

CHAPTER 8 ION EXCHANGE

8-1. General. Some naturally occurring and synthetic materials can exchange one type of ion for another dissolved ion of like charge, e.g., one positive ion for another positive ion. The number of charges on the ions removed from solution must equal the number of charges on the ions exchanged from the material. The major types of synthetic ion-exchange resins that have been developed are as follows: strong acid cation resins, weak acid cation resins, strong base anion resins, and weak base anion resins. Strong acid and weak acid cation resins exchange hydrogen ions (H+) for other cations. Strong acid cation resins may also exchange monovalent sodium ions (Na+) for such divalent cations as calcium (Ca⁺⁺) and magnesium (Mg⁺⁺). Strong base anion resins exchange hydroxyl (OH-) or bicarbonate (HCO₃) ions for other anions. Weak base anion resins adsorb acidic ionic materials, such as hydrochloric acid, sulfuric acid, and carbonic acid from solutions. Once adsorbed on the weak base anion resin, the anion part of the acid may be exchanged for other anions. These exchanges occur during the service cycle when treated water is produced. When the capacities of resins have been used up or exhausted, they are regenerated with acid or base or salt to restore the resin to the original ionic state. Illustrations of the strong acid cation resin hydrogen ion-cation exchange and the strong base anion hydroxyl ion-anion exchange that occur in the complete demineralization of water are shown in figure 8-1.

8-2. Pretreatment. Ion exchange can be used as a pretreatment method in the desalination process to reduce the levels of sparingly soluble salts. A strong acid cation resin in the sodium form and a weak acid cation resin in the hydrogen form can be used. In both processes the levels of alkaline earth metal cations, such as calcium (Ca⁺⁺) and magnesium (Mg⁺⁺), are reduced. The use of the strong acid cation resin in the sodium form is called water softening, and the use of the weak acid cation resin in the hydrogen form in conjunction with a carbon dioxide degasifier is called dealkalization-softening.

a. Softening. Water softening by sodium ion exchange can be used as a pretreatment method in a desalination process. During water softening, monovalent sodium ions on the strong acid cation resin are exchanged for the divalent calcium and magnesium in the water.

Although not desalination, the exchange of sodium ions for divalent cations produces a change in the type of salinity. This change in the salinity reduces the levels of the calcium and magnesium ions, such that the concentration of other ions in the reject or blowdown stream can be increased in the desalination process with a resultant increase in water recovery. Saturation of scale-forming materials, such as calcium carbonate, calcium sulfate, and magnesium hydroxide, is still reached, but the total concentration of salts in the reject attains a higher overall level than would be possible without softening.

b. Dealkalization-softening. Desalination processes can best utilize dealkalization-softening as a pretreatment method when the raw water contains high levels of alkalinity, bicarbonate and carbonate ions, and high levels of hardness, calcium and magnesium ions. A properly operated pretreatment that utilizes a weak acid cation resin will produce water with an alkalinity level of no more than 10 parts per million (as CaCO₃) and a residual hardness approximately equal to the original raw water non-carbonate hardness.

(1) *Treatment process.* The major benefit of dealkalization-softening using carboxylic (weak acid cation) resins lies in the actual reduction of the dissolved solids content of the water. Hydrogen (H+) ions from the resin exchange with the divalent calcium and magnesium ions in the water. This exchange occurs only if the anions of weak acid salts, such as bicarbonate or carbonate ions, are present. Carbonic acid is formed when the hydrogen and bicarbonate ions react. The carbonic acid is weakly ionized and reverts to its basic constituents of carbon dioxide and water. The dissolved carbon dioxide can be removed by using degasification methods, as discussed in paragraph 5-3. The combination of the weak acid cation exchange with degasification reduces both the calcium and magnesium levels as well as the alkalinity level in the raw water.

(2) *Dealkalization-softening uses.* This pretreatment should be investigated when pH adjustment of the raw water by an acid addition is indicated for the desalination process. Weak acid resins use about 10-percent more acid than that required for pH adjustment alone and will reduce the calcium and magnesium concentration as an additional advantage.

