

Chemistry - PI 24

MAKE-UP WATER TREATMENT PLANT

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Objectives:

1. From memory draw a block flow diagram of the water treatment plant for the station to which you have been deployed. In one or two sentences for each vessel, state its purpose.
  2. Outline a generalized regeneration sequence for a cation exchange vessel, anion exchange vessel, and a mixed bed stating the purpose of each step. Give example chemical reactions for regeneration of cation and anion resin.
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The purpose of water treatment is to "fit the water to the job". This process is usually two-fold, first, removing harmful constituents from the water, second, adding beneficial ingredients. Treatment may take place externally, before water is added to a system and/or internally when the water is in the system.

Water in or for make-up to the Secondary side is treated to:

- prevent formation of scale on boiler tubes.
- prevent corrosion or embrittlement in boiler steam and feed systems.
- prevent oxygen attack in boiler, steam and feed systems.
- minimize the effect of a condenser leak (between occurrence and repair).

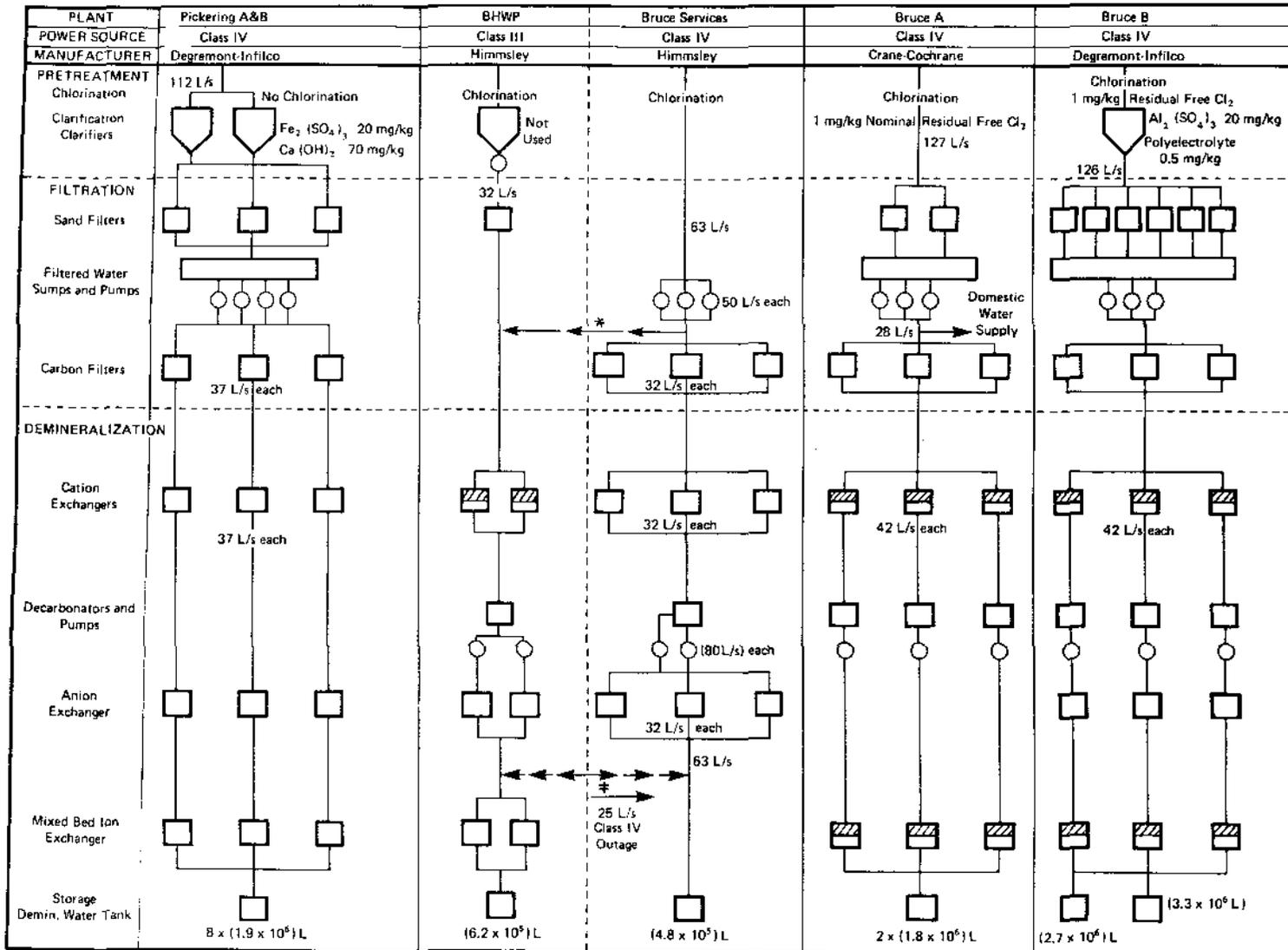
This module describes the external treatment for make-up water to the secondary side. Appendix A gives definitions of some of the more common terms.

