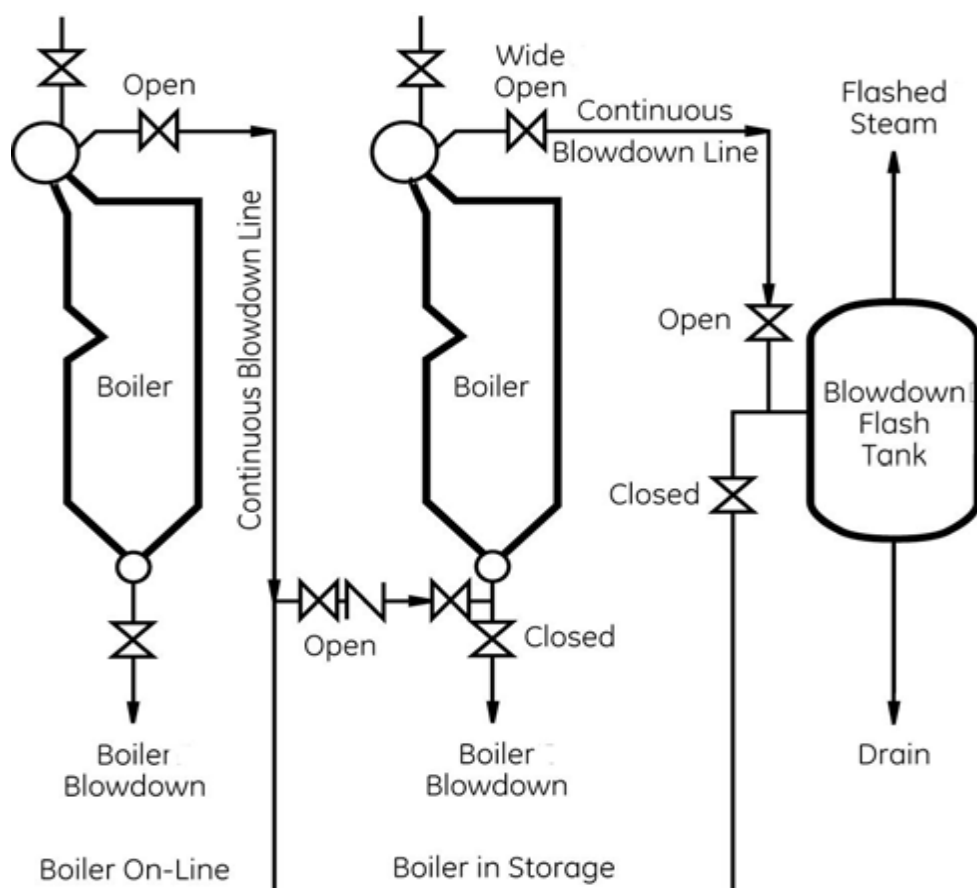
Fig-11, Wet Storage (Cascade)

References:

- Nalco water handbook, Daniel J. Flynn. Third edition.
- Knox, A. C., 'Venting Requirements for Deaerating Heaters," Chemical Engineering, January 23, 1984
- 2012 international water treatment seminar, USA, presentation, Deborah Bloom.
- Boiler failure analysis, second edition, James J. Dillon, Paul B. Desch, Tammy S. Lai, Daniel J. Flynn.
- Consensus for the lay-up of boilers, turbines, turbine condensers, and auxiliary equipment, ASME research report CRTD- Vol. 66.
- Rules of Thumb for Chemical Engineers, Third Edition, Carl R. Branan,

AFA
WORKSHOP
Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Advance in Corrosion Monitoring

Prof. Essam Khamis

Director, City of Scientific Research & Technological Applications- SARTA City

ADVANCES IN CORROSION MONITORING
متابعة تآكل الوحدات الصناعية

Prof. Essam Khamis Ibrahim

Director, City of Scientific Research and Technological Applications

SRTA-City

Former, Vice President of Alexandria University for Graduate Studies & Research

CORROSION MONITORING

CAPCIS *(Corrosion and Protection Centre, Industrial Services)* Originally a spin-out from the University of Manchester (formerly **UMIST**). **CAPCIS** is Europe's leading Materials Consultancy and Specialist Testing company, providing a diverse range of Integrity and Asset Management Services to the Oil and Gas, Utility, Infrastructure, Transport and Legal / Insurance sectors.

CAPCIS provide a range of services to support the selection, specification, development, supply, installation and operation of corrosion monitoring in field and laboratory application.

WHAT IS CORROSION MONITORING?

The regular measurement of corrosion or corrosivity as it effects an asset.

The asset may be pipeline network, a concrete bridge, an offshore oil & gas facility or a printed circuit in a computer.

It is most often used to make comparisons between actual and predicted corrosion rates.

BENEFITS OF CORROSION MONITORING

- Providing an early warning that damaging process conditions are developing.

- Studying the correlation between changes in process parameters such as *pressure, temperature, pH, flow rate, etc.* and their effect on system corrosivity.

- Evaluating the effectiveness of a corrosion control method such as chemical inhibition and the determination of optimal applications.

- Providing accurate prediction of equipment retirement date to facilitate scheduling of shutdowns and pre-ordering equipment items.

CORROSION MONITORING METHODS

Two main groups are available for monitoring methods:

Direct Techniques

- Corrosion Coupons.
- Electrical Resistance (ER).
- Inductive Resistance Probe.
- Linear Polarization resistance (LPR).
- Electrochemical Impedance Spectroscopy (EIS).
- Electrochemical Noise (EN).

- Harmonic Analysis.

- Zero Resistance Ammetry (ZRA).

- Potentiodynamic Polarization.

- Thin Layer Activation (TLA) & Gamma Radiography.

- Acoustic Emission (AE).

Indirect Techniques

- Corrosion Potential.

- Hydrogen Monitoring.

- Chemical Analysis.

Direct Techniques

Weight Loss Measurements

Specimen preparation *(important)*

⬇

Exposure to environment *(30 days)*

⬇

Specimen cleaning

⬇

Measurement of the weight change of the specimen

$$\text{mpy} = \frac{534\ w}{DAT}$$

w: weight loss, mg; D: density of specimen, g/cm³; A: area, inch², T: exposure time, hour.

Attractive features of weight loss method:

- **Simple,** No sophisticated instrumentation is required to obtain a result.

- **Direct,** A direct measurement is obtained, with no theoretical assumptions or approximations.

- **Versatile,** It is applicable to all corrosive environments, and gives information on all forms of corrosion.

Coupon after exposure

The visual appearance, the amount of deposit, fouling or presence of localized corrosion is as equally important as the weight loss value.

Microscopic examination can determine the degree of corrosion and the type of attack.
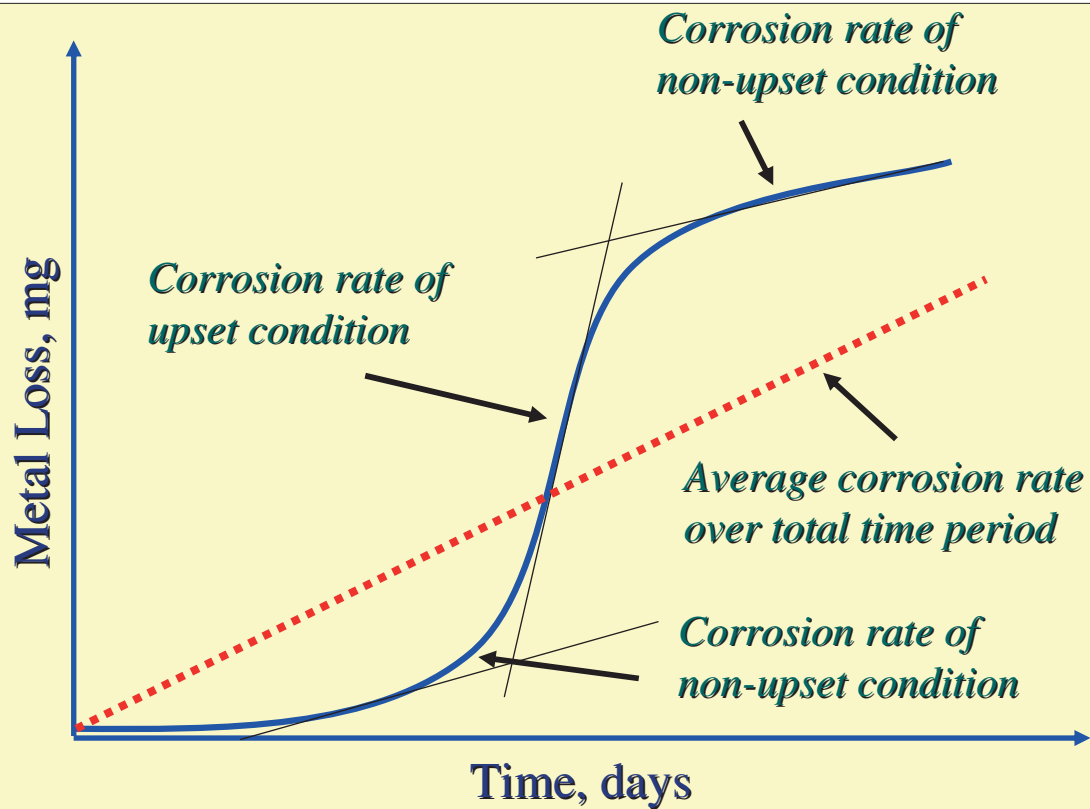
Typical plot of metal loss vs time

CORROSION RATE EXPRESSIONS

mmy : mm penetration per year

gmd : g/m² day

ipy : inches penetration per year

mpy : milli-inches per year

mdd : mg per square decimeter per day

For uniform attack and according to corrosion rate, metals are classified to:

- < 5 mpy *(0.15 mm/y)* , metals have good corrosion resistance. They are suitable for valve seats, pump shaft...

- 5 – 50 mpy *(0.15-1.5 mm/y)* , metals are satisfactory if a higher corrosion rate can be tolerated, e.g. for tanks, piping, valve bodies.

- > 50 mpy *(1.5 mm/y)* , usually metals are not satisfactory.

ELECTRICAL RESISTANCE (ER) , CORROSOMETER

ER is "on-line" method measuring total metal loss occurring in the interior of plant and pipelines. ER corrosion sensors have been likened to "intelligent" coupons, facilitating a simple corrosion measurement without the need to remove the coupon from service.

Measurement is achieved using ER probes with an element that is *"exposed"* to the corrosive fluid and a *"protected"* element sealed within the probe body. Measurement of the resistance ratio of the exposed protected element.
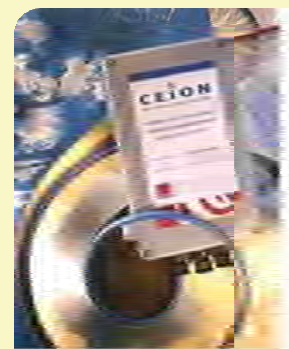
CEION® Technology

Cost between US$5000 and US$50,000 per monitoring point depending on the complexity of the system.
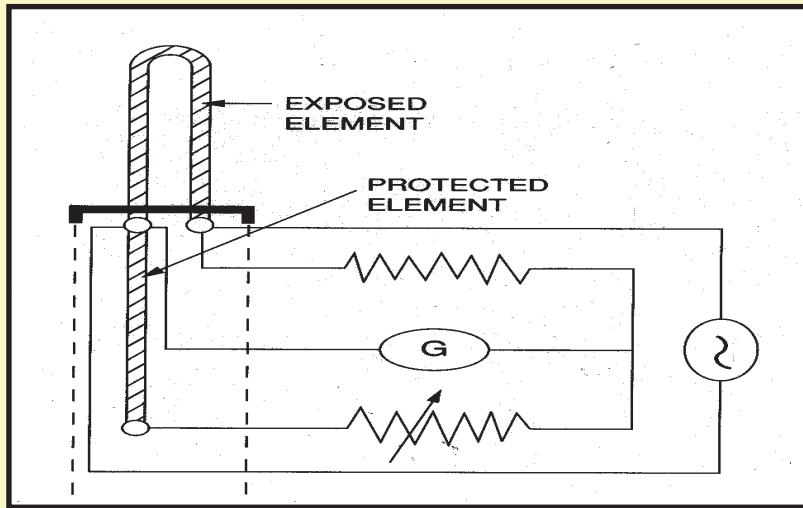
ER of the metal is given by: **ER = ρ l/A**
ρ : resistivity, l : element length, A : the cross sectional area. Reduction (metal loss) in the element's cross section due to corrosion will be accompanied by an increase in the element's ER.
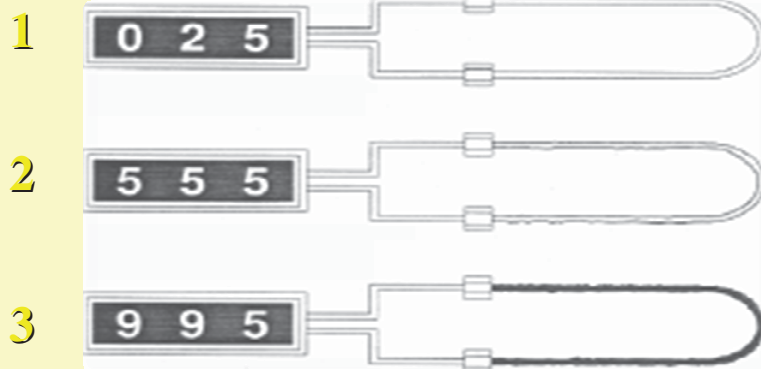
1- The wire loop is new with its total diameter of 40 mils.

2- The element has experienced about 5 mils penetration or about half of its useful life. The increased electrical resistance of the element will register as 5 mils metal penetration into the piping or process system.

3- Here the element has measured 10 mils of penetration and requires replacement.

Since temperature changes effect the resistance of both the exposed and protected element equally, measuring the resistance ratio minimizes the influence of changes in the ambient temperature. Therefore, any net change in the resistance ratio is attributable to metal loss from the exposed element.

ER method is applied to environments having poor electrolytes, vapors, soil, "wet" hydrocarbons, oil/gas production, transmission systems, refinery/petrochemical process streams, processing systems sub-sea pipelines, sub-surface wellheads and other formerly inaccessible locations.

ER generally do not respond rapidly to a change in corrosive conditions/change in corrosion rate.

CAUTION: Conductive deposits such as iron sulfide *(in sour oil/gas systems and certain forms of microbial corrosion, such as SRB attack)* or carbonaceous material on the sensor elements distort the readings.
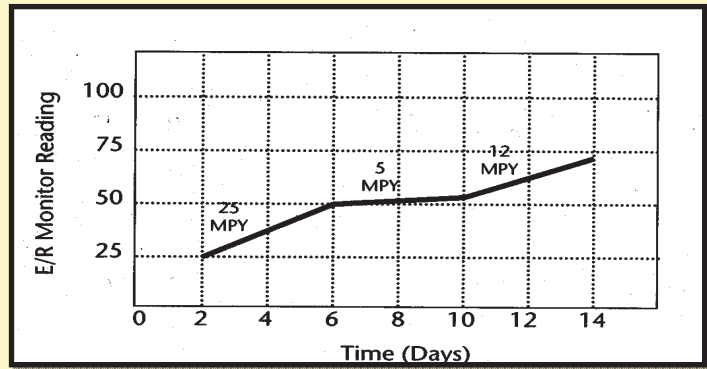
The ER probe *(electrical coupon)* is equipped with a sensing element having a composition similar to that of the process equipment of interest (*wire, tube, strip, cylinder and spiral*).

Electrical resistance probes

Manual graphing techniques are usually used to derive corrosion rate from periodically obtained data.

The Checkmate Corrosometer Portable Instrument is the latest addition to the industry-standard Corrosometer Product Line. Using "state of the art" surface mount integrated circuits, the sophisticated electronics provide higher resolution and measurement accuracy of Corrosometer (ER) corrosion probes.

INDUCTIVE RESISTANCE PROBES

- It is similar to ER probes. However, it is two orders of magnitude more sensitive than ER.
- Mass changes in the sensor element are detected by measuring changes in the inductive resistance of a coil, located inside the element.
- Sensor element tends to show-up a change in corrosion rate much sooner than the equivalent ER version.
- It is applicable for low conductivity and non aqueous environments, where electrochemical techniques are generally unsuitable.

OFF-LINE CORROSION RATE MEASUREMENTS

Chemical Analysis

Chemical analyses can provide valuable information in corrosion monitoring programs such as:

Metallic counts, pH monitoring, conductivity, dissolved oxygen, water alkalinity, concentration of suspended solids, and inhibitor concentrations.

Electrochemical Techniques

Corrosion can be monitored through the measurement of *potential* and *current* that characterize the corrosion process. This corrosion current can be converted to a corrosion rate by employing Faraday's Law.

$$mpy = \frac{0.13\ i\ e}{\rho}$$

i: current density, A;
e: equivalent weight of the metal, g;
ρ: density of the metal, g/cm^3.

BENEFITS OF ELECTROCHEMICAL METHODS

Measure an "instantaneous" corrosion rate.

Provide *faster* and more dynamic information than non chemical methods.

Used to obtain mechanistic information of the material in the environment (*identification of transitions between active and passive behavior in stainless alloys and the efficiency of chemical inhibition*).

Cell Design for Electrochemical Measurements
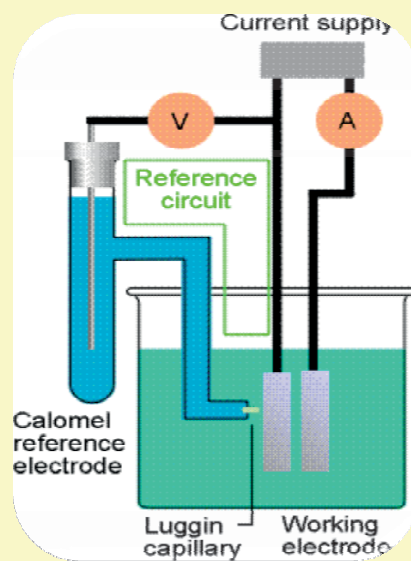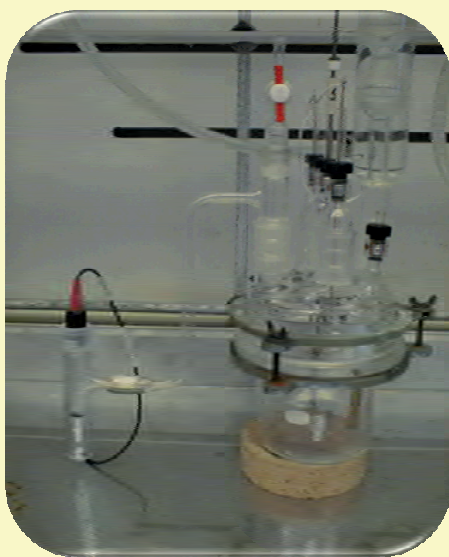
Electrochemical cell consists of three electrodes (*working, counter and reference*) together with features for the control of solution flow and state of aeration.

Corrosion Potential Measurements

E_{corr} is a useful indication of the corrosion state of an immersed metal.

The instrumentation is simple, comprising of milli-voltammeter with a high input impedance and a reference electrode.

The measurement of the corrosion potential is widely used in industry for monitoring reinforcing steel corrosion in concrete and structures such as buried pipelines under cathodic protection and monitoring of anodic protection systems.