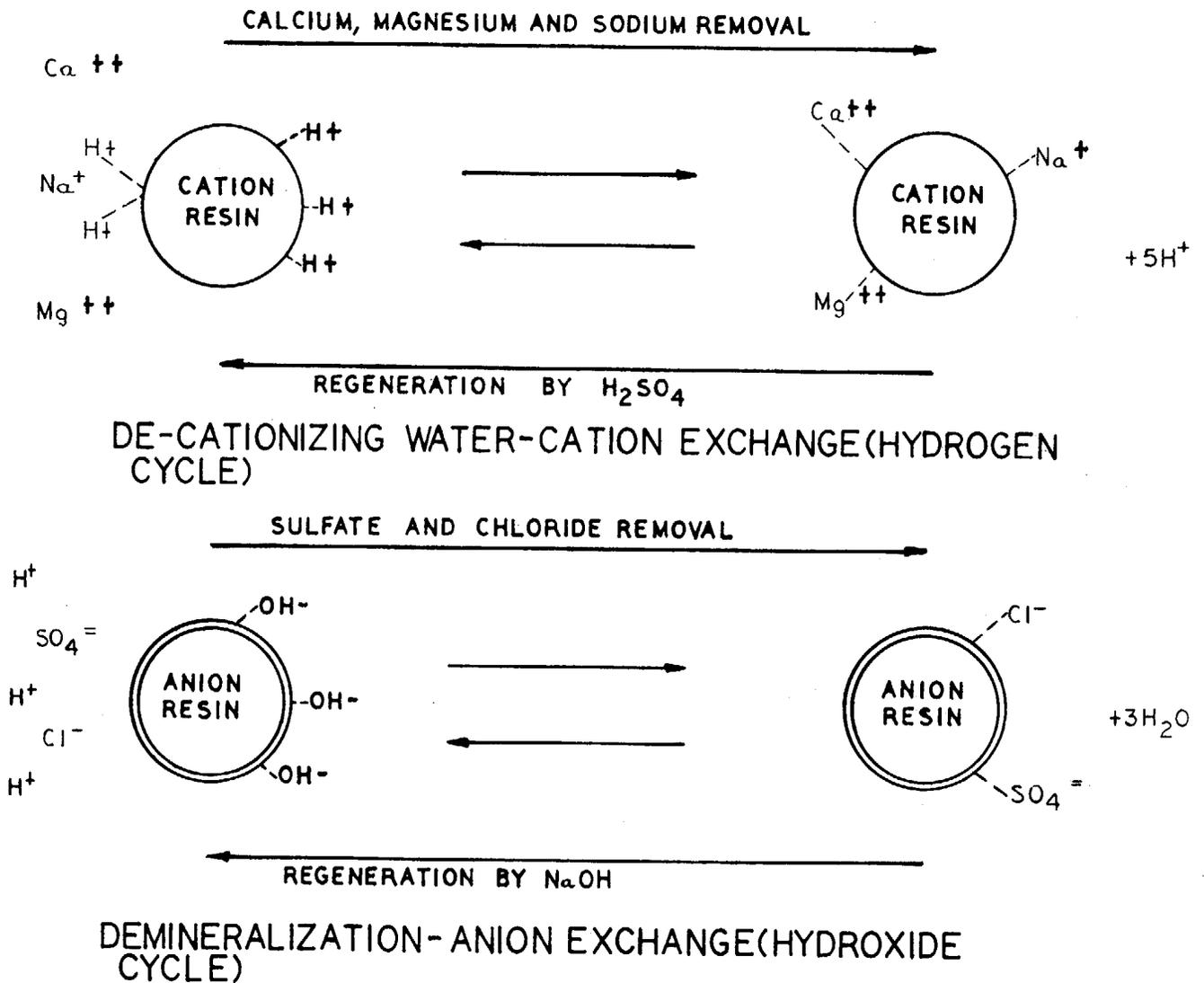


Figure 8-1. Principles of ion-exchange processes.