On the next page, there is a simplified flow sheet of the water treatment plant for the various NGD stations. At this point, you should study the drawings and ask yourself:

"What is the purpose of each vessel in the W.T.P. and why are they located in that sequence?"

"What chemicals are added? Why?"

### WATER TREATMENT PLANTS



\* Future feed for BHWP as well. Piping installed already but not tied in.

⊕ Piping installed already but not tied in.

Multilayer exchanger.

The answers to the questions will be found in the following sections.

**Chlorination:** The addition of chlorine gas (or sodium hypochlorite, ie, javex) to water to effect a bacteriological kill and oxidize other organic compounds which can foul ion exchange resins. Ahead of a clarifier, chlorination also puts the water in an "oxidizing condition" to promote better flocculation.

The action of chlorine is as follows:



Chlorine + water → hypochlorous acid + hydrochloric acid

It is the hypochlorous acid that is the "active ingredient" in the killing of bacteria.

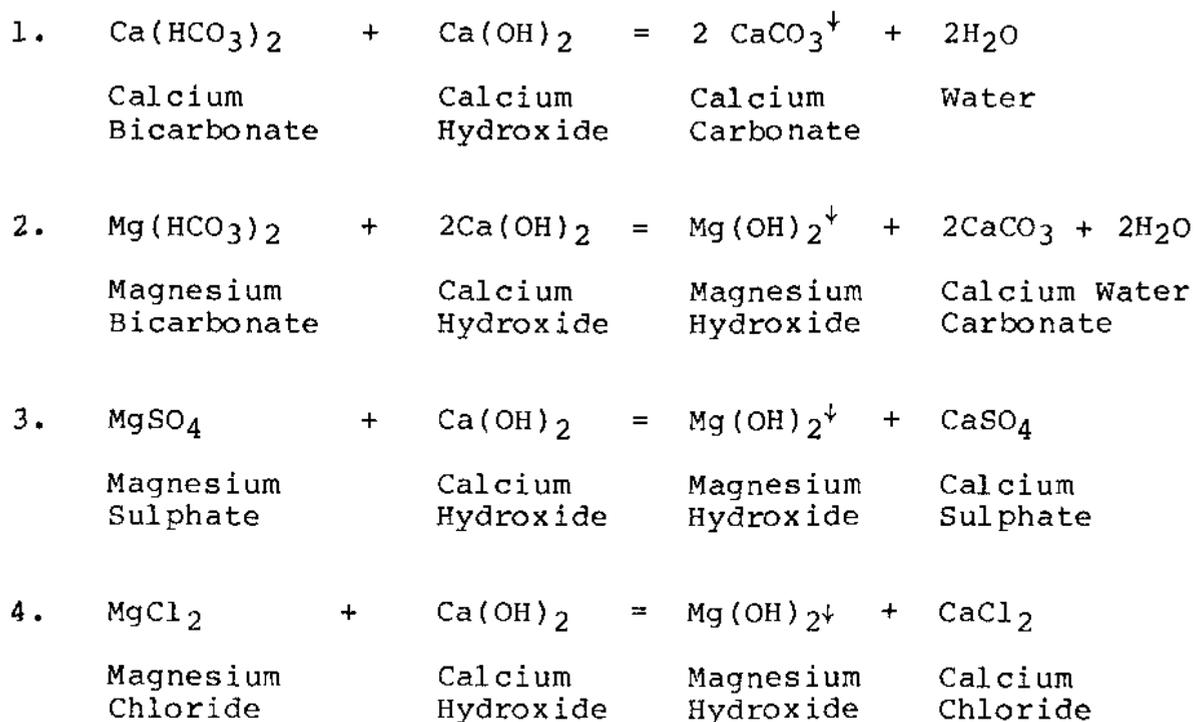
**Clarifiers:** Clarifiers are used to remove suspended solids and colloidal suspensions (particles suspended indefinitely due to their general size) from the raw water.