☞ THE ELECTRICAL DOUBLE LAYER
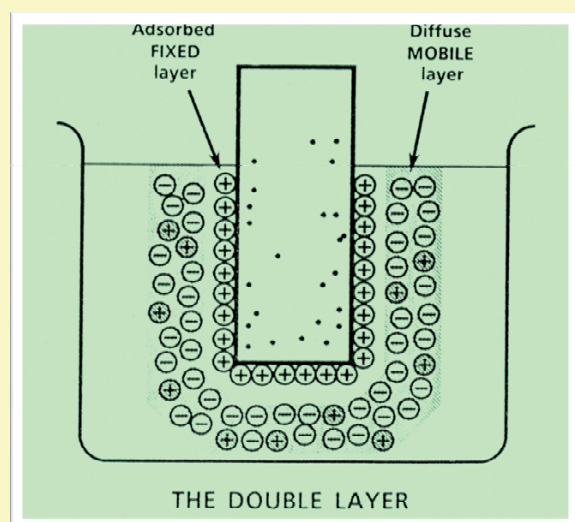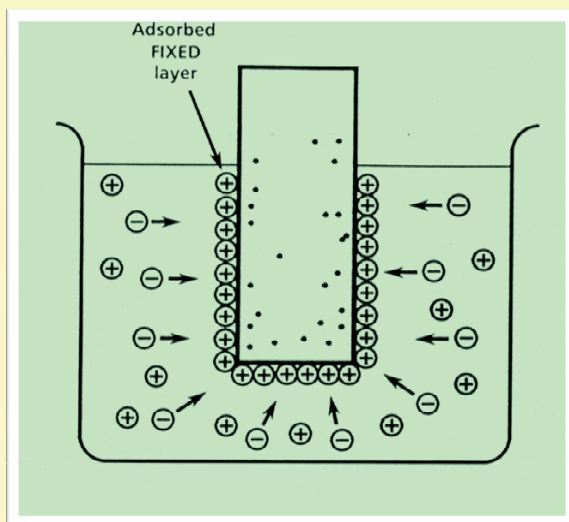
The adsorbed fixed layer and the diffuse mobile layer together are the ELECTROCHEMICAL DOUBLE LAYER acting as a capacitor.

The embedded probe comprises a Ag/AgCl/KCl reference electrode and a mixed metal oxide coated titanium counter electrode.

Surface Mounted Probe. Corrosion Potential & Corrosion Rate Mapping.

Concrete Probe measures the instantaneous corrosion rate of reinforcing steel in concrete by LPR method.

D.C Electrochemical Techniques

Laboratory measurements of corrosion include *Potentiostatic, Galvanostatic, Potentiodynamic and Linear Polarization Resistance.* These techniques have not translated well to on-line field use, except LPR used as continuous monitors.

The Potentiostat

Potentiostat changes the potential between the working and reference electrodes at a preset value, which in turns change the degree of corrosion of the metal.

Potentiostat forces the current to flow between the working and counter electrodes to keep the desired potential.

Potentiostats

MEASUREMENT METHODS

- Current control

Current path

V

AE

POTENTIOSTAT   RE

WE

Counter Electrode

R

Reference Electrode only used to monitor potential, **not** connected to potentiostat
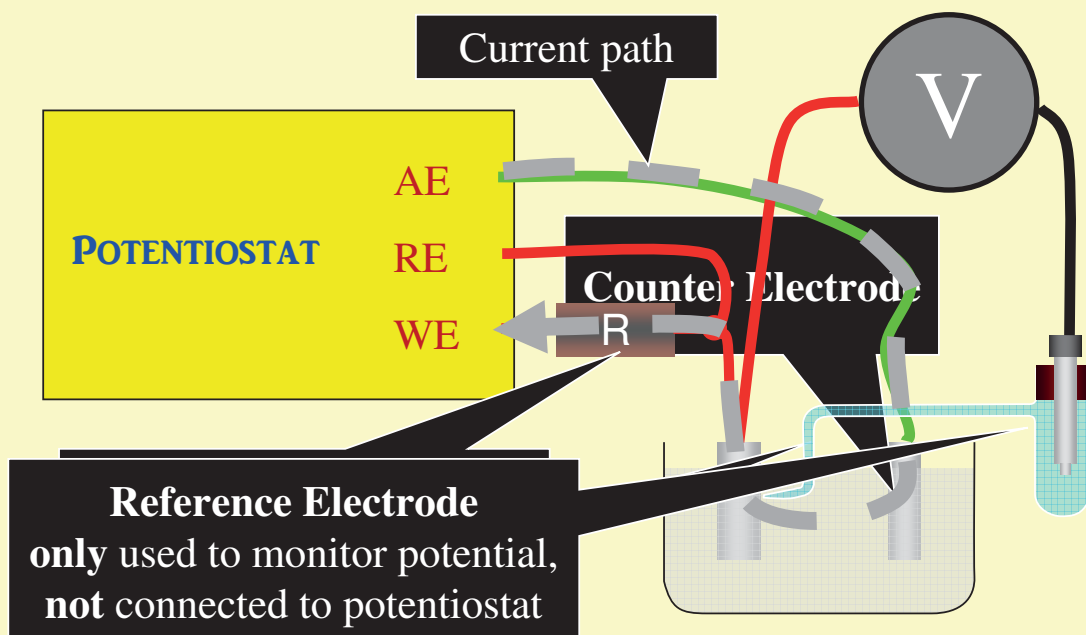
DC & THE DOUBLE LAYER

Surface atoms ionize and the electron flow towards the dc power supply.

DC POWER SUPPLY

− + ← • Electron Flow (Faradaic)

DC BEHAVIOUR:

The Capacitor "Leaks"
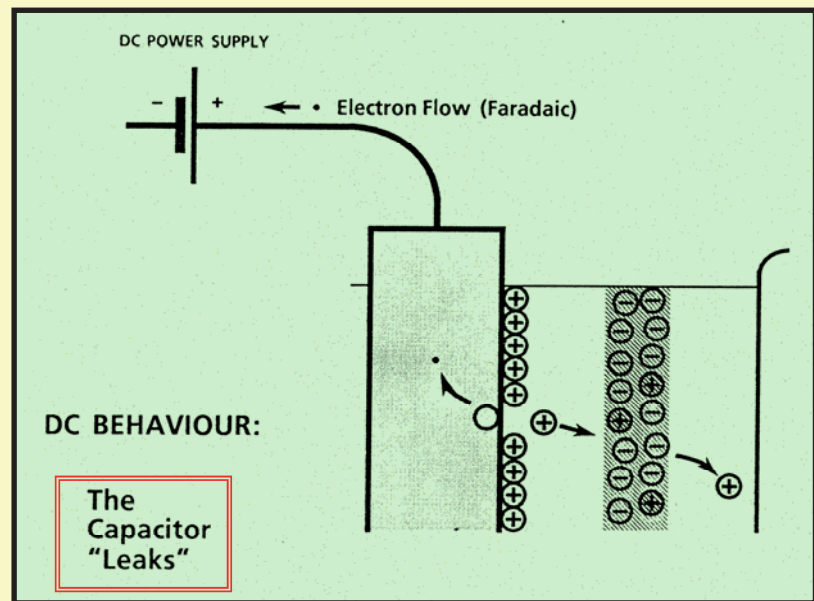
DC voltage makes a net current flow through the double layer, from plate (electrode surface) to plate (mobile layer).

i_{OH_2}

E_{H^+/H_2}

$H^+ \rightarrow H_2$

i_{corr}

E_{corr}

Applied current curve

E

i_{OM}

$M \rightarrow M^+$

Tafel region

E_{M/M^+}

log $i_{applied}$
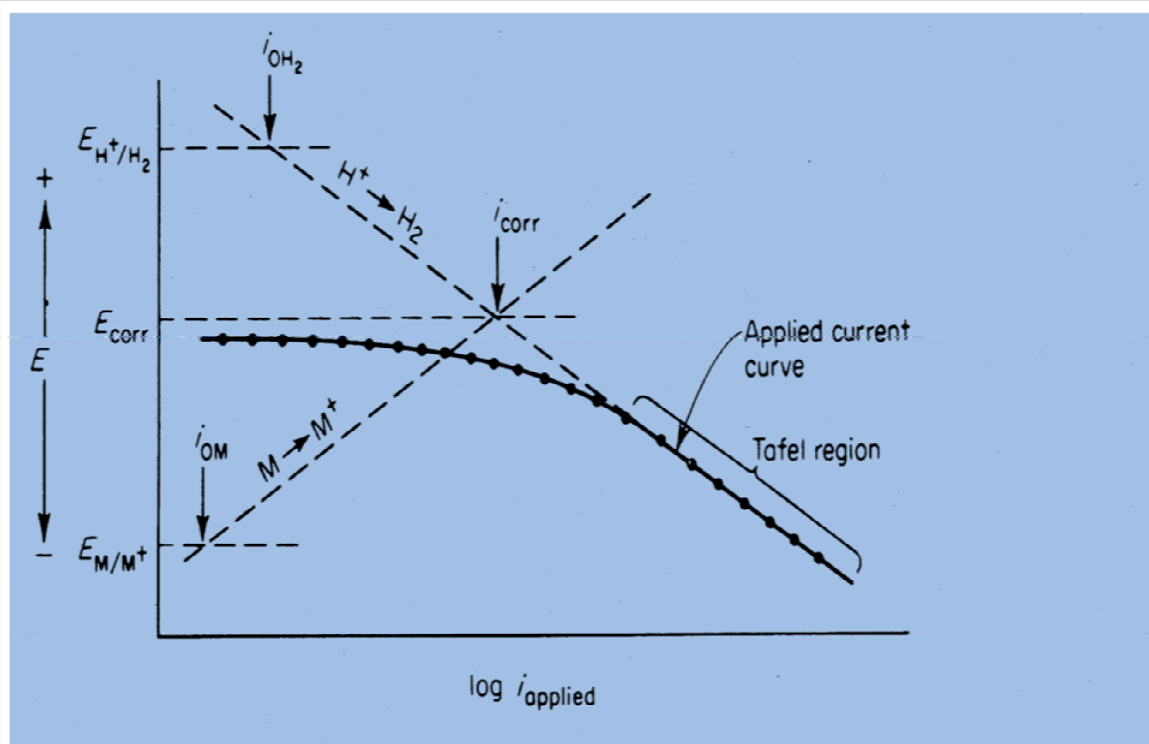
Tafel extrapolation for cathodic polarization curve

Tafel Potentiodynamic Polarization Curve

- ## Iron in hydrochloric acid
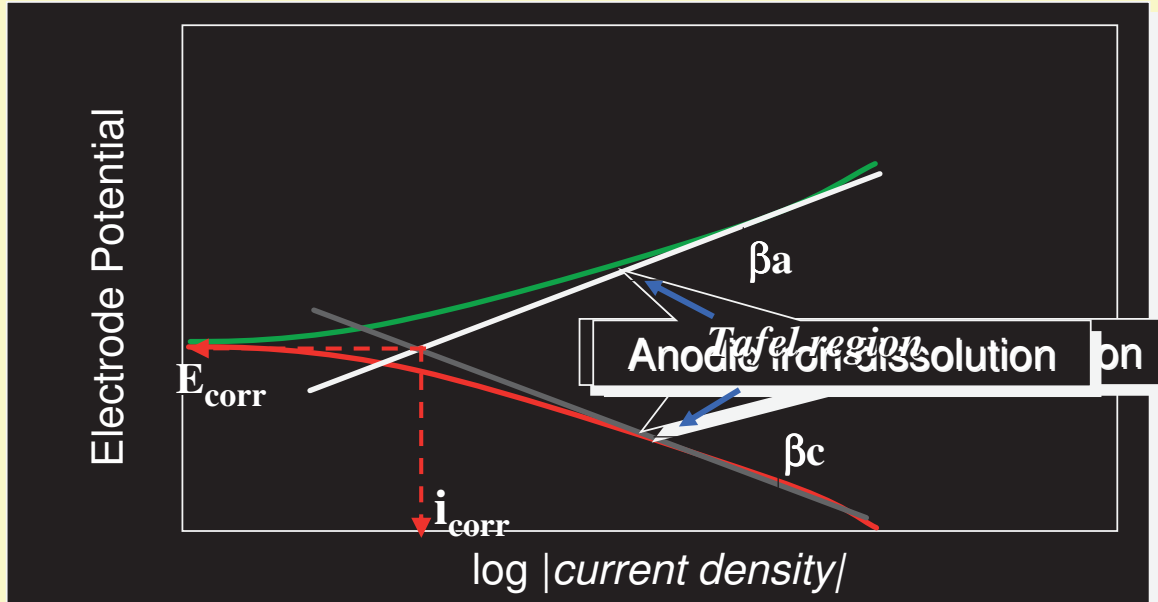
PASSIVATION

- ## Iron in sulphuric acid

18/8 Stainless steel in neutral Cl⁻

Increasing Mo

Fe-Cr alloys in oxidizing acid

Increasing Cr

Inhibitor addition

Mild steel in acid solutions
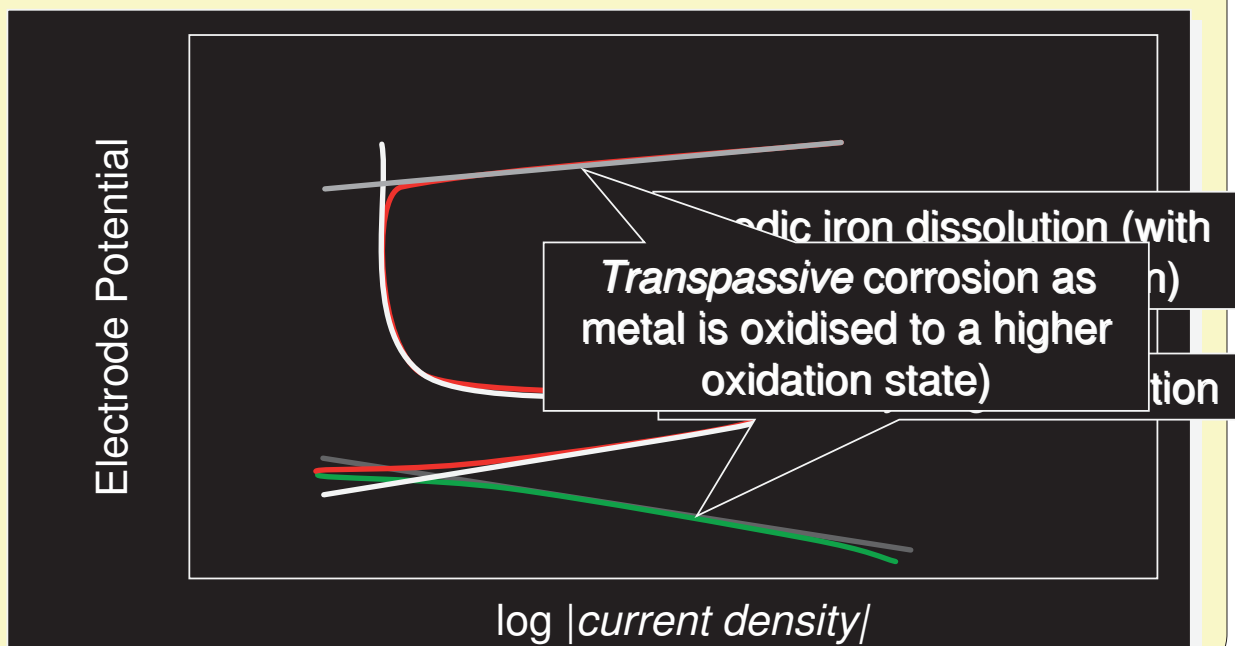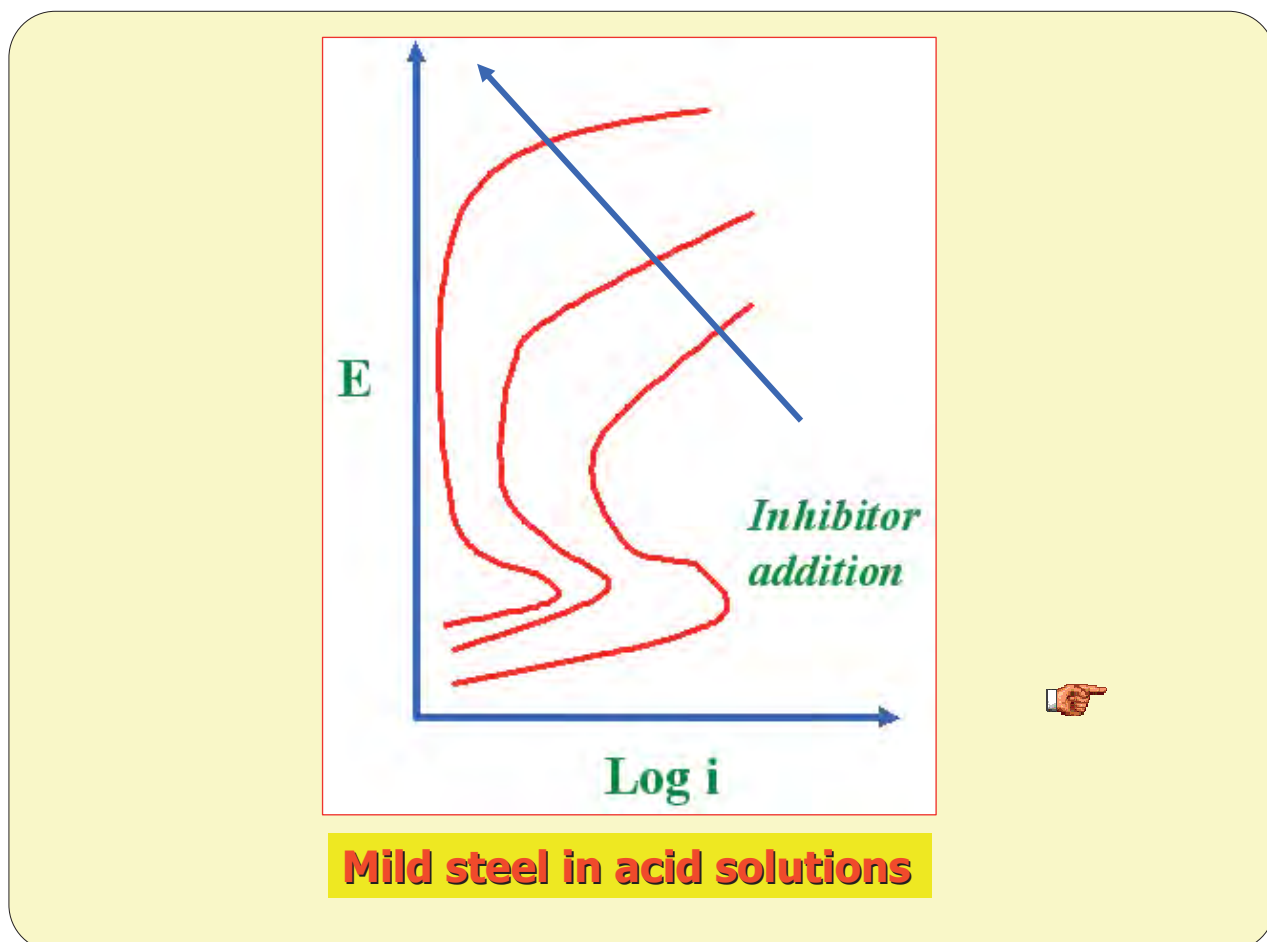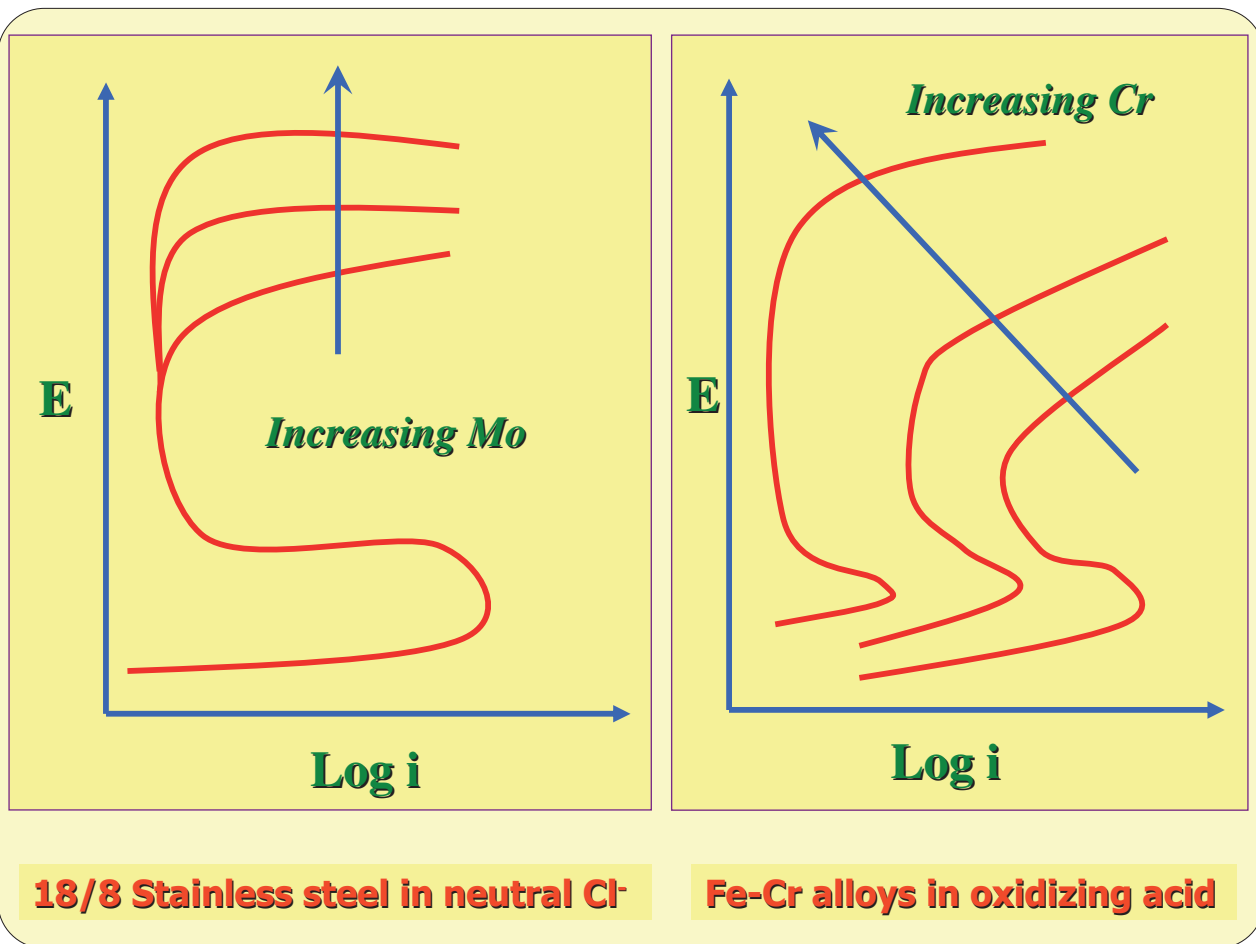
FLADE POTENTIAL AND THE STABILITY OF PASSIVITY