In brackish waters containing essentially only calcium, magnesium, and alkalinity, the use of weak acid cation resins with degasification could be considered as a possible desalination process. Since some types of weak acid cation resins also permit the efficient removal of sodium bicarbonate, the process becomes applicable as a desalination process when the raw water contains mainly sodium and alkalinity.

8-3. Desalination. Ion exchange can be used as a desalination process in the production of potable water.

a. Requirements. There are several basic requirements for the ion-exchange process to be used economically for the desalination of brackish waters.

- The ion-exchange resins should operate at high capacities.
- The ion-exchange resins should be regenerated close to the stoichiometric equivalence capacity.
- The acid and base regenerants should be low cost.
- The waste regenerants should be rinsed from the ion-exchange resins with a minimum of water, so that the capacity of the resin is not exhausted significantly.
- Regenerant waste volumes should be minimized, and unused regenerants should be recovered and reused to reduce the waste disposal volume.

b. Limitations. The use of ion exchange in the desalination of brackish water has several limitations. The volume of water treated is inversely proportional to the ionic concentration in the water. Regenerant consumption per unit volume of treated water is high and becomes higher as the salinity of the brackish water increases. The size of the ion-exchange equipment follows the same rationale—the more saline the water, the larger the ion-exchange equipment. A low salinity water, usually product water, is required for regeneration of the ion-exchange resins.

c. Treatment processes. The treatment processes employed have either been on a pilot plant scale or have been used in a limited number of full-size installations. The processes have generally utilized weak acid cation and weak base anion resins. These resins have higher capacities and require less acid and base regenerants than strong acid cation and strong base anion resins. Two ion-exchange desalination treatments that have been developed are the Desal Process and the RDI Process.

(1) *Desal process.* The Desal Process has several variations, but the main thrust of the process is the use of the weak base anion resins in the bicarbonate form.

(2) *RDI Process.* The RDI Process is a three-unit system using four different resins. The water first passes through a strong base anion resin where the strong acid anions, such as chloride, sulfate, and nitrate, are replaced with the bicarbonate ion from the resin. The water then moves through a layered ion exchange unit of weak acid cation and strong acid cation resins, where the calcium, magnesium, and sodium are removed, the bicarbonates are converted into carbonic acid, and the neutral salt leakage from the previous anion unit is converted into free mineral acidity, i.e., sulfuric, hydrochloric, and nitric acids.

Then, the water travels through a weak base anion resin, where the free mineral acidity is adsorbed but the carbonic acid passes through unaffected. The water is then degasified, which removes the dissolved carbon dioxide. The weak acid cation and strong acid cation resins are regenerated with either sulfuric or hydrochloric acid, first through the strong acid cation resin and then through the weak acid cation resin. The strong base anion and weak base anion resins are regenerated in series with sodium bicarbonate, first through the strong base anion resin and then through the weak base anion resin. The RDI Process is shown in figure 8-2.

d. Three-unit variation. In the three-unit variation, the strong acid anions in the water, such as chloride, sulfate, and nitrate, are replaced with the bicarbonate ion from a weak base anion resin in the bicarbonate form. The process then employs a weak acid cation resin that replaces the calcium, magnesium, and sodium in water with the hydrogen ion from the resin. The carbonic acid that is formed is adsorbed by a second weak base anion resin in the free-base form. When the system has exhausted its treating capability, the lead weak base anion resin is regenerated with ammonia, caustic, or lime, the weak acid cation resin is regenerated with sulfuric, hydrochloric, nitric, or sulfurous acid, and the tail-end weak base anion is not regenerated. The lead weak base anion resin is now in the free-base form and the weak acid cation resin in the hydrogen form. After its adsorption of carbonic acid in the previous service cycle, the tail-end weak base anion is in the bicarbonate form. The service flow direction is reversed for the next service cycle, with the former tail-end weak base anion in the lead position and the former lead weak base anion in the tail-end position. The direction of service flow is reversed on each succeeding service cycle after regenerating only the weak acid cation and the former lead weak base anion. This three-unit variation of the Desal Process is shown in figure 8-3, with the following sequence of operation: Service-A followed by Regeneration-B, Regeneration-B followed by Service-C, Service-C followed by Regeneration-D, Regeneration-D followed by Service-A, Service-A followed by Regeneration-B, etc., in a repeating sequence.

e. Two-unit variation. In the two-unit variation, carbon dioxide is fed to the raw water. The carbon dioxide in the water (carbonic acid) converts the weak base anion resin in the lead unit to the bicarbonate form and the strong acid anions in the water, such as chloride, sulfate, and nitrate, are replaced with the bicarbonate ion from the resin.