Some clarifiers have polyelectrolytes added to assist coagulation and some have lime and/or Ferric or Aluminum Sulphate added to effect flocculation → coagulation → sedimentation.

If the water is in an oxidizing condition, Ferric Sulphate will react with lime to form a fluffy Ferric Hydroxide precipitate (flocculation) which acts as a moving filter in the clarifier, coagulating the suspended solids and colloids. Coagulated particles fall to the bottom of the clarifier from which they are eventually transferred to the W.T.P waste treatment system.

The addition of lime to the clarifier has a secondary effect of providing partial softening of the raw water which will give a significant reduction in loading on the ion exchange vessels to follow.

The mechanism which you need not memorize is as follows:



The symbol † represents formation of a precipitate which settles along with the rest of the clarifier sludge.

Clarifier effluent is then free of suspended solids and colloids and in some cases, partially softened.

**Sand Filters:** Sand filters act as safe guards to catch anything in the way of solids passing the clarifier. Most modern sand filters are fitted with automatic backwash which is initiated by bed pressure differential.

**Filtered Water Sumps:** These act as storage vessels for the filtered, partially softened water. Flow to the clarifier is usually controlled by the filtered water sump level indicator.

**Carbon Filters:** The purpose of the carbon filter is to remove residual free chlorine from the filtered water. Free chlorine can break down the resins in the ion exchange vessels which follow. The organic molecules formed when resin is degraded are small enough to enter the body of the anion exchange resins and cause "organic fouling" by blocking the ion exchange sites.

**Cation Exchangers:** As the name implies, these vessels contain cation exchange resin, usually in the hydrogen form.

Cations entering the vessel displace hydrogen from exchange sites in the resin, eg.

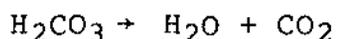


The cations stay with the resin while the released hydrogen ions now travel with the process water.

**Decarbonator:** The decarbonator is a vacuum degassing tower. Its purpose is to reduce the loading on the anion exchanger by removing carbonates. Note that any carbonates entering the cation exchanger will be converted to carbonic acid, eg.

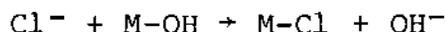


If carbonic acid is subjected to a vacuum, it decomposes



The carbon dioxide is vented to atmosphere and the water carries onto the next stage.

**Anion Exchanger:** In this vessel, anions are exchanged for hydroxyl ( $\text{OH}^-$ ) ions, eg.



Note here that raw water has an equal number of anions and cations; therefore ion exchange will simply produce an equal number of  $\text{H}^+ + \text{OH}^-$  ions which will form  $\text{H}_2\text{O}$ .

**Mixed Bed:** Due to equilibrium considerations, the single bed cation and anion exchangers are not 100% efficient, therefore, there are some residual cations and anions leaving the "primary train" and entering the mixed bed ion exchanger. The mixed bed is an intimate mixture of cation and anion exchange resins. In effect, as water passes through the MB, it sees an infinite chain of cation and anion exchange vessels and the removal of ionic species in exchange for  $\text{H}^+ + \text{OH}^-$  approaches 100%.