When the applied potential is removed, passivity decays within a short time as shown in the figure. The noble potential arrived at just before decay to the active value is the Flade potential.
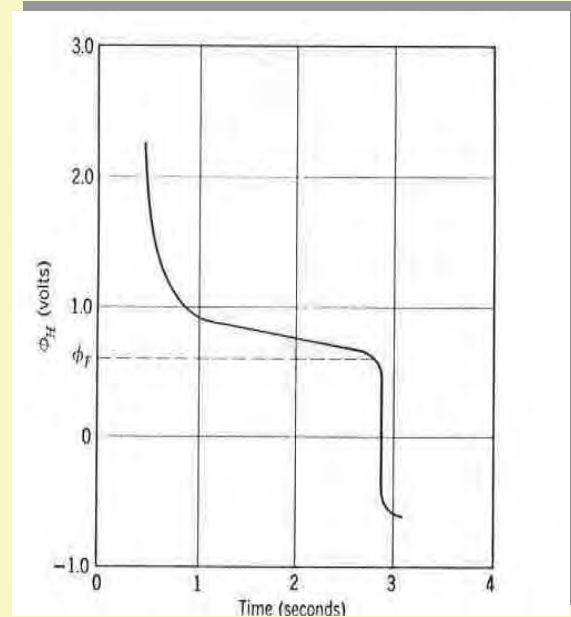
- *Stability of passivity is related to the Flade potential*

- The positive value of E_f for Fe (+0.63 V) indicates the tendency for the passive film to decay,
- The negative value of E_f for Cr (-0.2 V) indicates conditions more favorable to passive film formation and hence greater stability of passivity.
- For Cr-Fe alloys, E_f values lowers from 0.63 for pure iron to more negative values as Cr is alloyed.
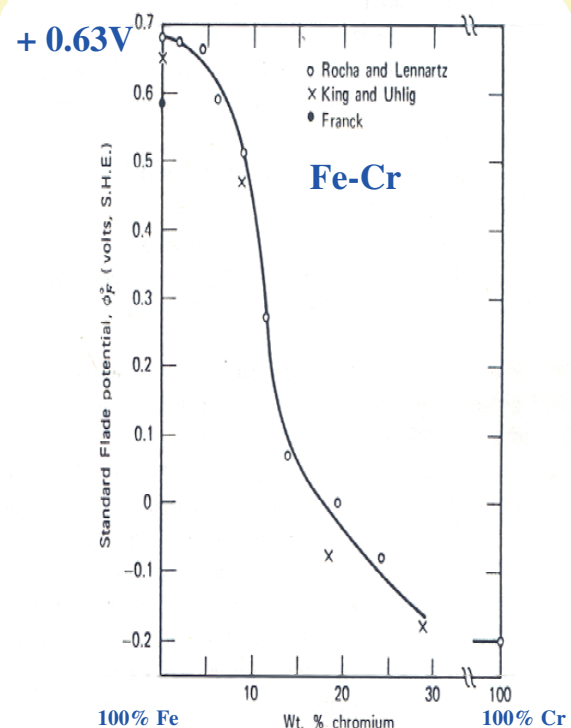
FIGURE 4. Standard Flade potentials for chromium-iron alloys and chromium.

orrosion rate values measured for steel in concrete is related to the ris of corrosion as follows

corr . cm   *assive condition*

corr . to . cm   *ow corrosion*

corr . to . cm   *oderate corrosion*

corr cm   *igh corrosion rate*

Linear Polarization Resistance *(LPR)*, CORRATER

is useful as a method to rapidly identify corrosion upsets and initiate remedial action.

This techni ue has been used successfully for over thirty years, in almost all types of water based, corrosive environments, some of the more common applications are

LPR Corrosion Rate Meter

9030 Plus

ooling water systems.

Secondary recovery system.

otable water treatment and distribution systems.

mine sweetening.

inear polari ation resistance probes

Waste water treatment systems.

ic ling and mineral e traction processes.

ulp and paper manufacturing.

ydrocarbon production with free water.

---

has advantages over metal loss methods, but is limited in the scope of its application. Since the fluid must be conductive *a ueous solutions* .

are must be ta en to avoid using   in applications where the electrodes can become coated in oil or covered with scale.
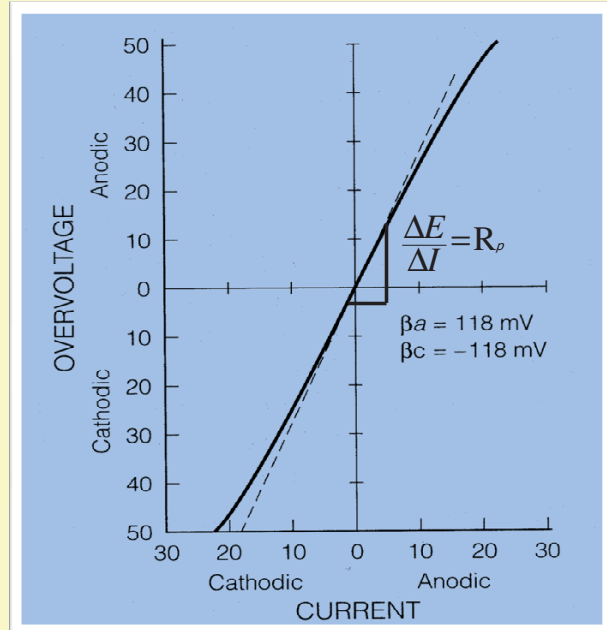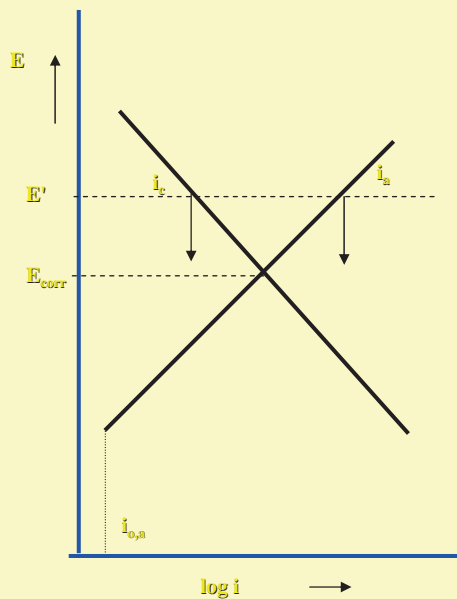
$$R_p = \frac{\Delta E}{\Delta I} = \frac{\beta a\ \beta c}{2.3\ i_{corr}\ (\beta a + \beta c)} \qquad \text{"Stern - Geary equation"}$$

β_a & β_c : Tafel constants

$\Delta E = \pm\ 20$ mV around Ecorr

Electrical Impedance Spectroscopy (EIS)

S utili es an   signal to perturb a corroding specimen. S monitors the electric response of the metal environment interface to the applied   signal over a fre uency spectrum usually in the range of   to m   in order to measure the charge transfer resistance across the corroding interface, $_{ct.}$

$_{ct}$ is inversely proportional to the corrosion rate.

$$i_{corr} = \frac{Constant}{R_{ct}}$$

AC & The Double Layer

AC POWER SUPPLY
Rising ½-cycle

AC POWER SUPPLY

OSCILLATING MOBILE LAYER
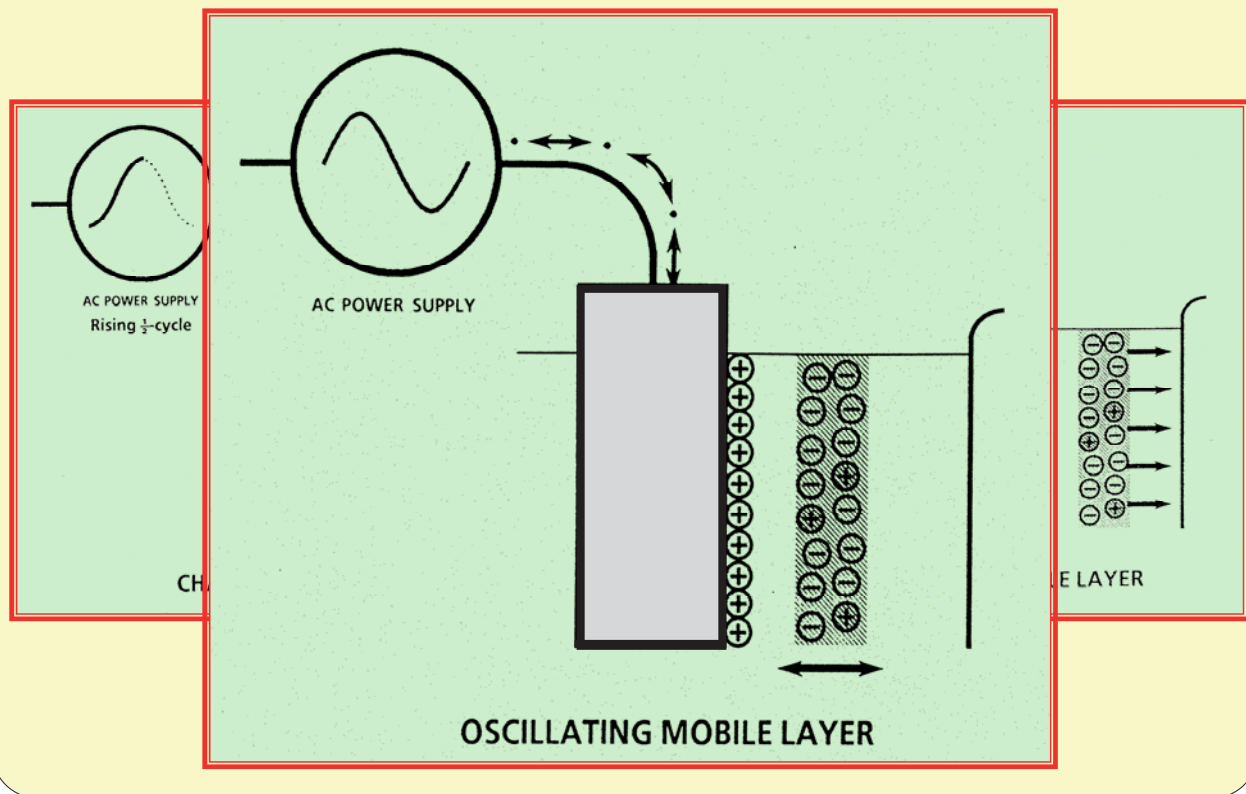
Behavior of The Double Layer

C_{dl}
I_c
Charging Current

WE

I_c
ac

• No "LEAKAGE";
(Only Charge/Discharge of Double Layer)
• No Nett Current Flow
• No Chemical Reaction

AC BEHAVIOUR

R_f
I_f
Faradaic Current

WE

I_f
dc

• Nett Current Flow
• Chemical Reaction (Corrosion)

DC BEHAVIOUR
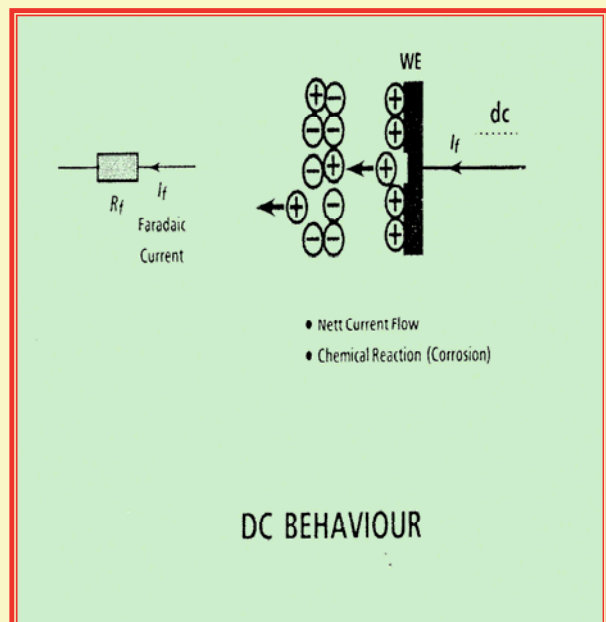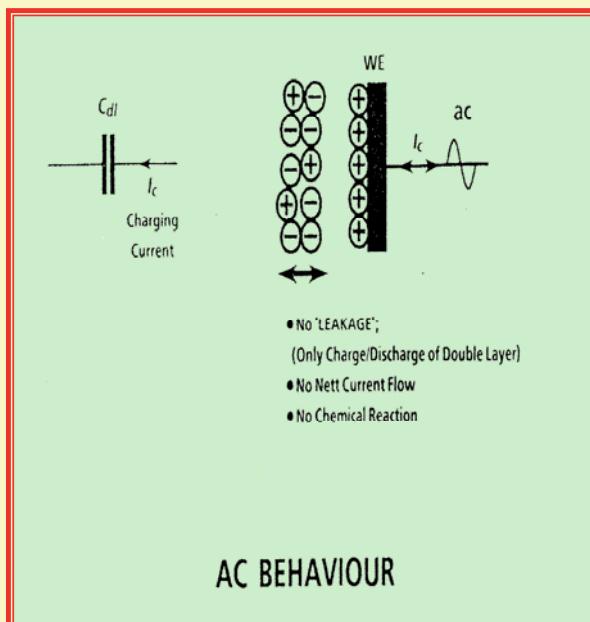
With *AC*, The double layer behaves like a capacitor (C_{dl})
With *DC*, The double layer behaves like a resistor R_f
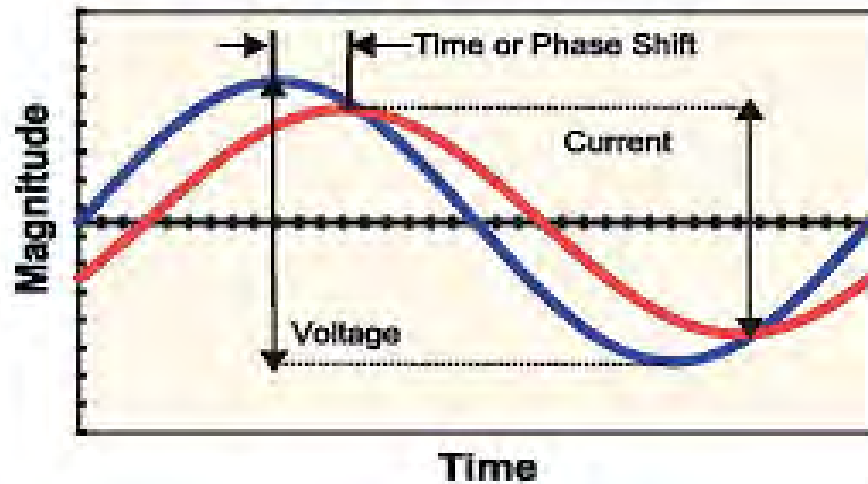
Sine wave voltage is applied, the current response having a sine wave is shifted in time (*phase angle, θ*) due to the slow response of this system.

If one cycle (360°) of the sine wave takes 1 sec, and the time shift between the current and voltage sine waves is 0.1 sec, then the phase angle is 36°.

The ratio of the si e of the voltage sine wave in volts to that of the current sine wave in amperes gives the *magnitude*, or *si e*, or *modulus* of the impedance in ohms of this system .