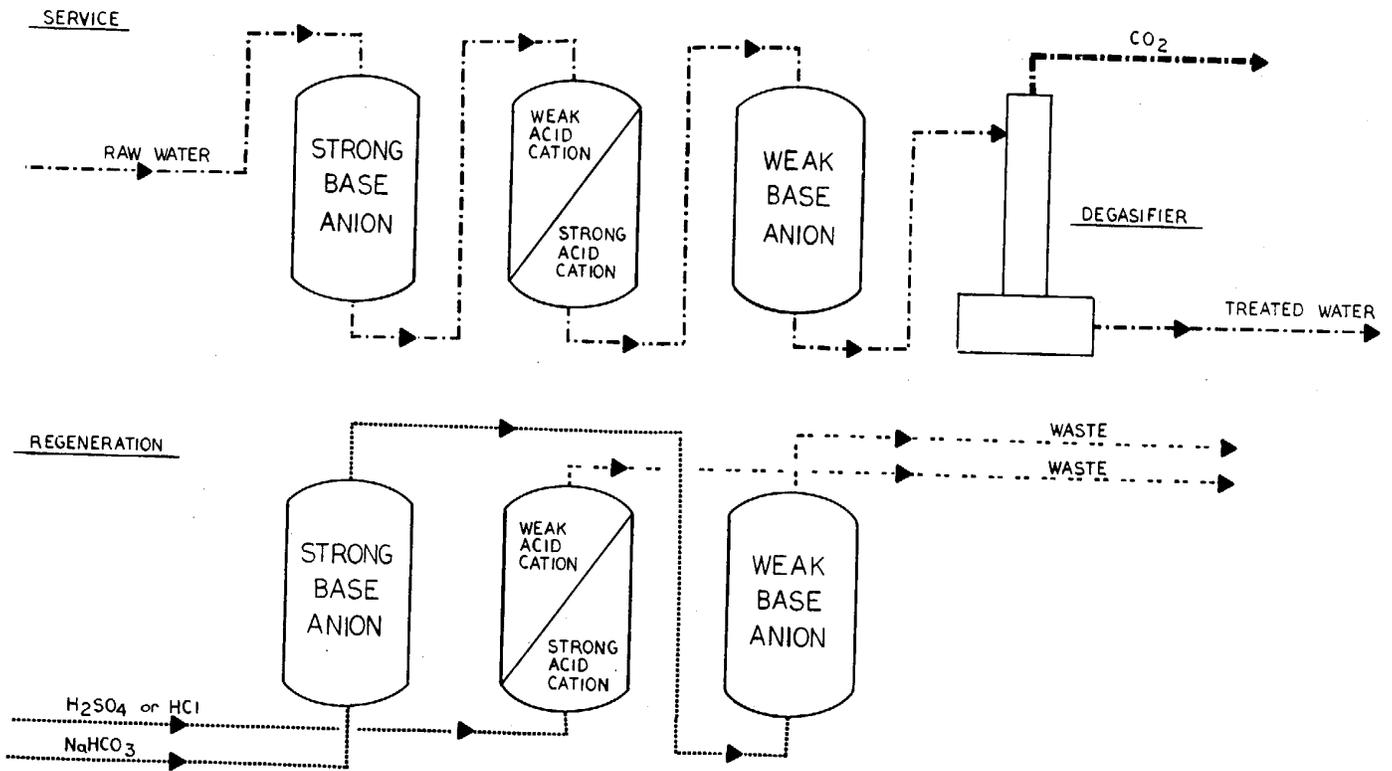


Figure 8-2. RDI Process.