It should be noted that the anion resin in the MB is strong enough to remove silica (see 21-1 Impurities) from the raw water.

From the mixed bed, demineralized water goes to a storage tank which supplies the unit requirements for make-up water. At full flow, a WTP should produce about 3% of plant steam flow. Normal make-up requirements are in the 2% range.

At this point you should consider the questions:

1. What happens when a cation exchanger runs out of H<sup>+</sup> or all the sites are filled with foreign cations?
2. As above, for anion exchanger and mixed beds.

An average primary train (cation + anion) would run about 24 hours at full flow before running out of exchange capacity. An average mixed bed will run about 5 days at full flow.

When an ion exchange resin runs out of exchange capacity (known as exhaustion) the ions that would normally be removed just pass right through. Evidence of this happening is easily seen in the effluent from mixed beds and anion exchangers by **rising** conductivity. (Why?) But for a cation exchange vessel, exhaustion is indicated by **falling** conductivity. (Why?)

As there is considerable capital investment in resin, it is fortunate that both types of resin can be **regenerated** by passing a large concentration of:

H<sup>+</sup> ions for cation exchange resin

OH<sup>-</sup> ions for anion exchange resin

over the resin bed.

For cation resins, this is done using dilute acid, usually sulphuric, eg.



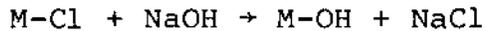
The steps in a regeneration would then be:

1. Remove from service.
2. Backwash (upflow using normal influent) to loosen bed and remove any fines or silt.
3. Pause to allow the bed to settle.
4. Acid introduction\* to regenerate the resin.

\*When using sulphuric acid, it is the general practice to introduce the acid in a stepwise manner with respect to concentration, ie, 2% followed by 4% then 6%. This method elutes calcium from the resin without the precipitation of Calcium Sulphate which coats the resin and renders it useless.

5. Slow rinse to displace left-over acid and wastes.
6. Fast rinse.
7. Service.

For anion resin regeneration is effected using dilute caustic soda ( 5%):