, θ and f at which impedance was measured often plotted on what is nown as a ode plot which usually used to display S data. 👉

$$|Z| = Z' + jZ''$$

$$Z' = Z \cos \theta \qquad Z'' = Z \sin \theta$$

$$\omega_{max} = \frac{1}{R_{ct} C_{dl}}$$

ω *(angular frequency)*

Z''

θ

Z'

Argand diagram

C_{dl}

R_s

R_{ct}

Equivalent Circuit

$$\omega_{max} = \frac{1}{R_{ct} C_{dl}}$$

Z''

R_s

R_{ct}

Z'

Solution resistance

Nyquist complex diagram
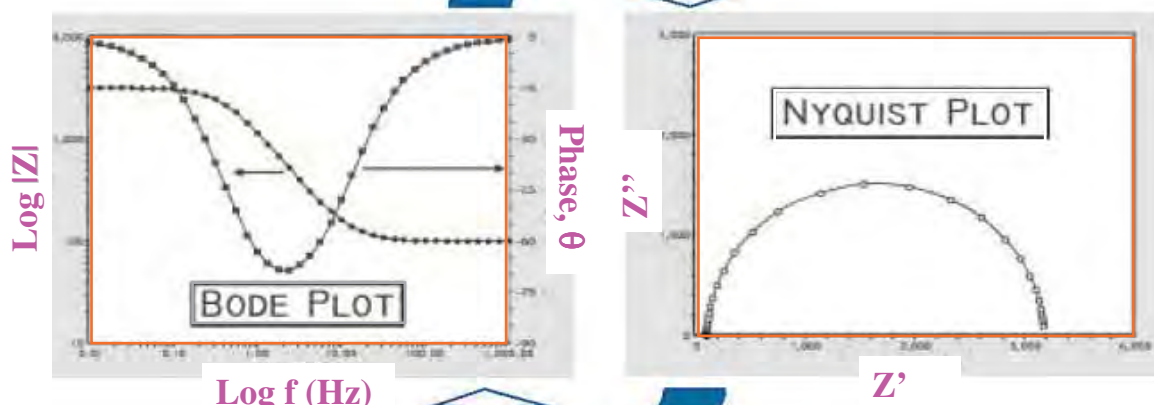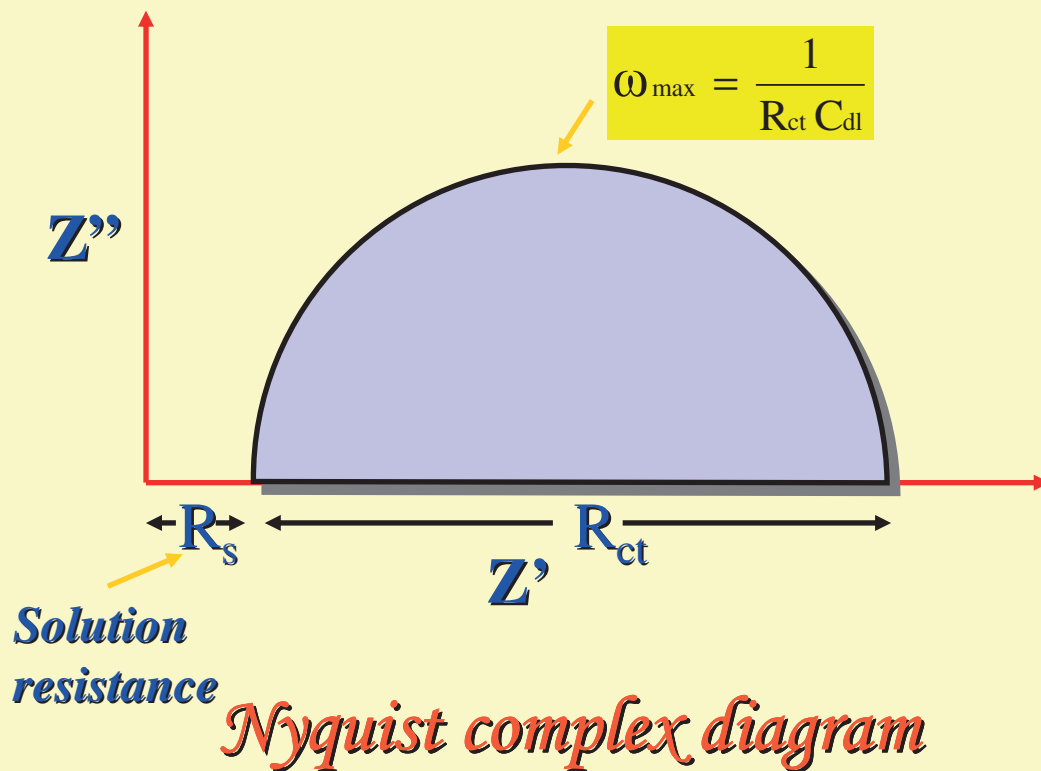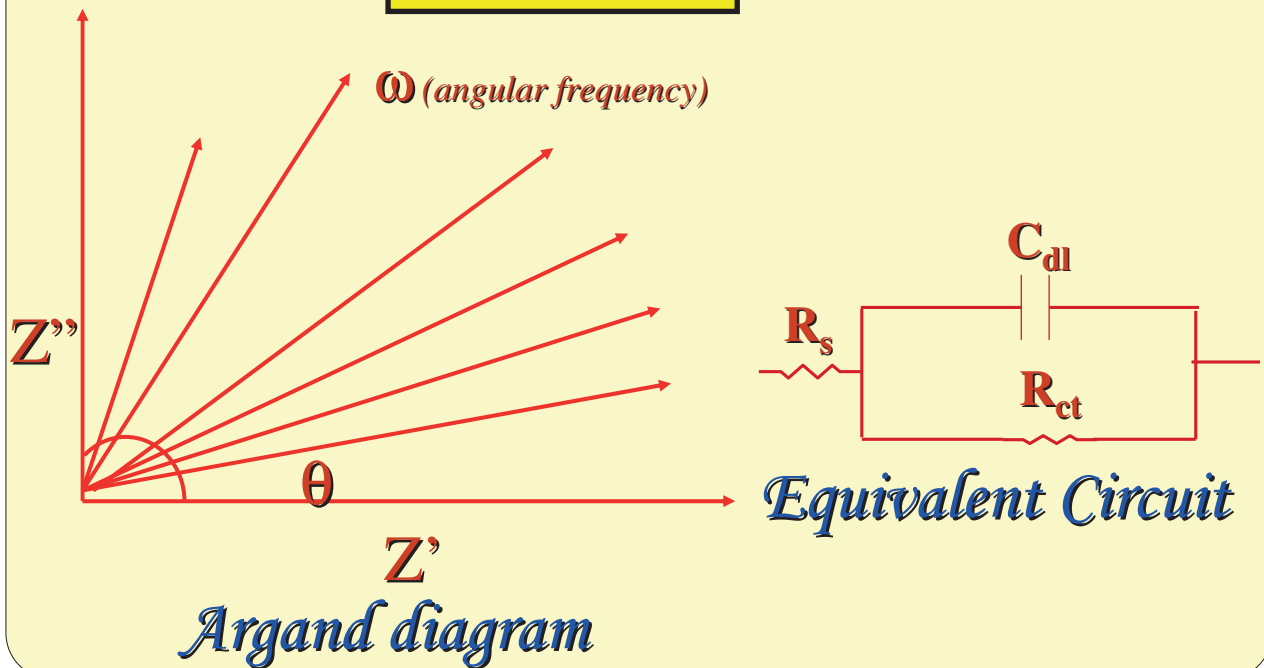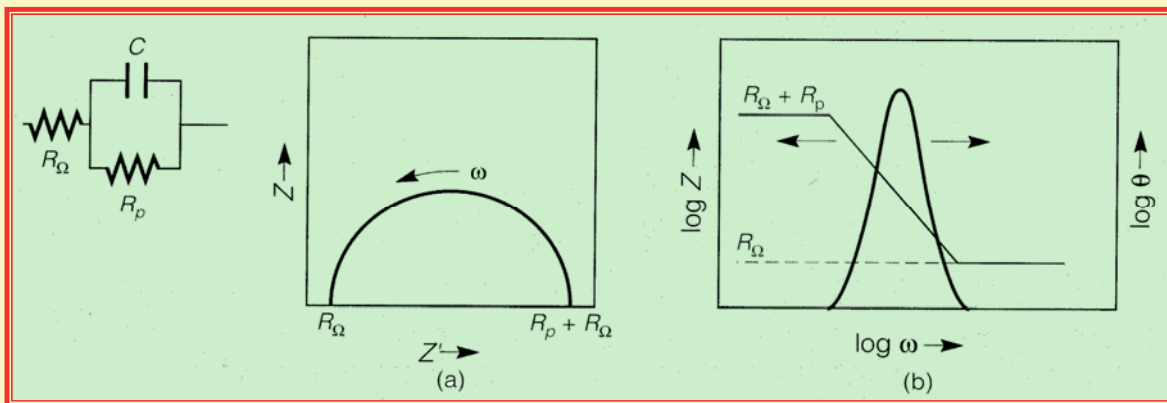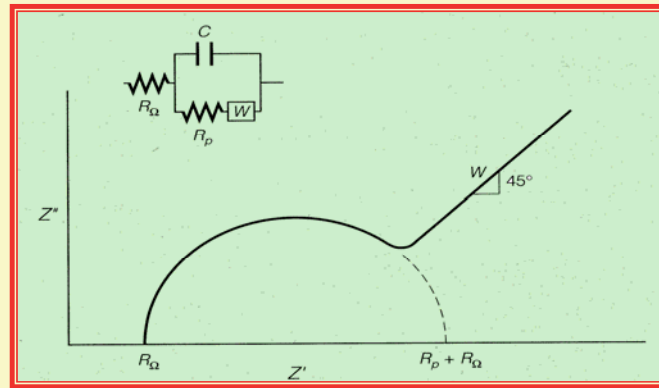
Nyquist & Bode Plot

Nyquist & Bode Plot
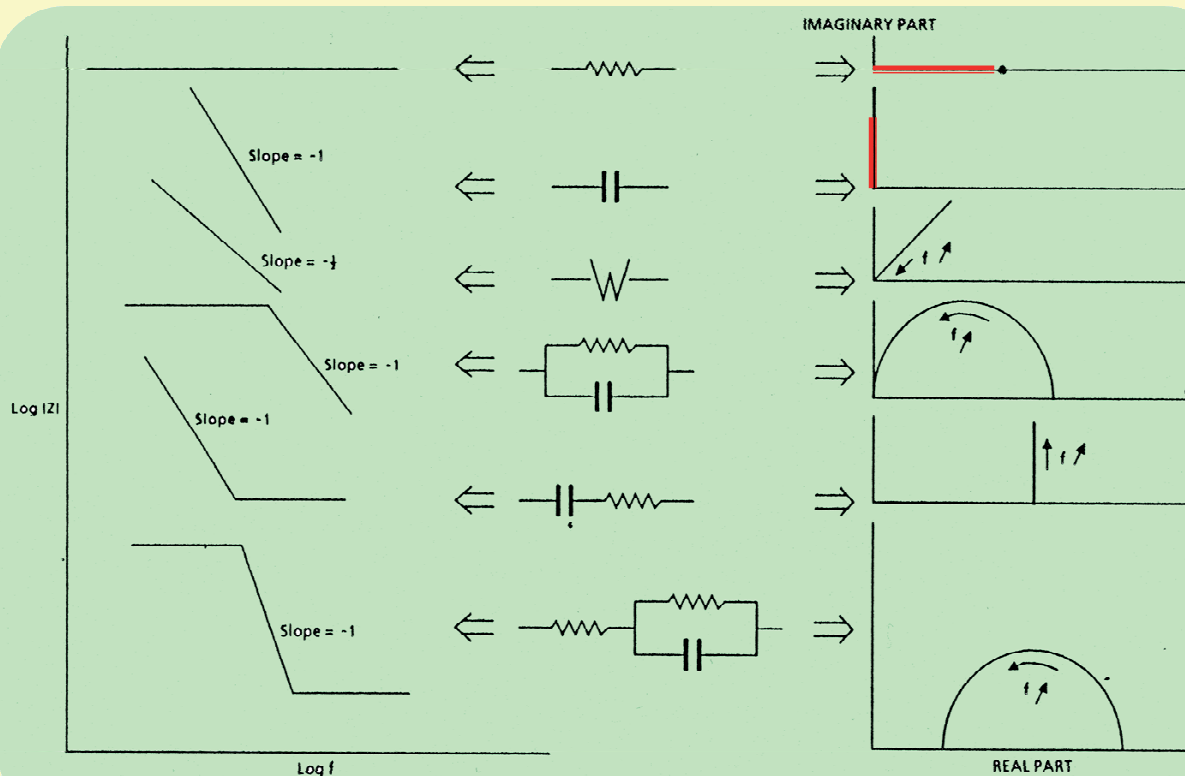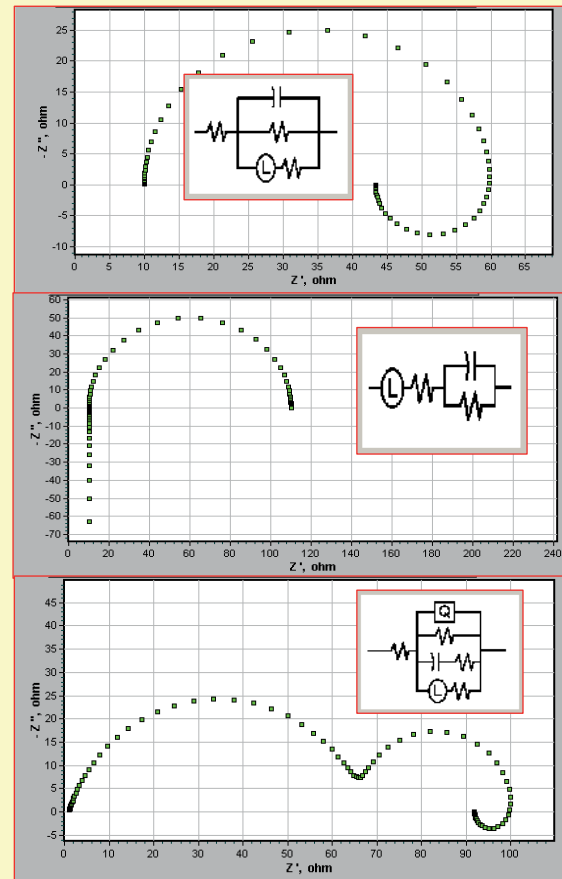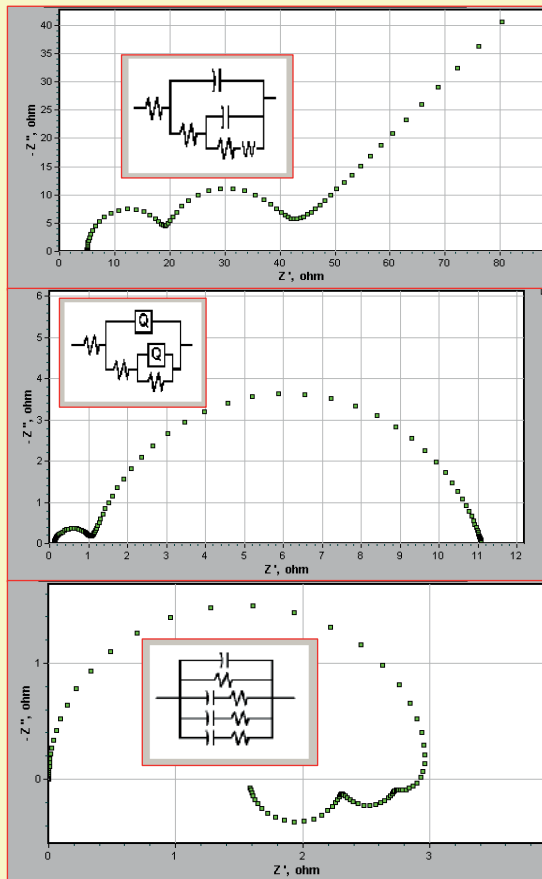
   S e amines *coated* or *inhibited* materials much more effectively than with   techni ues.   ther areas of applications are evaluation of corrosion of steel in *concrete* structures and in the evaluation of *cathodic protection*.

   S can also be used to determine the properties of the surface layers such as pore resistance and film capacitance.

The main limitations
   nalysis and the interpretation of the data are comple   compared to   . They re uire application of a theoretical e uivalent circuit to analy e and interpret the data.

شكراً لحسن المتابعة والاهتمام

THANK YOU FOR YOUR ATTENTION

Day 3: Wednesday: December 24th, 2013

Session V

APPROACHING ZERO LIQUID DISCHARGE WITH CLEANER PRODUCTION

Dr. Samia Massoud Mohamed

Eng. Nagwa Monsef Mohamed

AFA Workshop-Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

25th December 2013 - Aswan

Environmental & Water Engineering Consultants- EWATEC

PRESENTATION OUTLINES

- What does Cleaner Production mean ?