The process then employs a weak acid cation resin, in the same manner as the three-unit variation, which replaces the calcium, magnesium, and sodium in the

water with the hydrogen ion from the resin. The carbonic acid or dissolved carbon dioxide that is formed is now removed by a degasifier.

Ammonia, caustic, or lime can be used to regenerate the weak base anion resin and sulfuric, hydrochloric, nitric, or sulfurous acid can be used to regenerate the weak acid cation resin. The two unit variation of the Desal Process is shown in figure 8-4.

water as pure as does ion exchange. In the production of steam, it is sometimes necessary to use water with a lower level of total dissolved solids. Ion exchange should be considered if water with less than approximately 300 milligrams per liter of total dissolved solids must be purified further.

8-4. Demineralization. No other demineralization or desalination technique can, in a single pass, produce

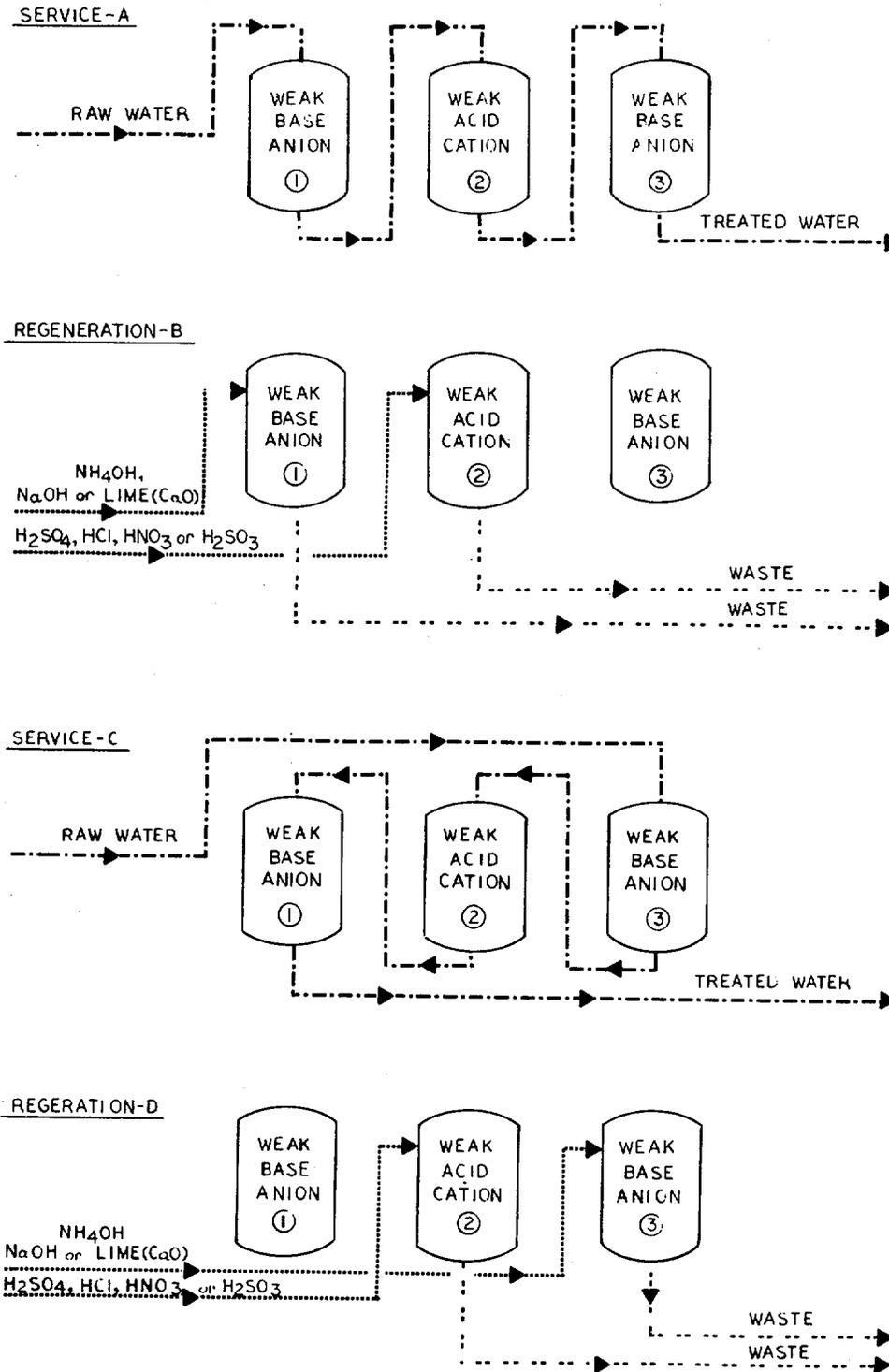


Figure 8-3. Three-unit variation Desal Process.

Source: Rohm and Haas Co.

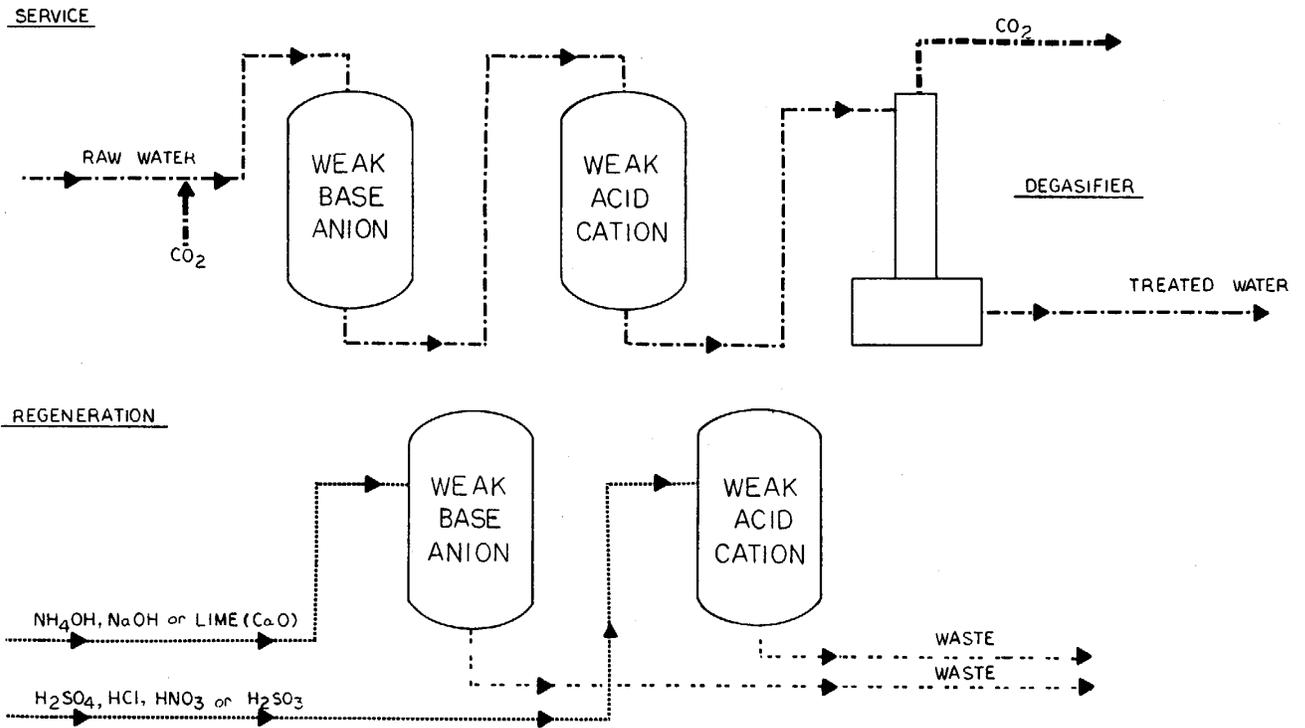


Figure 8-4. Two-unit variation Desal Process.

A typical cation-anion two-bed demineralization flow sheet is shown in figure 8-5. The cost of ion-exchange regeneration, including regeneration waste disposal, is directly related to the amount of dissolved solids to be

removed. For many small users, such as laboratories, replaceable mixed-bed ion-exchange cartridges are the most economical method used to obtain ultrapure water.