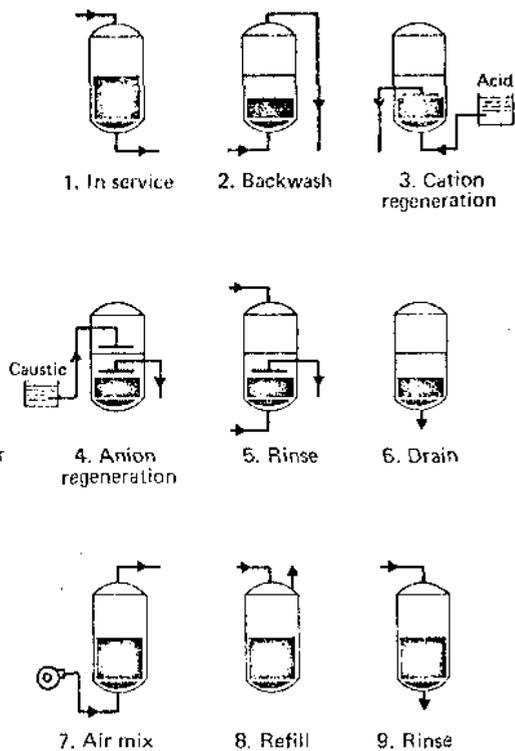
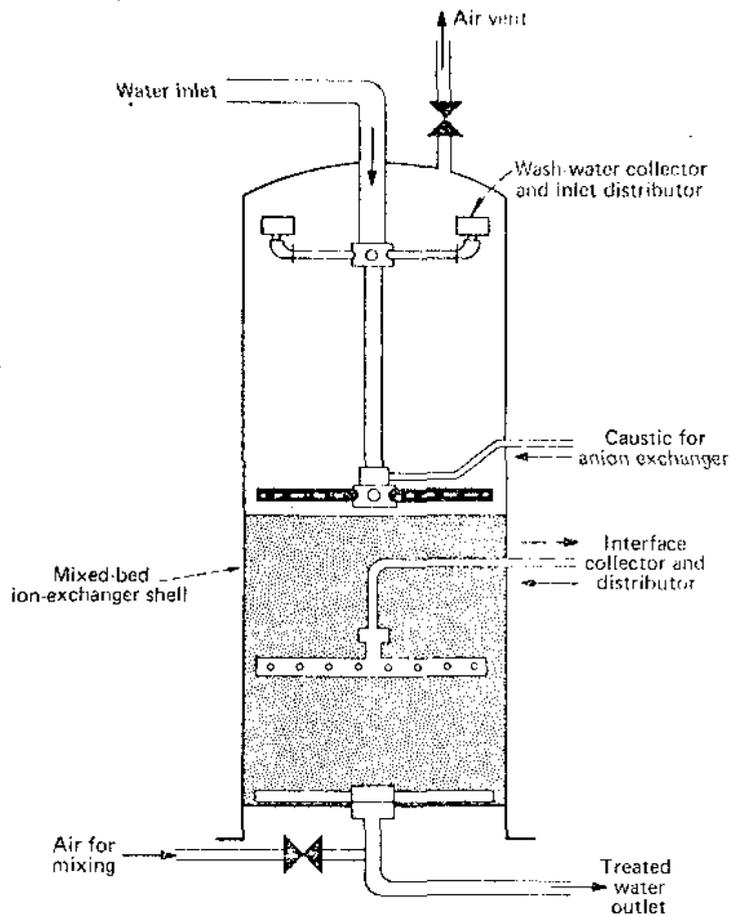


Steps for regeneration are similar to those for a cation vessel.

For mixed beds, there is a problem in regeneration. If acid (eg, H<sub>2</sub>SO<sub>4</sub>) is introduced to regenerate the cation resin, then the large excess of SO<sub>4</sub> = ions will use up all the anion resin. Similarly, if NaOH is introduced to regenerate anion resin, then large excesses of Na<sup>+</sup> ion will use up all the cation resin.

How do we solve this problem?

If the mixed bed is backwashed, at the appropriate rate, the anion resin will rise because of its lower density to the top of the vessel and the cation resin remain at the bottom. If the resins are then allowed to settle and if in the design stage a mid-bed distributor had been installed at the interface of the two resins, regeneration could be accomplished as in the following diagram:



Regeneration of mixed resin bed is illustrated from initial backwash to end of rinse and return of unit to service. Light shading represents lighter anion resin, dark tint is heavier cation beads. Entire process can take anywhere from two to four hours.

Mixed-bed demineralizer houses intimate mixture of cation and ion exchange resins.

A typical regeneration sequence for a mixed bed is as follows:

1. Remove column from service.
2. Backwash to separate resins.
3. Isolate bed and allow resins to settle into layers.
4. Acid introduction to regenerate cation resin.
5. Caustic introduction to regenerate anion resin.
6. Slow rinse anion resin.
7. Drain bed through bottom to bed level. This rinses cation resin and gets the bed ready for the next step.
8. Air mix resins.
9. Air mix resins and drain off water. This promotes intimate mixing and removes water which would allow layering of resins when air is stopped.
10. Pause - allows resin to fall intimately mixed to bottom of vessel.
11. Slowly fill with water to top of vessel. This slow fill does not disturb the bed.
12. Slow rinse.
- 13.\* Fast rinse to service conductivity.
14. Service.

\*Some designs call for a step 13(a) called rinse recycle which saves water by recycling the rinse outlet to the inlet of the MB and recirculating the same water until the effluent conductivity is suitable for service.

Primary train regeneration is usually done by regenerating cation and anion vessels simultaneously, a process taking about 2 hours.