- Cleaner Production Concept

- Zero Liquid Discharge Definition & Concept

- Zero Liquid Discharge Goals

- Cleaner Production Tools for Achieving ZLD

- General ZLD System in Chemical/Petrochemical Industries

Environmental & Water Engineering Consultants- EWATEC
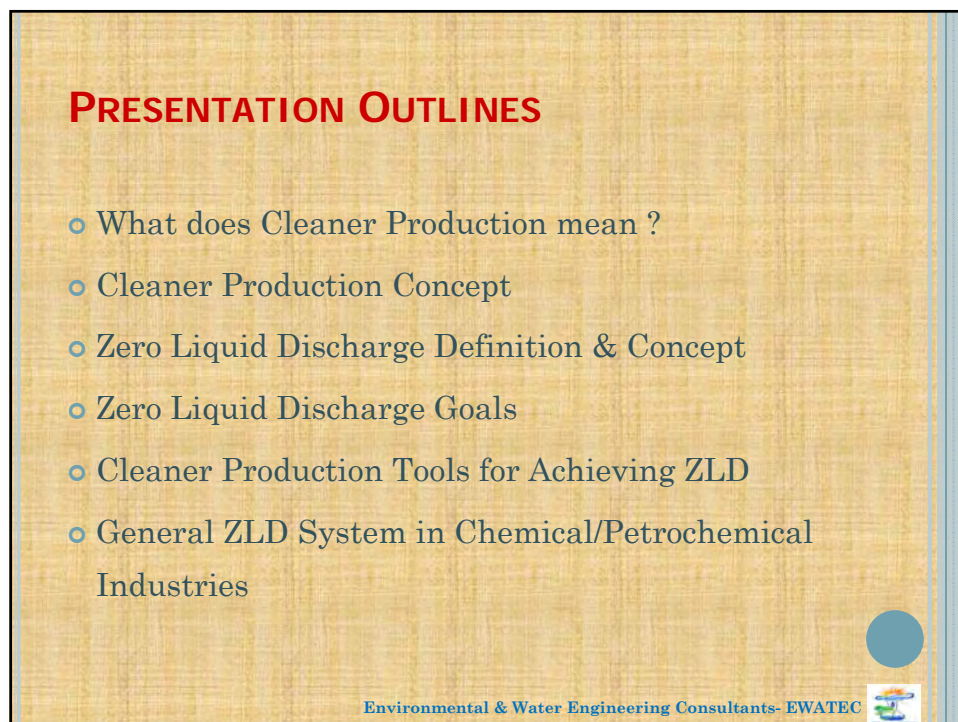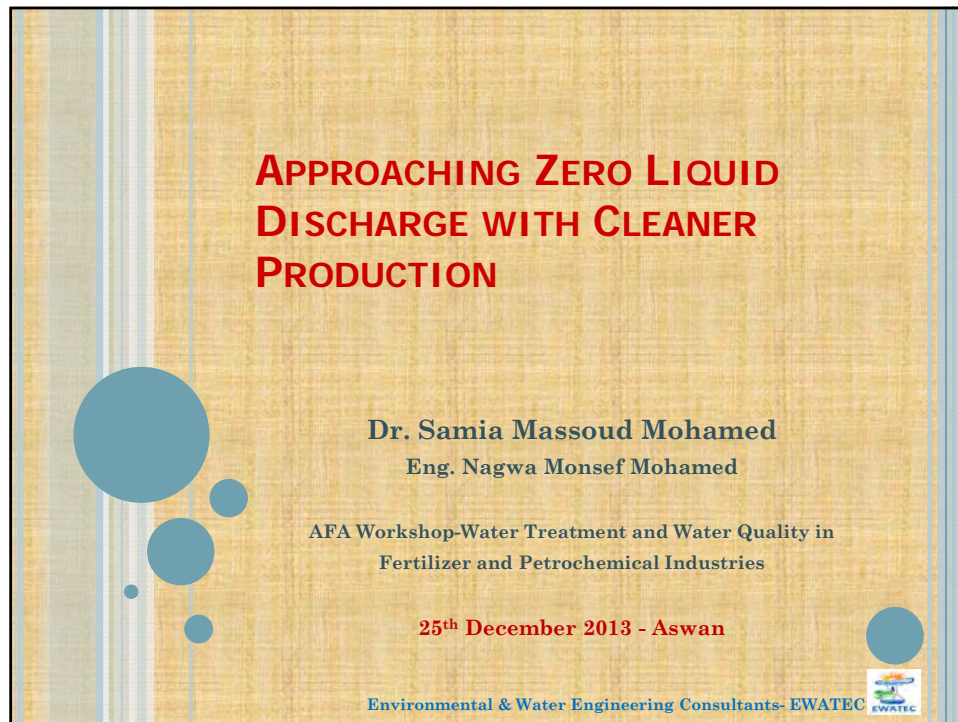
PRESENTATION OUTLINES (CONT.)

- Zero Liquid Discharge Limitations

- Relation between CP & ZLD

- Costs and Efforts of CP Options for achieving ZLD

- Case Studies on Partial & Integrated ZLD

- Recommendations

Environmental & Water Engineering Consultants- EWATEC

What does Cleaner Production mean ?

Environmental & Water Engineering Consultants- EWATEC

What is waste WASTE !

Waste = Non-Product-Output

A profitable company will do
the best, to avoid such
undesired non-product-outputs.

Environmental & Water Engineering Consultants- EWATEC

Reduction of waste

=

Increasing profit

=

Cleaner production

Environmental & Water Engineering Consultants- EWATEC

DEFINITION OF CLEANER PRODUCTION

➢ Cleaner Production is…

- ▪ A **problem-solving strategy** that uses a collection of analytic tools to improve the **efficiency** of production processes and improve profitability.

- ▪ **Relevant to all** sizes of enterprise, from home-based to multi-national.

➢ **Many CP improvements require little or no initial investment or have rapid payback.**

CLEANER PRODUCTION IS QUITE SIMPLE

Increase production efficiency

while at the same time

Eliminate or at least minimize wastes and emissions at their source rather than treat them after they have been generated.

CLEANER PRODUCTION CONCEPT

Minimizing Input

Maximizing Output

➢ Raw materials

Sellable products ➢

➢ Energy

Rate of reuse ➢

➢ Water

Rate of recovery ➢

➢ Hazardous substances

Rate of renewables ➢

➢ Costs

Benefits ➢

This is Cleaner Production!

Environmental & Water Engineering Consultants- EWATEC

Before Applying Cleaner Production

Emissions

Materials

Products

Energy

Manufacturing Processes

By-Products

Water

Hazardous Waste

Heat Loss

Solid Waste (trash)

Waste-water

After Applying Cleaner Production
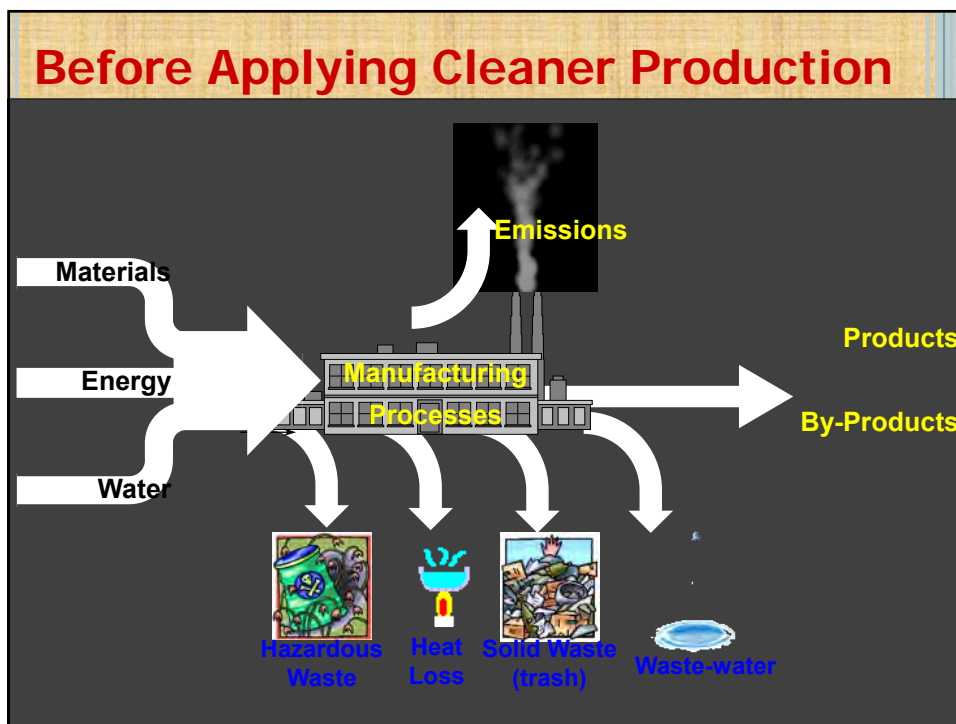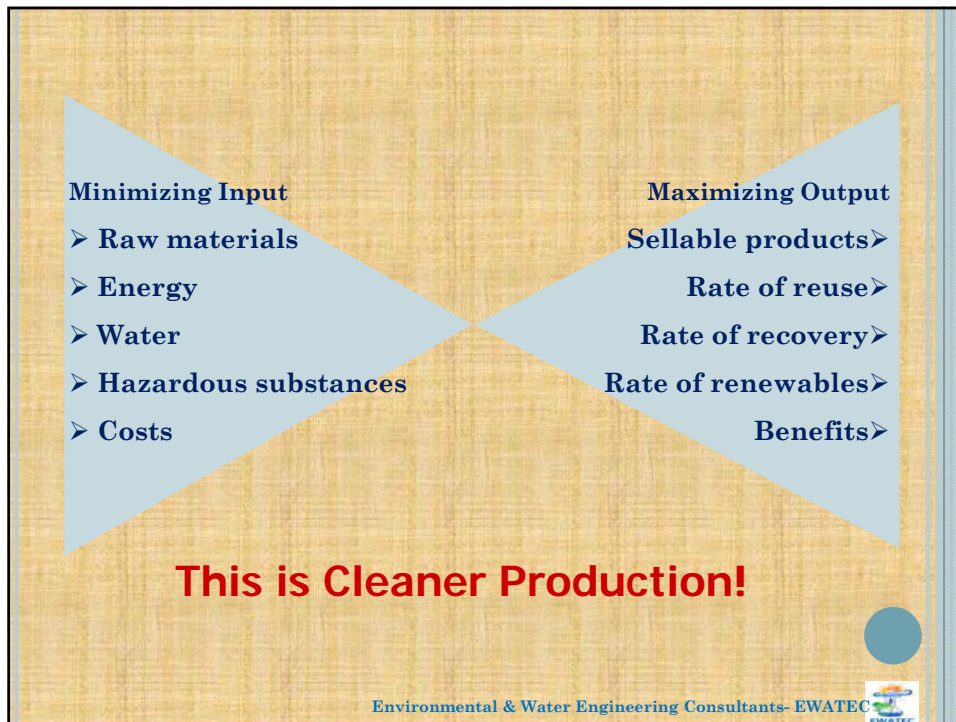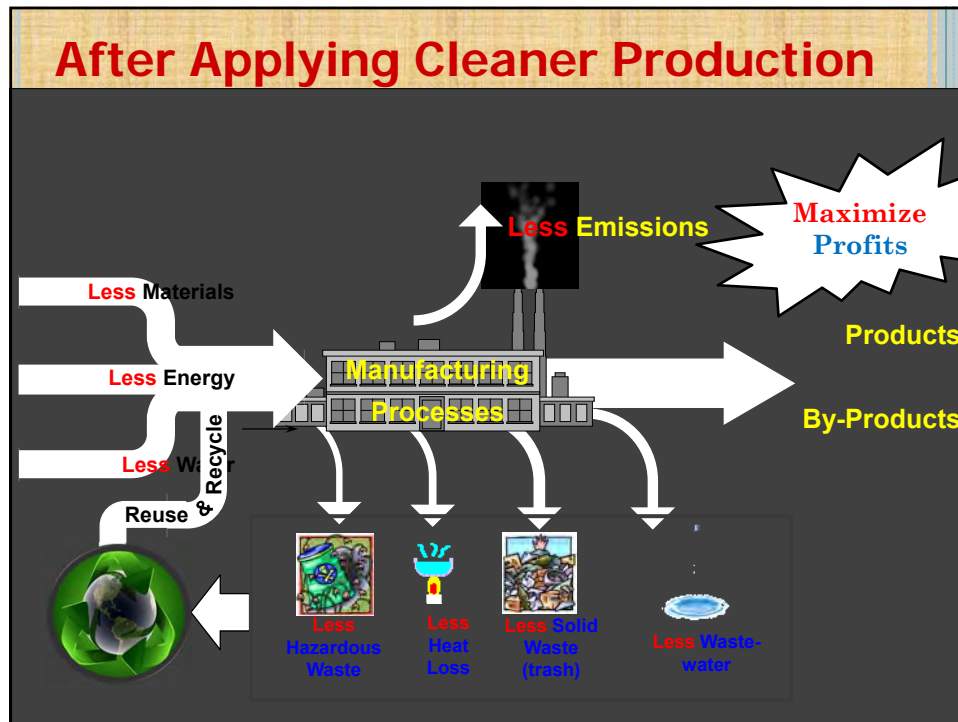
ZERO LIQUID DISCHARGE

DEFINITION & CONCEPT

○ ZLD refers to a process that completely eliminates liquid from a system. The end product of a ZLD system is a solid residue of precipitate salts that needs to be transferred to an appropriate solid waste disposal facility (such as Landfill).

○ Recently, ZLD has been introduced especially to large industries for ultimate treatment of wastewater to produce clean streams suitable for reuse in the plant.

Environmental & Water Engineering Consultants- EWATEC

ZERO LIQUID DISCHARGE

GOALS

Environmental & Water Engineering Consultants- EWATEC

- Minimize process wastewater in an economically feasible manner by producing clean streams suitable for reuse.

- Comply with the tightening wastewater disposal regulations.

- Fulfill the green industry initiatives for achieving sustainable development.

- Achieve economic benefit through recycling of treated water and selling the produced solids if sellable.

Environmental & Water Engineering Consultants- EWATEC

CLEANER PRODUCTION TOOLS

FOR

ACHIEVING ZLD

Environmental & Water Engineering Consultants- EWATEC

Apply Good Housekeeping plan	- Prevent Leaks / Spills
Reduce process water consumption	- Limit the amount of wastewater that needs to be treated through improving the quality of the feed water (pre-treating water going to cooling towers to reduce hardness and silica which leads to delaying of bleeding times).
Reduce wastewater volume	- Segregation of clean streams. - Improve feed water quality.
Reduce pollution load	- Point source treatment. - Reuse & Recycle
Equipment Optimization	- Control Operation parameters.
Wastewater treatment (End-of-pipe)	- Chemical treatment. - Biological treatment. - Membrane.
Waste Disposal	- Solids disposed to a landfill / sell if valuable

Environmental & Water Engineering Consultants- EWATEC

GENERAL ZLD SYSTEM IN

CHEMICAL/PETROCHEMICAL INDUSTRIES

Environmental & Water Engineering Consultants- EWATEC

Wastewater Effluent from the plant

Wastewater Treatment
Physicochemical or Biological

Pre-Treatment for membrane separation

Membrane Separation
- Reverse Osmosis, RO
- Ultra filtration, UF
- Electro dialysis ED
- EDR, Reversal

Recycled Distillate to process

Integrated ZLD　　**Reject**　　**Partial ZLD**

Evaporation & Crystallization　　**Disposal to Evaporation ponds**　　**Disposal to receiving media**

Solids　　　　**Comply with Law Limits**

Sellable if valuable　　Disposed to landfill

ZERO LIQUID DISCHARGE

LIMITATIONS

Environmental & Water Engineering Consultants- EWATEC

- Difficult to treat certain types of wastewater.

- The equipment to dewater the concentrate slurry tends to be extremely expensive which limits the cost effectiveness to only those with large volume streams.

- ZLD fast payback period only in case of water demand scarcity.

- Feasible only for large scale enterprises.

Environmental & Water Engineering Consultants- EWATEC

DIFFERENCE BETWEEN

CLEANER PRODUCTION

&

END OF PIPE/ZLD

Environmental & Water Engineering Consultants- EWATEC

Cleaner Production (CP)	End of Pipe / ZLD
Where do waste and emissions come from?	How can treat existing waste and emissions?
Stands for action	Stands for re-action
Can help to reduce costs	Leads to additional costs
Environmental protection is everybody's business.	Environmental protection is a matter for competent experts
Is an innovation developed within the company	Is bought from outside
Reduces material and energy consumption	Increase material and energy consumption

Environmental & Water Engineering Consultants- EWATEC

RELATION BETWEEN CP & ZLD

Environmental & Water Engineering Consultants- EWATEC
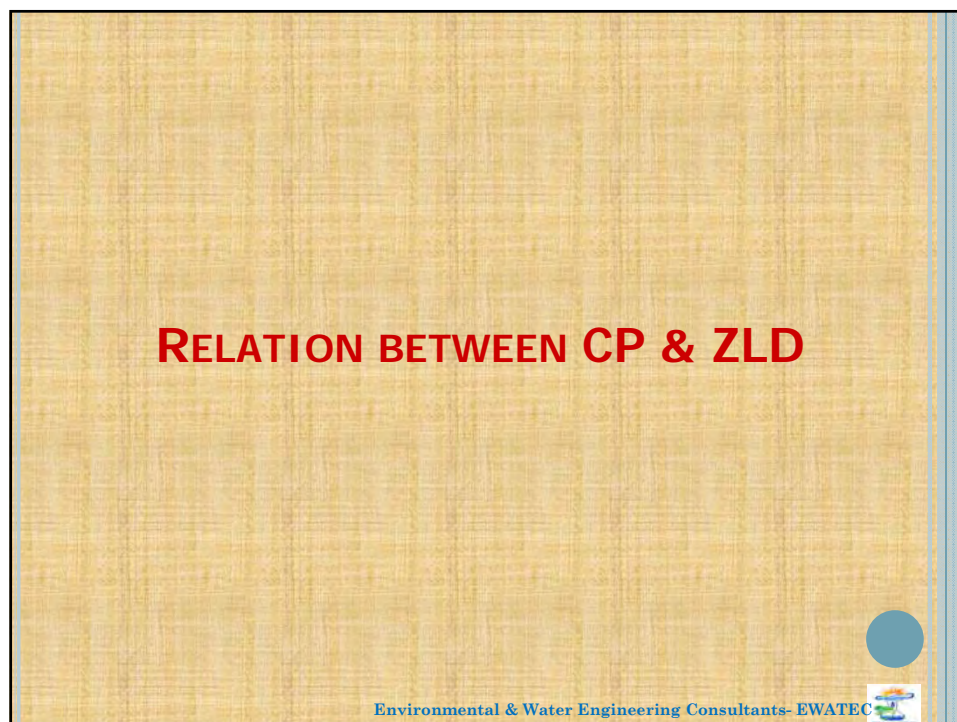
○ ZLD can be considered among the high cost tools of cleaner production for reuse of wastewater.

Example: Reducing water consumption using No/Low cost CP tools will minimize generated wastewater thus reducing ZLD cost.

○ Feed water quality improvements can lead to reduction in both capital and operating cost of ZLD.

○ No / Low cost CP options is the most economic solution for wastewater problems with small / medium enterprises while ZLD techniques is the most suitable solution for recovery of wastewater in large enterprises with high wastewater volumes (Power plants-fertilizers-…etc).

- CP improvements should be applied prior implementation of ZLD to reduce the capital and operating cost of ZLD.

- CP improvements require little or no initial investments compared to ZLD with high investments.