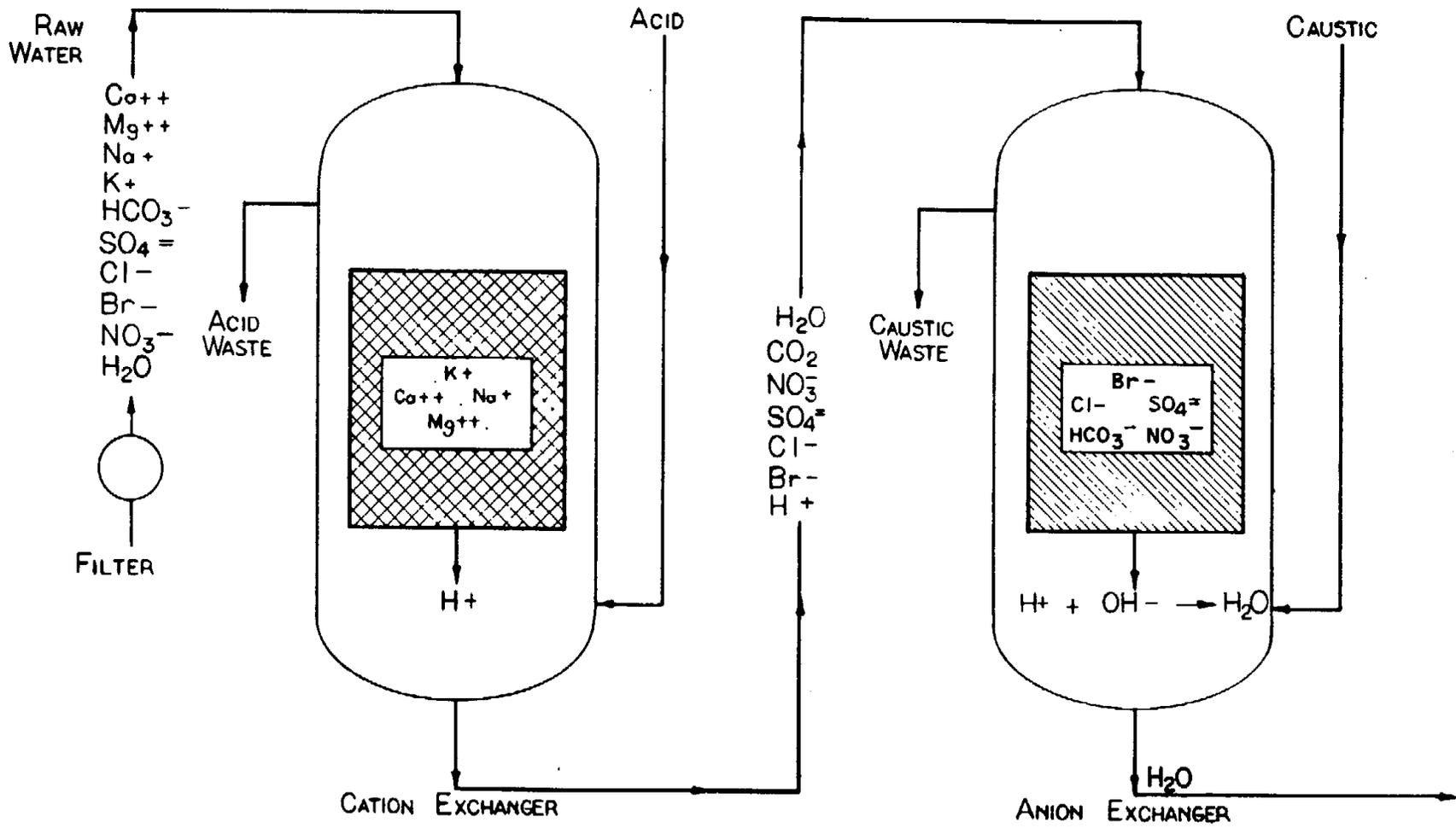


Figure 8-5. Demineralization two-bed flowsheet.