Mixed bed regeneration takes about 4 hours.

#### Practice Exercises:

Consider the objectives at the front of the text as questions. From memory, jot down your answers in point form, then compare what you have with the data in the text.

APPENDIX A

General Definitions

**Corrosion:** Metal wastage caused by attack from the environment in which a metal resides, eg, a rusting car fender. The usual forms of corrosion are:

1. Oxidation of the metal by atmospheric or dissolved oxygen.
2. Acid attack (or basic in the case of metals such as aluminum).
3. Electrolytic decomposition caused through action with a dissimilar metal, (eg, iron will corrode before copper where both are present).

**Deposition:** As the name implies, this is the build-up of deposits of:

1. entrained solids
2. corrosion products
3. dissolved solids by evaporation
4. organic growth.

**Erosion:** Metal wastage by the "high" velocity passage of a liquid over it.

**Specific Conductance or Conductivity:**

A measure of the dissolved ionized substances in a liquid, usually water. Conductance is inversely proportional to resistance.

**pH:** A measurement of the relative acidity or basicity of a liquid. The classic definition is:  $\text{pH} = -\log_{10} [\text{H}^+]$

ie, pH is equal to minus the logarithm (base 10) of the hydrogen ion concentration in gram equivalent weights per litre.

**Ion:** A charged atom or group of atoms either positive or negative at large in a solution.

**Ion exchange:** The process whereby an organic compound "trades" a charged ion for a similarly charged ion in a solution.

Ion Exchange Resin:

The usual commercial form of an ion exchange medium. The compound is made into beads about the size of beach sand.

Cation: A positively charged ion so named because it is attracted to the cathode of an electrolytic cell.

Anion: A negatively charged ion (cf. anode).

Water Treatment:

The process applied to water or the substance added to water to:

1. Make it suitable to the work intended.
2. Make it non-harmful to the equipment involved.

Aeration: Mixing intimately water and air to remove gases and odours.

Subsidence: Removal of suspended material by allowing them to settle in a holding tank.

Coagulation: The process of removing finely divided particles or colloidal particles of turbidity and colour capable of staying in suspension indefinitely. These particles are combined in masses sufficiently large to effect removal by settling or filtration.

Filtration: Passing a liquid material containing suspended solids through a bed of material such as sand, gravel, charcoal in such a manner as to effectively remove any suspended matter.

Chlorination: The addition of chlorine gas or hypochlorous salts to water or sewage usually for the purpose of disinfection.

Softening: The process by which the Calcium, Magnesium, and Bicarbonate constituting the hardness of a water are chemically removed by precipitation or ion exchange.

Evaporation: Distillation of a water, usually softener effluent, to produce fairly high purity water. (Not in vogue anymore.)

Demineralization:

Removal of ionic species from water by ion exchange.

As pH and conductivity are very important, a brief word of explanation is in order:

**Conductivity:** is measured by polarizing two electrodes in water and measuring how well current passes between them. A water high in mineral content will have a high conductivity. Examples are:

Lake Ontario Water: 350  $\mu$  mhos/cm<sup>3</sup>  
Well Water: 600  $\mu$  mhos/cm<sup>3</sup>  
Demin.Water: 0.2  $\mu$  mhos/cm<sup>3</sup>.

**pH:** is the relative acidity or alkalinity of a water. It is measured on a scale from 0 - 14 with 7 being neutral. Going towards 14 from 7 represents increasing alkalinity. Going towards 0 from 7 represents increasing acidity. It should be noted that a 1 unit change in pH represents a 10-fold change in relative acidity or alkalinity, (eg, a solution with a pH of 2.0 is 10 times more acid than a solution of pH 3.0).

Examples of pH are:

Lake Ontario Water: 8.2  
Apples: 2.9 - 3.3  
Beer: 4.0 - 5.0  
Milk of Magnesia: 10.5  
5% Sulphuric Acid: 0.3

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