COSTS AND EFFORTS OF CLEANER PRODUCTIONS OPTIONS FOR ACHIEVING ZLD

Achieving
Zero Liquid
Discharge

New Technology

New Equipment

Resource Conservation
Water, Energy,…etc

On-site reuse/ recycle/ Recovery

Process optimization

Good Housekeeping

Technology requirements

Low Cost,
Easy to Implement

High Cost,
Strategic Advantage

Invistments to be put in

Environmental & Water Engineering Consultants- EWATEC
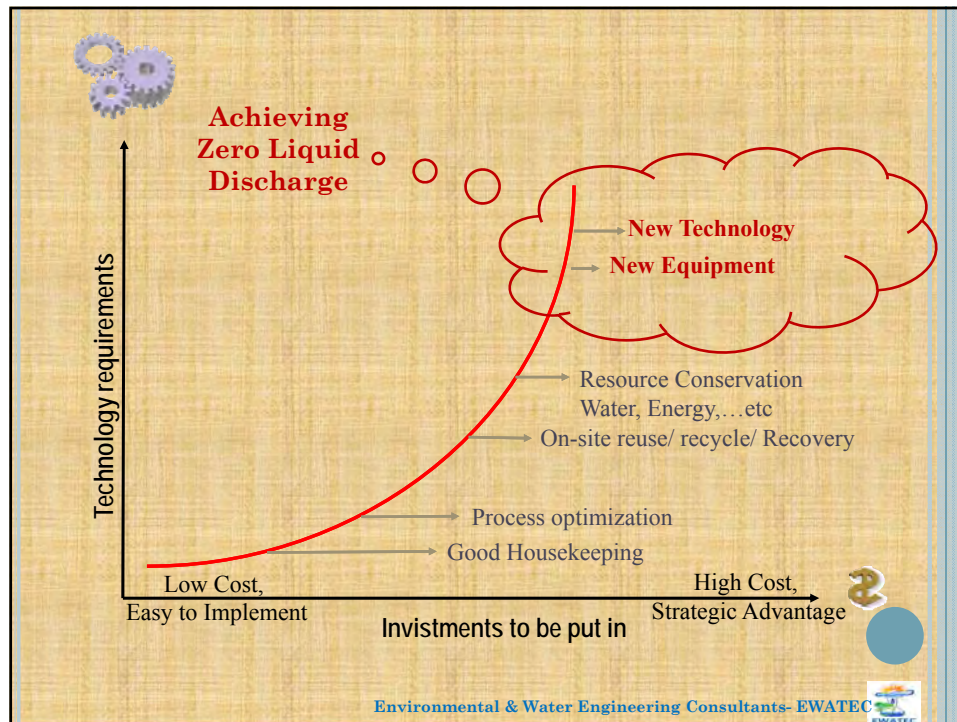
CASE STUDIES ON

PARTIAL & INTEGRATED ZLD

Environmental & Water Engineering Consultants- EWATEC

1- Pharmaceutical Industry
(Partial ZLD)

Environmental & Water Engineering Consultants- EWATEC

Environmental & Water Engineering Consultants- EWATEC

Influent

Equalizing tank

50%

To sewer

1st storage aeration sedimentation

Effluent pit

Sludge tank

Filter press

Sludge to disposal

2nd storage aeration sedimentation

Chlorination → Filtration → Irrigation tank

50% For Irrigation

Environmental & Water Engineering Consultants- EWATEC

Installation of Industrial Wastewater Treatment Plant (IWWTP) with a capacity of 800 m³/day

Total Cost : 2,232,540 EGP

Saving From Treated Water Reuse in Irrigation : 50%

Daily Water Saving   : 400 m³/day (132,000 m³/year)

Yearly Saving : 528,000 EGP /Yr

Payback Period : 4 Years

Environmental & Water Engineering Consultants- EWATEC

2- Chemical Industry

(Lead-Acid Batteries)

(Integrated ZLD)

Environmental & Water Engineering Consultants- EWATEC

Receiving of used Batteries

Recycled acidified water

Crusher

Water storage tank

Lead parts + plastic pieces

Vibrator

Lead paste + acidified water

Recycled Water

Hydrodynamic Separator

Thickening Tank

Dry lead paste

Na_2CO_3

Plastic pieces (Polypropylene small pieces)

Lead Parts

De-Sulfurization Unit

Smelter

sodium carbonate (Solution)

Lead carbonate

Recycled Washing water

Grinder Chamber

Lead Refining Pots

Washing Unit

Crystallization Unit

Smelter

Crushed Polypropylene + water

Centrifuge

Lead Alloys

Lead Refining Pots

Crushed Polypropylene For packaging & selling

Sodium Sulphate Crystals for selling

Lead Alloys

3- Engineering Industry
(Partial ZLD)

IWWTP Design Max Capacity: 300 m³/ day

Environmental & Water Engineering Consultants- EWATEC
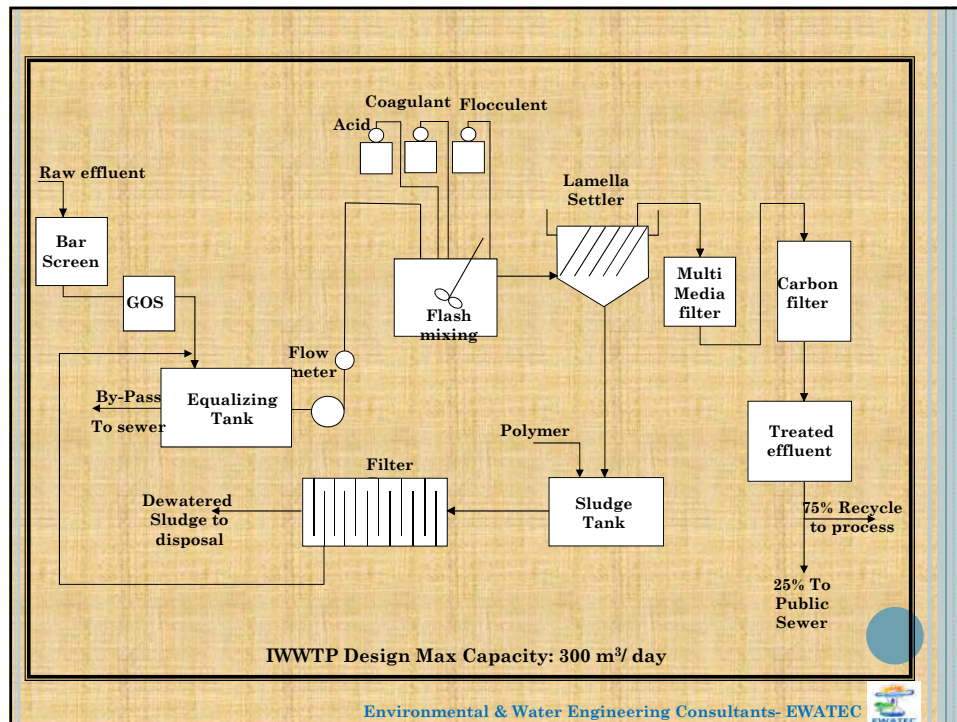
Installation of Industrial Wastewater Treatment Plant (IWWTP) with a capacity of 300 m³/day

Total Cost   : 2,300,000 EGP

Saving of Treated Water Recycled back to process: 75%

Daily Water Saving   : 186 m³/day (61380 m³/year)

Yearly Saving   : 245520 EGP /Yr

Payback Period :   9 Years

Environmental & Water Engineering Consultants- EWATEC

4- Beverage Industry
(Partial ZLD)

Environmental & Water Engineering Consultants- EWATEC

Environmental & Water Engineering Consultants- EWATEC
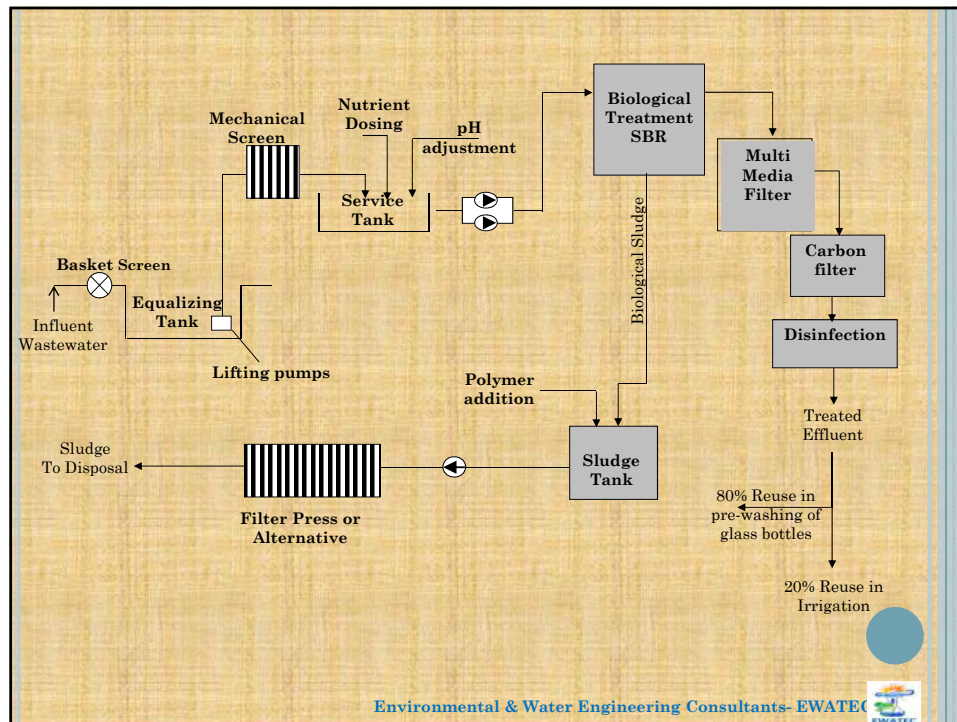
Installation of Industrial Wastewater Treatment Plant (IWWTP) with a capacity of 1400 m³/day

Total Cost   :   3,000,000 EGP

Saving From Treated Water Reuse in bottles Pre-washing process= 60%

Daily Water Saving due to recycling : 840 m³/day (277,200 m³/year)

Yearly Saving   : 1,108,800 EGP /Yr

Payback Period : 2.7 Years

Environmental & Water Engineering Consultants- EWATEC

Recommendations

○ Applying Cleaner production options with No/Low cost should be implemented prior ZLD.

○ Cost reductions are necessary for application of most high recovery and ZLD processing schemes. Research should be conducted with this goal in mind. In particular , the goals should include a reduction in capital cost and a reduction of operating costs due to energy and chemical requirements.

o Detailed water quality analyses need to be done at the concentrate level to determine whether contaminants present at low levels in feed water will result in brine or solids being hazardous or containing problematic levels of radionuclides.

o There is a need to develop a knowledge base for high-recovery and ZLD processing and to acknowledge the real cost and environmental consequences of large-scale concentrate disposal.

Environmental & Water Engineering Consultants- EWATEC

THANK YOU FOR LISTENING

Environmental & Water Engineering Consultants- EWATEC

AFA
WORKSHOP
Water Treatment and Water Quality in
Fertilizer and Petrochemical Industries

Case Study ≪Zero liquid Discharge≫

Eng. Amr Saber

Abu Qir Fertilizer Co. - Egypt

ZERO LIQUID DISCHARGE APPROACH

BY
ENG. AMR EL-ADAWY
Vice Utilities Sectors Head
Abu Qir Fertilizer Co.

ABU QIR I: Urea(prilled) on stream 1979

Abu Qir Fertilizer Co.   ZLD

ABU QIR II. Ammonium nitrate (granulated) On stream 1991

Abu Qir Fertilizer Co.   ZLD

ABU QIR III. Urea (granulated) on stream 1998

Abu Qir Fertilizer Co.   ZLD

The Main VISION is

Environmental

National

Economical

We have to make environmental project with economic payback

Abu Qir Fertilizer Co.   ZLD

1st Stage

Basis of design

- Approach or reach zero liquid discharge (no evaporation pond)
- Minimum amount of water recycled for re-use 80%
- Achieve compliance with Environmental Regulations regarding:
  - Emissions of ammonia to surrounding environment must comply with legal limits (17.4 mg/m3).
  - Emissions of ammonia through stacks must comply with legal limits (50 mg/m3)
- Alternative solution is accepted
- Area of ZLD project should be considered.

Basic Data

•	Flow at standard operation:	500 – 650 m3/h
	Flow if maintenance on fertilizer production plants:	400 – 450 m3/h
•	Temperature fluctuation mainly due to seasonal effects	
•	Ammonia depending on pH existing as - dissolved ammonia gas (NH_3) - dissolved ammonium ion (NH_4^+)	

Abu Qir Fertilizer Co.   ZLD

Treatment Criteria : Effluent Quality (limits)

Parameter	Unit	Water Reuse	Sea Discharge
pH	-	6.5 - 6.7	6 - 9
Chemical Oxygen Demand (COD)	mg/l	10	100
Biochemical Oxygen Demand (BOD$_5$)	mg/l	3	60
Total Dissolved Solids (TDS)	mg/l	200	±5% of sea TDS
Total Suspended Solids (TSS)	mg/l	5	60
Phosphate-Phosphorus (PO$_4$-P)	mg/l	2	2
Total Hardness (as CaCO$_3$)	mg/l	22	
Total Ammonia (NH$_3$)	mg/l	0.7	
Nitrate (NO$_3^-$)	mg/l	2	
Sodium (Na$^+$)	mg/l	26	
Calcium (Ca^{2+})	mg/l	7	
Magnesium (Mg^{2+})	mg/l	1.5	
Chloride (Cl$^-$)	mg/l	25	
Total Ammonia-Nitrogen (NH$_3$-N)	mg/l		3
Total Nitrogen (TN)	mg/l		10

Abu Qir Fertilizer Co.   ZLD

Bidding Stages

- Bid Advertisement
- Pre–Bid meeting
- Bidders Clarification requests.
- Bid Submissions
- AFC request for clarification.

AFC Request for Clarification

Process & Technology
Functional Guarantee
Design, Equipment Manufacture & Delivery
Operational Performance
Implementation Schedule
Clarification Meeting
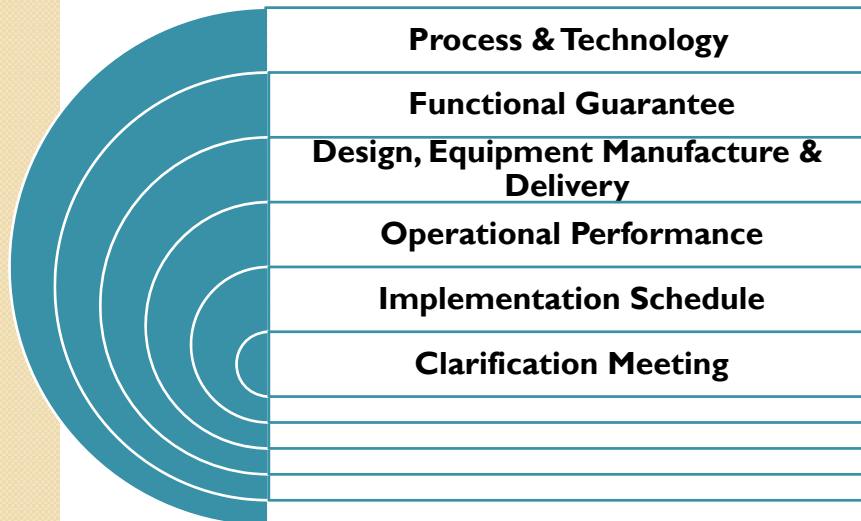
Abu Qir Fertilizer Co.   ZLD

Main Techniques

Biological Treatment
- Nitrification/De-nitrification for ammonia and nitrate removal

Chemical & Physical Treatment
- Nitrogen removal by stripping followed by Sulphuric acid scrubbing with production of Ammonium sulphate by-product

Combination of both processes

Crystallization
- Without nitrogen removal

Abu Qir Fertilizer Co.   ZLD

Biological Treatment

Equalization → Nitrification MBBR → Denitrification MBBR → Nitrification MBBR → Denitrification MBBR → Post Aeration

Treated Water to Reuse ← RO ← UF ← Dissolved Air Floatation ← Post Aeration

De-Nitrification → Nitrification → Clarification → To Sea for Disposal

RO → Sludge Dewatering

Abu Qir Fertilizer Co.   ZLD

Chemical-Physical Treatment

Balancing Tank → Ammonia Stripper → Cold Lime Multiflo Softener → Multimedia Filter

Cold Lime Multiflo Softener → Sludge Thickner

Backwash

Sludge Cake ← Sludge Thickner

Treated Water to reuse ← High RO Skid ← Nitrate Removal Ion Exchange ← Softener ← Multimedia Filter

Sea Water

Discharge to Sea Water ← Collecting Tank

Abu Qir Fertilizer Co.   ZLD

Chemical-Physical & Biological Treatment

Equalization → Micro Sieving → Sand Filtration → pH-adjustment

pH-adjustment → (from) Chemical-Physical Treatment

Denitrification ← pH-adjustment ← Chemical-Physical Treatment

Denitrification → UF

UF → RO → Final Storage Tank → Treated Water to Reuse

UF → Neutralization

Neutralization → Blending with Sea water

RO → Blending with Sea water

Blending with Sea water ← Sea Water

Water Discharge to Sea

Abu Qir Fertilizer Co.   ZLD

Comparison Between Different Technologies

Available Technology	Advantage	Disadvantage
Air Stripping	•Can take advantage of high pH effluent •Small footprint	•Hard to remove the N_2 to very low levels •Can't remove organic and other contaminants
BNR	•Can remove N_2 to very low levels •Can remove organics & other contaminants	•Need extremely high chemical consumption due to high pH & low C/N ratio •Need large footprint
Combination of air stripping & BNR with MBR	•Can remove organics & other contaminants •Remove N_2 to very low limits •Need less chemicals •Relatively small footprint	•Need complex configuration

Abu Qir Fertilizer Co.   ZLD

Technical Evaluation

- Eight bidders met the requirements of References & qualifications with 4 main techniques and invited to participate on stage 2 of the bidding process.

Abu Qir Fertilizer Co.   ZLD

2nd Stage

Basis of design

- Approach or reach zero liquid discharge (no evaporation pond)
- Minimum amount of water recycled for re-use 80%
- Achieve compliance with Environmental Regulations regarding:
  - Discharge to the sea with ammonia less than 3 ppm, N less than 10 ppm & compliance with environmental law.
  - Increase TDS to be ±5% of the sea.
  - Dilution with sea water mainly considered.
  - Emissions of ammonia to surrounding environment must comply with legal limits (17.4 mg/m3).
  - Emissions of ammonia through stacks must comply with legal limits (50 mg/m3)
- Alternative solution is not accepted
- Area of ZLD project should be considered.

Abu Qir Fertilizer Co.   ZLD

Performance Criteria

1. Expected recycled water amount (minimum 80%) and quality
2. Expected effluent flows and quality after each treatment step.
3. Amount and quality of reject wastewater (if any)
4. Consumption of chemicals per m^3 of raw WW.
5. Power requirements at start up and full capacity
6. Control system
7. Lifetime and cost of membranes
8. Number of workers required.
9. Warranties offered by bidder

Abu Qir Fertilizer Co.   ZLD

STAGE 2 EVALUATION

Capex

Opex
(for 2 years)

Abu Qir Fertilizer Co.   ZLD

Summary Treatment Process

Treatment comprising

- Equalisation / Mixing
- pH adjustment to 11
- Decalcification (Softening)
- Chemical-physical treatment for ammonia removal and recovery
- Neutralisation to pH 8
- Biological denitrification
- Ultra filtration and two-stage Reverse osmosis
- Treated water collection and return to existing cooling towers
- Final concentrate treatment and discharge to sea
- Gravity thickening and mechanical dewatering for biological sludge
- Mechanical dewatering for lime sludge

Abu Qir Fertilizer Co. ZLD

Our Target Achievement

Pretreatment → Ammonia Removal

OPEX Reduction

Fertilizer

Economical Aim

Distribution for reuse (85%) ← TDS Reduction ← Biological Treatment

National Aim

TDS Adjustment → Environmental Aim
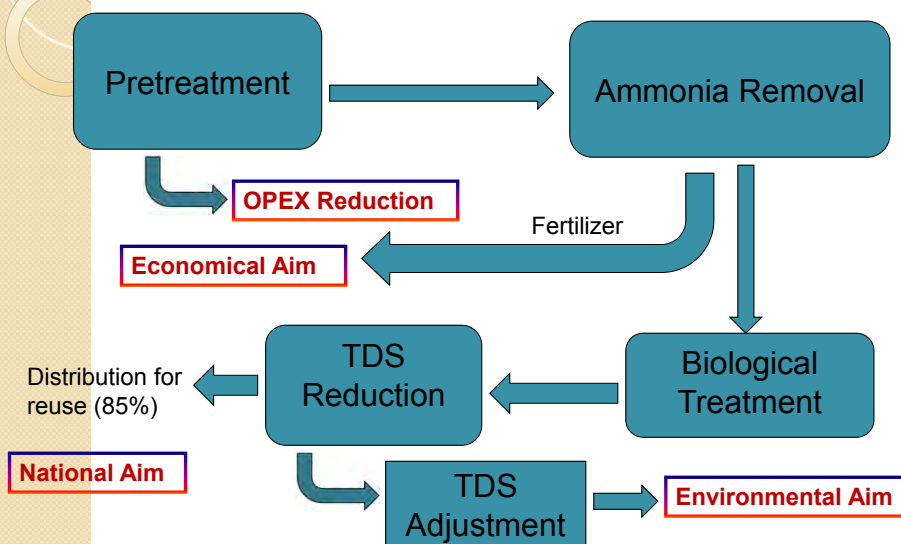
Abu Qir Fertilizer Co. ZLD

Project Site at 25-11-2013

Abu Qir Fertilizer Co.   ZLD

Thank You

Welcome to the 30th
Water Treatment Technology Conference
In May 2014

W.T.T

48

Abu Qir Fertilizer Co.   ZLD

Case Study

≪Zero liquid Discharge Unit in NCIC≫

Eng. Ahmed Samir

Head Production Sector - NCIC – Egypt

جهاز مشروعات الخدمة الوطنية
شركة النصر للكيماويات الوسيطة
مجمع انتاج الكيماويات بالفيوم

مراحل انشاء محطة معالجة الصرف الصناعى بشركة النصر للكيماويات الوسيطة

إجراءات إنشاء محطة الصرف الصناعى المعالج

إجمالى كمية مياه الصرف المطلوب معالجتها 70 م3/ساعة عبارة عن:-

- 26 م3/ساعة صرف صناعى وتتميز بـ (نسبة الأملاح الذائبة والغير ذائبه 24000 ملجم/لتر ودرجة حامضية 1.5-2 درجة حامضية)

- 44 م3/ساعة عبارة عن صرف المرافق المتمثلة فى صرف أبراج التبريد /الغلايات /وحدات التناضح العكسي/وحدات المياه الغير أيونية وتتميز بـ (نسبة الأملاح الذائبة 6000) ملجم/لتر.

- لذلك تعتمد عملية المعالجة على عدم الخلط ولكن على فصل مياة الصرف الصناعى (26) م3/ ساعة مياه ملوثة عن المياه الخاصة بصرف المرافق (44 م3/ساعة) مياه نظيفة قابلة لإعادة التدوير لتسهيل عملية المعالجة والحصول من خلال المعالجة على مياه بالمواصفة اللازمة لتشغيل المصانع.

إجمالى التكلفة المالية لإنشاء محطة الصرف الصناعى (10) مليون جنيهاً.

أقسام محطة معالجة الصرف الصناعي

الطاقة التصميمية لمحطة معالجة الصرف الصناعي 70م3 / ساعة. وتتكون المحطة من قسمين :

القسم الأول ويتم فيه معالجة مياه صرف المصانع عن طريق :

- ضبط الأس الهيدروجيني.
- اضافة مساعدات الترسيب على مرحلتين.
- فصل الرواسب عن المياه المعالجة.
- المياه المعالجة تتميز (نسبة الأملاح الذائبة اقل من 4000 ملجم/لتر).

القسم الثاني ويتم فيه معالجة مياه المرافق الصناعية عن طريق :

- إزالة الأملاح الذائبة عن طريق مجموعة من الفلاتر ووحدة تنقية المياه بالخاصية الغشائية .
- المياه المعالجة (نسبة الأملاح الذائبة أقل من 200 ملجم/لتر).
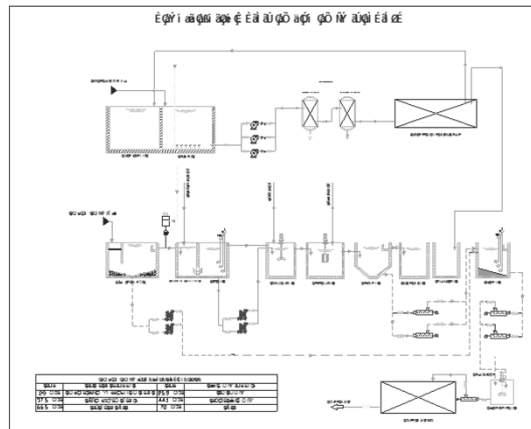
أقسام محطة معالجة الصرف الصناعي

القسم الأول من محطة معالجة الصرف الصناعي

القسم الأول يتكون من المراحل التالية :

- الترسيب الابتدائي.
- ضبط الأس الهيدروجيني.
- خزان الاتزان.
- خزان التقليب السريع.
- خزان التقليب البطيء.
- خزان الترسيب النهائي.
- خزان المياه المعالجة.
- خزان التدوير.
- تجميع ومعالجة الحمأة.
- مضخات نقل حمأة خزان الترسيب الابتدائي.

القسم الأول
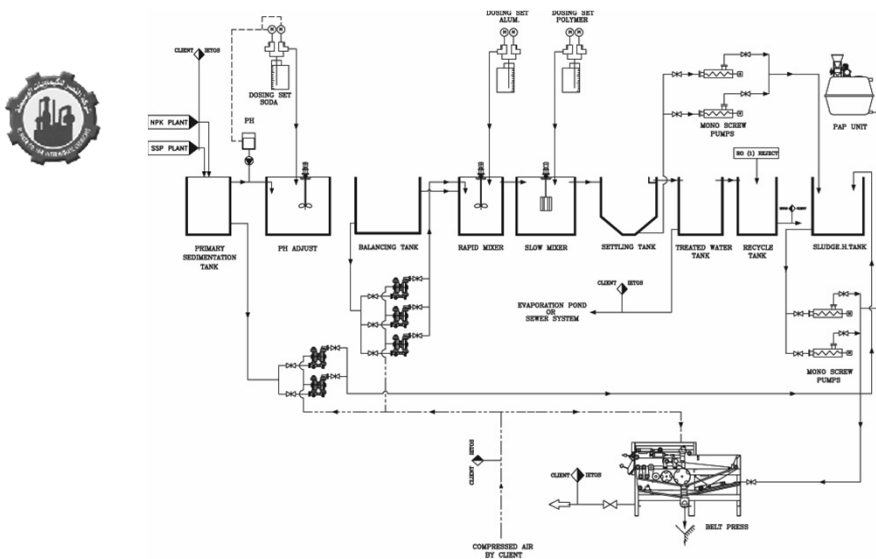
القسم الثاني من محطة معالجة الصرف الصناعي

القسم الثاني يتكون من المراحل التالية :

- خزان التجميع.
- المرشحات الرملية.
- مرشحات الكربون النشط.
- وحدة تنقيه المياه .
- وحدة رفع نسبة الاستعادة.
- خزان التدوير.

القسم الثاني
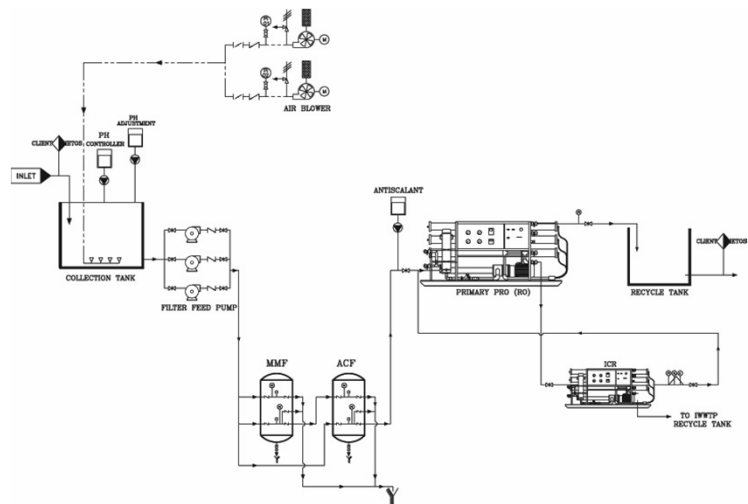
صور من داخل محطة معالجة الصرف الصناعي خلال مراحل الإنشاء

البــدايــة في 25 – 8 – 2012

شركة النصر للكيماويات الوسيطة
المنطقة الصناعية بكوم أوشيم - الفيوم

صور من داخل محطة معالجة الصرف الصناعي خلال مراحل الإنشاء

شركة النصر للكيماويات الوسيطة
المنطقة الصناعية بكوم أوشيم - الفيوم
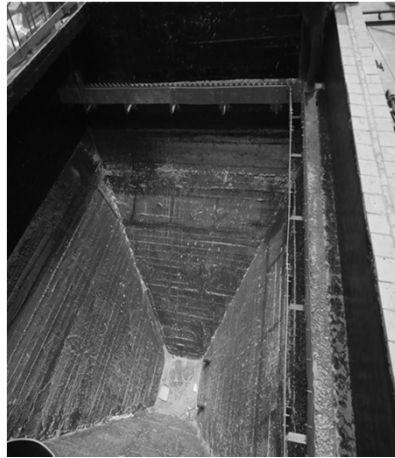
صور من داخل محطة معالجة الصرف الصناعي

محطة معالجة الصرف الصناعي

صور من داخل محطة معالجة الصرف الصناعي

صور من داخل محطة معالجة الصرف الصناعي

صور من داخل محطة معالجة الصرف الصناعي

مرشح الحمأة و فصل الرواسب

الجدوى الاقتصادية

م	النشاط	حجم التوفير سنوياً	التكلفة الكلية	مدة استرداد الاستثمارات
1	محطة معالجة الصرف الصناعي	1.3 مليون جنية	10 مليون جنية	8 سنوات

شركة النصر للكيماويات الوسيطة
المنطقة الصناعية بكوم أوشيم – الفيوم

AFA

WORKSHOP

Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Startup and 7 years post experience in water treatment units in Alexfert complex

Eng. Ibrahim A. Elshibiny

Alexfert Co. - Egypt

Startup and 7 years post experience in water treatment units in Alexfert complex

IBRAHIM A. ELSHIBINY
ALEXANDRIA FERTILIZERS CO.

* Introduction

Alexfert is one of the important nitrogenous fertilizer complex in Egypt.

It was established in 2003 as a joint stock co.

The plant started at 2006 ,several case studies were faced along Seven years of operation in water treatment units

This paper will focus on the different methods followed at both operational & maintenance trends to enhance water treatment performance .

Also will cover the technical & economic aspects of operation units as well as environmental aspects

* **The Alexfert complex consists of:**

- **Ammonia plant** (1,200 t/d)

- **Urea synthesis plant** (1,925 t/d)

- **Urea granulation plant** (2,000 t/d)

- **Granuler Ammonium sulphate plant** (720t/d)

- **Utilities, storage, bagging, loading units.**

---

* WATER treatment unites in Alexfert.co.

1. pre treatmnt unit.
2. cooling towers for both ammonia & urea plants.
3. deminerlization unit.
4. waste water treatment unit.
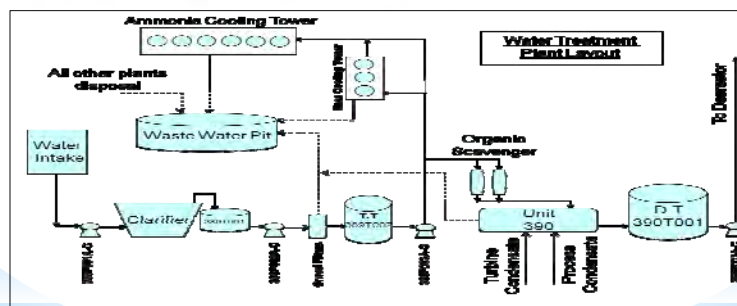
* Case studies in Pretreatment unit

TREATED WATER Analyses

PH	P-alk	M-alk	TH	CL	Fe	Turb	TDS
	ppm	ppm	ppm	ppm	ppm	NTU	ppm
10.2	25	50	65	43	0.03	1.2	225

RAW WATER Analyses

PH	M-alk	TH	CL	TDS	KMno	TUrb	FreCL2
7 : 9	200 ppm	210 ppm	80 ppm	500 ppm	14 ppm	16 NTU	1.0 ppm
7.5	141	150	42	250	12	6	0.3

Case 1:

Problem: Blocking in Inlet line to Gravel Filters Due to precipitations from Ca- Mg sulfate from raw water & chemicals additives.

- The water flow rate decreased from 120 to 50 m³/hr. from one gravel filter.
- The other one flow rate are decresed to 70 m3/hr .
- The total flow rate are 520 from 620 m3/hr (6 gravel filters).

- **Solution**:
- 1.Chemical cleaning was done by HCL 30% conc.
- 2. Modifing the inlet line by adding flanges
- Result:
- It,s easy to do chemical cleaning without shutdowen.

Case 2:

Problem : **Intermediate pump trouble & low effenicey du to Ca-Mg sulfate ppt. in both impller & suction line.**

Solution:

1. **Chemical cleaning by HCL 5% conc.**
2. **Ceramic coating was applied to the pump impeller the ideal solution after investigation to avoid ppt.& enhance roughness.**

The Result:

-**The chemical cleaning interval become every 3-4 monthes instead one month.**
-**No pump trip occurred.**

Case 3:

Problem: Sludge produced from wet softining Clarifier &Environmentalp Aspect.

In the plant Design the huge amount of Slude produced from clarifier was mixed with industrial waste water disposed directaly to the sea.
[**wich produse high T.D.S.& high S.S.**

According the eq: Ca(Hco3)+ Ca(oh)2= 2Caco3+2H2o(6 ton/day ppt.)

Solution:

1.**A sludge pit was constructed with volume 25 m3 capacity.**
 2. **According the contract with the Alexandria Sanetary Co. , The Sludge are transferd to the legal manusebilaty Landfill.**

Result:
 Alexfert are comply with environmental laws 4 /94 & law 48/82.

Case 4:

Problem: **Alum dosing nozzle failure**.

The Alum PVC injection connection 0.5 inch was broken inside raw water inlet floculator& the corrosion occurred at the first point contact with CS main line (around welding area).
It,s dificult to repair with the plant runing &may occure many times.

Solution:

Making shell&injection in one connection 1 inch, using ST.ST. instead of PVC old one .wich has the corrosion resistance ,& has more strenth withstand the bending stress.

Result: **ther is no problem from this point since 5 years ago.**
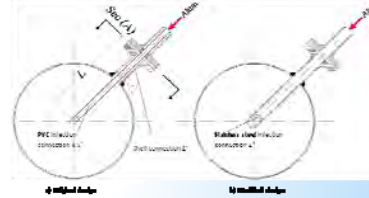
Case 5:

Problem : **Lime dosing &Sludge pumps failure many times in short period.**
This is due to variable lime quality & sludge composition.
-Screw pump become inefficient as the clearance between the stator and rotor increases &the stator must be replaced with new one / 2 month.

Solution:
Modification was done by made Tighten 3 clamps over stator pushing stator inside to rotor reducing the clearance & increasing stator lifetime(referred to new stator design).

Result:
1.**Maintenance done many times for the stator before replacement need.**
2.**The stator replacement intervals becomes 8-10 month .**

Modified stator

Original stator

COOLING TOWER UNITS & Case studies

Ammonia Cooling Tower

Fan

Hot Water   Cold Water

Make-Up Water

Cell

Blow Down   Basin

High Tension Pumps

Filtration Pump

Side Stream Filtration 5%   Chemical Dosing Station
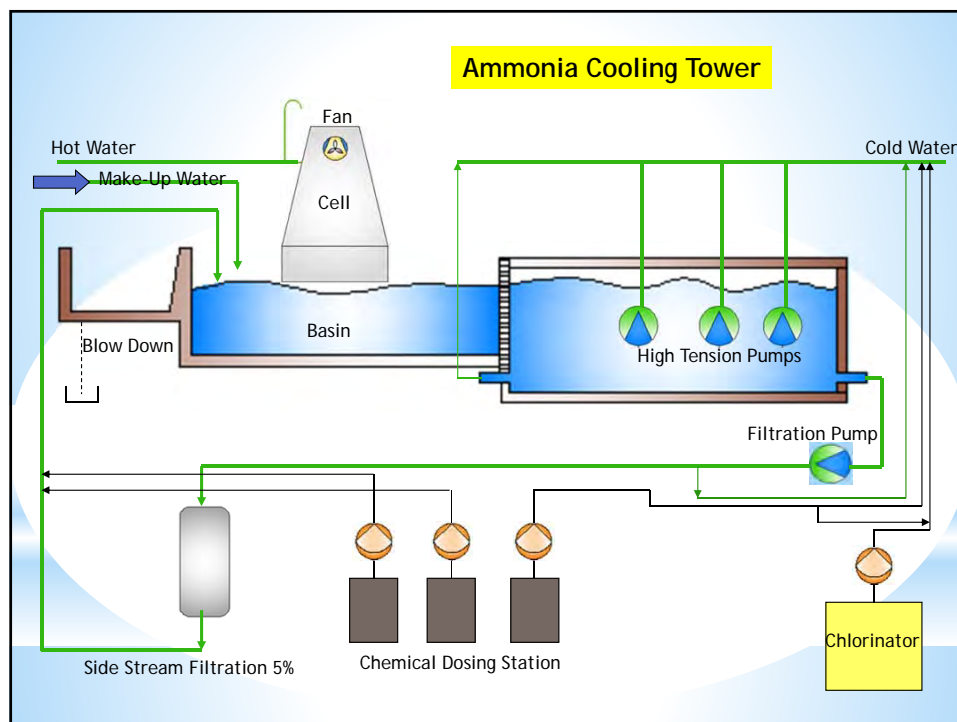
Chlorinator

Case 6:

Problem: Blocking in liquid chlorine line in chlorination unit.
The chlorine line inlet to evaporator was blocked by rust & freezing inside the chlorine cylinder.

Solution:
-Change the operation by vapor chlorine instead of liquid CL_2.
-the evaporator temp.was changed from(60-80) to (15-25)$_0$C.
Result:
There is no blockage done.
Chlorine gas handling is more safe than liquid.

Case 7:

Problem: Gearbox (cooling fan) failure.

It,s difficult to detect the vibration inside cooling fan housing on gearbox to predict the problem before occurred.

Solution:
Installed on line vibration set on gearbox with outside display screen,

Result:
-operators &technicians monitor the vibration readings periodically in the shift & repot the case of the gearbox,

-early monitoring prevent gearbox damage.

Case 8:

Modified cooling water treatment program:

Since plant start-up in June 2006 to the end of 2007 the method for monitoring and controlling chemical dosage in cooling water system depends on manual control for corrosion inhibitor dosage based on analysis of grab sample taken once eight hours and control is based on manual adjustment of treatment pump stroke.

At the end of 2007 a new apparatus (automation system) was established on line to monitor and control cooling water treatment program, its available methods of continuous monitoring and precise automatic feed control of chemical additives.

Treatment

Scale and corrosion inhibitor Zinc Phosphate high stress polymer.

• **Stabilizing agent polymer and phosphate.**

• **Biocide.**

• **Mixture from (Bromine and chlorine).**

• **Side stream filtration about 5%.**

Cooling water control

• **The equipment is the controller module for the cooling water inhibitor programs.**

• **It monitors and controls based on the equipment components in the re-circulating water.**

• **By continuously reading the exact level of equipment proportional to actual product level, a feedback control signal is generated also.**

Previous Chemicals	**New Chemicals**

- N-23201T Corrosion Inhibitor & Dispersant alkaline zinc family with polymer technology.
 	
- The corrosion protection by high level of Zn combined with low level of phosphates.
- Dose:
    Amm = 30 ppm
    Urea = 30 ppm
	-3DT190 Dispersant.
	- It is a product using high stress polymer to control iron, manganese, calcium phosphate, and zinc.
	- Water temperature > 57˚c
	  Skin temperature > 71˚c
	  Phosphate > 30˚c
	- Dose:
	    Amm = 25 - 30 ppm
	    Urea = 20 - 25 ppm

- N-73440 corrosion inhibitor.
- The product contains: polymer, phosphate, and organic compounds.
- Dose:
    Amm = 25 ppm
    Urea = 20 ppm
	-3DT129 corrosion inhibitor.
	- It is a multifunctional scale & corrosion inhibitor contains Zn, O-PO4, and phosphonate (PSO Polymer).
	- Zn as cathodic corrosion inhibitor.
	  O-PO4 as anodic corrosion inhibitor.
	  Phosphates as CaCO3 scale inhibitor.
	- Wide range PH, low alkalinity, and corrosive water.
	- Dose:
	    Amm = 35 ppm
	    Urea = 30 ppm
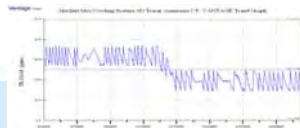
Waste Water Pit

The blow-down of both cooling towers goes directly to the waste water pit which led before to an increased concentration of Zn inside the pit due to high dosage of chemicals added, sometimes these concentrations may reach to 1.5 ppm (the law 4/94 is 1 ppm). After the new chemicals applied with less dosage (with lowest Zn and PO4 content), the concentration of Zn decreased 3 times lower than the environmental limits reached to less than 0.3 ppm, which is environmentally target and apply the environment law.

Zn Concentration in Waste Water Pit
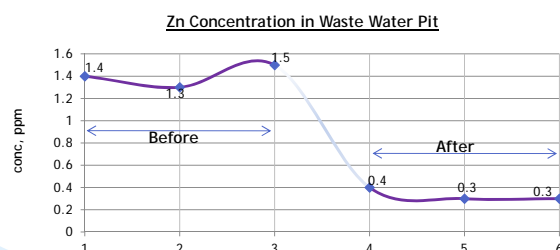
Case 9:

Problem: Fouling in heat Exchangers plate coolers.
This problem was appeared in specific units such as plate cooler 329E004 in urea plant , in Co2 plate cooler in ammonia plant ,Aso in gas cooler 308 E003 in ammonia plant.

Fouling in plate cooler 329E004(uria plant).

The urea plant suffered from process water high temperature, reading 114 c (normal operation is 80 c) that an % increase in temperature will lead to reduction of CO2 and NH3 to carbamate, reducing urea production (lost production) and loading to lot gases to the flare system causing an environmental impact.

No bypass was available to take the cooler offline to perform chemical cleaning.

No unscheduled shutdown is allowed to make mechanical cleaning.

FOULIG

Mechanical cleaned

Solution:

Based on plant requirements was studied with **NALCO co**. the water flow, system design, also the skin temperature for this cooler in order to find away to perform the online cleaning and restoring the process water side to its normal temperature in the shortest period.

We used different types of anti-scale chemicals which are used in cooling system with concentrated dose as shock dose.

Chemicals which are used (anti-corrosion chemicals):
N-23201 (200lit/30min) [phosphoric acid & zinc chloride, > PH 0.5]
N-73400 (200lit/30min) [phosphoric acid & zinc chloride, > PH 0.5]
N-68 sulphamic acid 3%, PH 0.2

When cleaning the cooler online with the plant in normal operation there is a big risk, as this could affect the water quality of the entire cooling circuit and by turn affecting the performance of the other units and heat exchangers (PH changes and high suspended matter)

, it was recommended to use the sulphamic acid (N-68) being the fastest acid to do the job.
This weak acid will not affect the material of the gasket or the cooler.

Result:
A- Temperature Decreasing

N-23201	N-73400	N-68
4-6 °c	6-10 °c	9-13 °c

B- Chemical used to adjust PH at cooling tower (NaOH) 50% concentration

N-23201	N-73400	N-68
~ 60	~ 40	~ 10
kg/time	kg/time	kg/time

C_In case we used N-23201 or N-73400 we should close the automatic dosing system of Zn and phosphate throw anti-corrosion chemical dosing station about 24 hrs due to high concentration of chemicals in circuit.

E- In case we used N-68 the new chemical type is no disturbance on the cooling system.

D-No additional chemical adjustment for PH (slightly very few quantities)
No shut off chemical dosing of automatic system.

DEMINERALIZATION UNIT
&CASE STUDIES

Case 10 :

Problem: Organic Fouling Defect Ion Exchange Productivity.

According to the annual variation in Nile water specifications are detected at raw water supply to the AlexFert plant (T.D.S, Chlorides and organic matter).

The efficiency of demineralization unit is degraded. AlexFert Established their own scheme for maintain normal operation.

This scheme a trial to solve the problem of the organic load increase in case study regarding the removal of organic fouling in demineralization unit.

So, the efficiency of demineralization unit decreased by 30% comparing designed efficiency before treating.

Organic Fouling

No. of regenerations/year & chemical consumptions
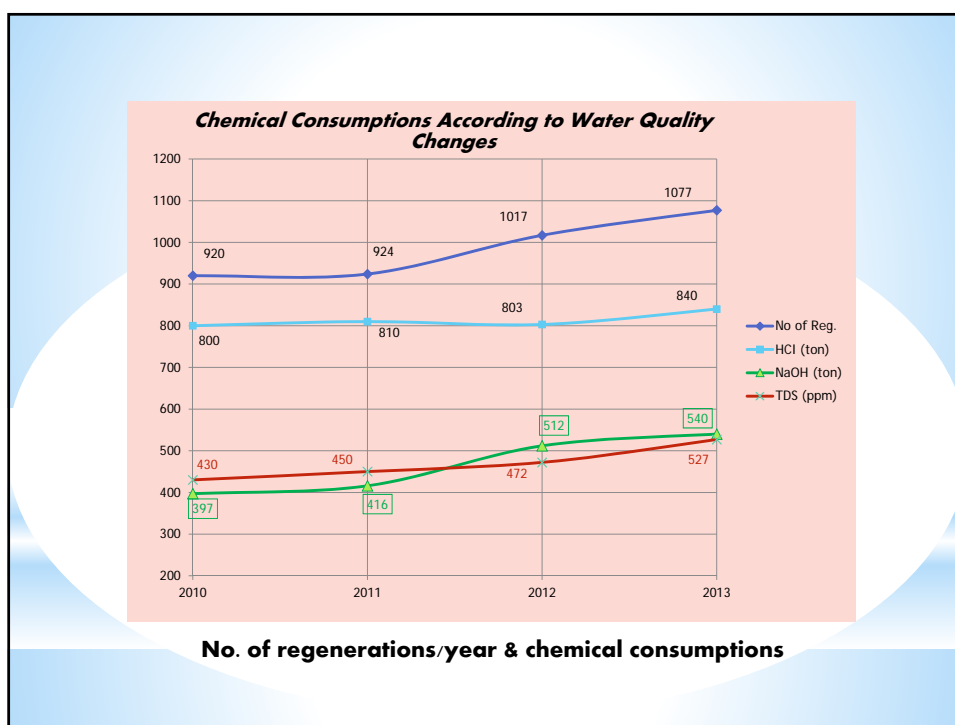
Most pretreatment systems are not fully effective in removing organic with this controlling parameters. The clarifier and gravel filters remove about 60% of organic matter.

The ion exchange resins are coated with condensed organic layer leads to decreased operating capacity and decreased performance.

Solution:

Activity	Scheduled
Cation Backwash	Once / 2 months
Strong Anion Backwash	Once / 6 months
Weak Anion Organic Removal	Once / 6 months
Acid Cleaning of Organic scavenger	Once / 6 months
Organic scavenger Regeneration	Once / 4 days

Alex-Fert preventive scheme for ion exchange unit

Organic scavenger :

Steps of cleaning process :

Prepare a batch of alkaline common salt with consists of (NaOH 2% & NaCl 10-12% with 40 °c) its volume is relative to the bed volume of resin volume overnight if possible or less depend on the plant conditions.

Result:

Operating capacity increased, regeneration times decreased & regenerant is also decreased.

Resin life increased and water quality improved.

Conclusion :

The corporation between operational, instrumentation and mechanical team works to investigate any problem in the plant then recommend the correct solution in the best time to keep the plant running in high efficient mode.

Alex-Fert experience in water treatment management gave the ideal integrated system with focusing also in environmental aspect.

Now Alex-Fert thinking and discussing in details to achieve the minimum emissions and the optimum level of liquid discharge.

*THANK YOU

AFA
WORKSHOP

Water Treatment and Water Quality in Fertilizer and Petrochemical Industries

Delegate List

Water Treatment and [Water Quality](#) In Fertilizer and Petrochemical Industries

#	COUNTRY	NAME	POSITION	COMPANY	TELEPHONE	FAX	E-MAIL
1	Egypt	Maged AL-KOMY	GM, Production Ammonia 1	Abu Qir Fertilizers Co.			
2	Egypt	Mohamed FAWZY	Vice Chairman, Production Sectors	Abu Qir Fertilizers Co.			
3	Egypt	Amr AL-ADAWY	Vice Chairman, Utilites Sector	Abu Qir Fertilizers Co.			
4	Egypt	Hassan FATHI	GM, Production	Abu Qir Fertilizers Co.			
5	Egypt	Hani KAMAL	GM, Water Treatment	Abu Qir Fertilizers Co.			
6	Egypt	Islam AWAD	Chemist	Abu Qir Fertilizers Co.			
7	Egypt	Tarek TAHA	Head Sector	Abu Qir Fertilizers Co.			
8	Egypt	Mahmoud RAMADAN	Utilities Manager	Abu Qir Fertilizers Co.			
9	Egypt	Mohamed SHABOURY	Finance & Adminstration Manager	AFA	+202 23054467	+202 23054466	info@afa.com.eg
10	Egypt	Mohamed Mohmoud ALI	Studies Manager	AFA	+202 23054467	+202 23054466	info@afa.com.eg
11	Egypt	Mushira MOHARAM	Manager, Publishing & Doc. Section	AFA	+202 23054467	+202 23054466	info@afa.com.eg
12	Egypt	Wael MAZEN	Manager, Adminstration Section	AFA	+202 23054467	+202 23054466	info@afa.com.eg
13	Egypt	Mazen GHONIEM	Head Section , IT	AFA	+202 23054467	+202 23054466	info@afa.com.eg
14	Egypt	Ibrahim ABDEL HAKIM	Manager, Environment & Utilities	ALEXFERT			
15	Egypt	Ahmed ISMAIL	Ammonia Superint. Head	ALEXFERT			
16	Egypt	Islam KHALIL	Eng. Ammonia Superint.	ALEXFERT			
17	Egypt	Faiza ABOU ZEID	General Manager	Aqua Trust	+201223217535		
18	Egypt	Tarek MAHRAN		Aqua Trust			
19	Egypt	Samar YASSEN		Aqua Trust			
20	Egypt	Hossam ETMAN		Aqua Trust			
21	Egypt	Abdel Hakim EL-MENHAWY		Aqua Trust			
22	Egypt	Mahmoud EL-MENHAWY		Aqua Trust			

23	Egypt	CIHC		[Chemical Industries](#) Holding Company			
24	Egypt	Alaedin ABBAS	Managing Director	COME	+201223163965	+203 5556147	alaedin.abbas@comeconsult.com
25	Egypt	Ahmed EL-SHAZLY		E-JUST	+201002598756	+203 4599842	ahmed.elshazly@ejust.edu.eg
26	Egypt	Mohamed ISMAIL		Egyptian Electricity Holding Co.	+201228374398		ismaileea@yahoo.com
27	Egypt	Abdel Aziz KONSOWA	Chairman	ENCO	+20122162806	+203 5468506	akonsowa@encoegypt.com
28	Egypt	Samia MASSOUD		EWATEC	+201003449530		ewatecteam@gmail.com
29	Egypt	Tarek SHAHIN	Director of Mechanics	Helwan Fertilizers Co.	+202 29730936	+202 25950370	publicrelations@hfc-egypt.com
30	Egypt	Aly SALEH	Director of Electricity	Helwan Fertilizers Co.	+202 29739515	+202 25950370	publicrelations@hfc-egypt.com
31	Egypt	Nagy BADAWI	Chemist	Helwan Fertilizers Co.	+202 29739034	+202 25950370	publicrelations@hfc-egypt.com
32	Egypt	Mohamed MANSOUR	Chemist	Helwan Fertilizers Co.	+201026656575		publicrelations@hfc-egypt.com
33	Egypt	Ehab YOUSSEF	Chemist	Helwan Fertilizers Co.	+201007951013		publicrelations@hfc-egypt.com
34	Egypt	Mamduh ZAKY		KIMA	+20 97 2314500	+2 097 2314505	info@kimaegypt.com
35	Egypt	Sayd A. MOHAMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
36	Egypt	Hegazy M. HEGAZY		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
37	Egypt	AbuKrisha M. HUSEEN		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
38	Egypt	Adel A. SADEK		KIMA	+2 097 2314500	+2 097 2314505	
39	Egypt	Ahmed M. ABDELMUTLEB		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
40	Egypt	Saber A. ELSAYED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
41	Egypt	Ahmed H. ESMAIL		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
42	Egypt	Asem A. HUSEEN		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
43	Egypt	Mustaf S. FRRAG		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
44	Egypt	Ahmed S. AHMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
45	Egypt	Ahmed M. ELTAYB		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
46	Egypt	Hasan M. AHMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com

47	Egypt	Salim SALIM		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
48	Egypt	Mohamed S. MUSFATA		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
49	Egypt	Mohsen AHMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
50	Egypt	Esameldeen A. KHODERY		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegype.com
51	Egypt	Mahmud A. ABDELMUTY		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
52	Egypt	Ahmed A. MOHAMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
53	Egypt	Taha M. SAYED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypy.com
54	Egypt	Eshak A. LABYB		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
55	Egypt	Ahmed Abdelaziz MOHAMED		KIMA	+2 097 2314500	+2 2314505	info@kimaegypt.com
56	Egypt	Mahmud MOHAMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
57	Egypt	Mohamed ABU ELHASAN		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
58	Egypt	Muner F. TADRWS		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
59	Egypt	Mamduh S. FAHMY		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
60	Egypt	Mahmud A. ZAHRY		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
61	Egypt	Gamal Ismail MOHAMED		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
62	Egypt	Saed Mohamed HASAN		KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
63	Egypt	Eid ELHOT	Chairman	KIMA	+2 097 2314500	+2 097 2314505	info@kimaegypt.com
64	Egypt	Mohamed MASOUD	Sector Manager	MOPCO	+201001755528	+202 26731184	mohdyouf@mopco-eg.com
65	Egypt	Mahmoud RAMZY	Section Head	MOPCO	+201001755528	+202 26731180	mohdyouf@mopco-eg.com
66	Egypt	Waleed EL-SEWEFY	Engineer	MOPCO	+201001755528	+202 26731180	mohdyouf@mopco-eg.com
67	Egypt	Ahmed SAMIR	Production, Head Sector	NCIC			ncic@nasrchemicals.com
68	Egypt	Wissam MAHGOUB	Sales Manager	Pall Corporation	+20170703949		wissam_mahgoub@europe.pall.com
69	Egypt	Alaa ALI	Application Engineer	Pall Corporation	+971 48849420		alaa_ali@europe.pall.com
70	Egypt	Ibrahim ABDEL HAI	Chairman & Managing Director	SEMADCO			
71	Egypt	Mahmoud KHATTAB	Production Sector	SEMADCO			

		KHATTAB	Sector			
72	Egypt	Sayed HELMY	Medical, Head Sector	SEMADCO		
73	Egypt	Abdel Nasser GOMAA	Minerals, Head Sector	SEMADCO		
74	Egypt	Mahmoud YOUSSEF	GM	SEMADCO		
75	Egypt	Mohamed MAAET	Engineer	SEMADCO		
76	Egypt	Abdel Latif ABBASS	Chemist	SEMADCO		
77	Egypt	Abdallah MATTAR	Chemist	SEMADCO		
78	Egypt	Ayman EL-MOGHLY	Senior Sales Manager	Uhde Engineering Egypt S.A.E	+201017601223	+202 22662885	ayman.el-moghly@thyssenkrupp.com
79	Jordan	Fouad ALZOUBI	Power & Water Manager	Arab Potash Company (APC)	+962 77111159	+962 32305132	fuad.z@arabpotash.com
80	Jordan	Osama KHALIL	Chemical Supervisor	Arab Potash Company (APC)	+962 775482536	+962 6 5200520	osama.k@arabpotash.com
81	Jordan	Haroun KHASOUNA	Engineer	JPMC		
82	Jordan	Safwan AL-MADANY		JPMC		
83	Jordan	Abdel Karim SHEYYAB		JPMC		
84	Jordan	Radwan AL-LAKAYDA		JPMC		
85	Jordan	Qassem AL-SHABOUL		JPMC		
86	Jordan	Ramzi SINNOKROT	Technical Sector Manager	KEMAPCO	+962 797313486	+962 64601995	ramzi.sinnokrot@kemapco.com
87	Jordan	Abdelhaleem SRIHIN	Production Engineer	KEMAPCO	+962 797313486	+962 64601995	abdelhaleem.srihin@kemapco.com
88	Jordan	Waleed JARADAT	Shift Supervisior	KEMAPCO	+962777632292	+96264601995	belal.alnsour@kemapco.com
89	Kuwait	Mohamed FOULAD		PIC		
90	Kuwait	Hussien AL-AJAMI		PIC		
91	Kuwait	Khaled AL-OTAIBI		PIC		
92	Kuwait	Ahmed Al-AZMI		PIC		
93	Morocco	Hicham HASSOUNE	Researcher	OCP Group	+212 5233453	+212 523345445	h.hassoune@ocpgroup.ma
94	Morocco	Khaoula KHALESS	Researcher	OCP Group	+212 661965815	+212 523345445	k.khaless@ocpgroup.ma
95	Qatar	Abdulaziz ALJABRI	Field Env. Eng	QAFCO	+974-44228888	+974-44770347	aaljabri@qafco.com.qa

96	Tunisia	A. OMIRI	Engineer	TIFERT	+216 98367710	+216 74667090	nejha.hammouda@yahoo.fr
97	UAE	Mohamed ABU TALEB	Utilities-1 Dep. Manager	FERTIL			
98	UAE	Waleed BIN SUMAIDA	Utilities-2 Supervisor	FERTIL			
99	UAE	Salem AL-MENHALI	Utilities-2 Supervisor	FERTIL			
100	UAE	Khalid AL-MARZOUQI	Utilities-2 Sr. Operator	FERTIL			
101	UAE	Ali AL HOSANI	Ammonia-1 Process Engineer	FERTIL			
102	UAE	Hamdan AL-KATHERI	Urea-1 Process Engineer	FERTIL			
103	UAE	Mohamed AL-HAMADI	Utilities-1 Supervisor	FERTIL			

Subscribe to our newsletter

email [   ] [Subscribe] ↻