ION EXCHANGE
PROCESS CONFIGURATIONS

Ion exchange is used extensively in both water and wastewater treatment. Some of the common applications are

1. water softening,
2. demineralization
3. desalting
4. ammonia removal
5. treatment of heavy metal wastewaters
6. treatment of some radioactive wastes.

1. Split-flow Softening

One of the largest uses of ion exchange in environmental engineering is the softening of water by the exchange of sodium ions for calcium and magnesium ions.

Removal of all of the hardness is undesirable for a domestic water supply. Therefore, a portion of the flow may bypass the exchangers to give a blended water of the desired hardness. This process is called **split-flow softening**.

2. Demineralization

Ion exchange is used for the removal of all cations and anions from a water.

In total **demineralization**, the cationic resins are charged with the hydrogen ion and the anionic resins are charged with the hydroxyl ion.

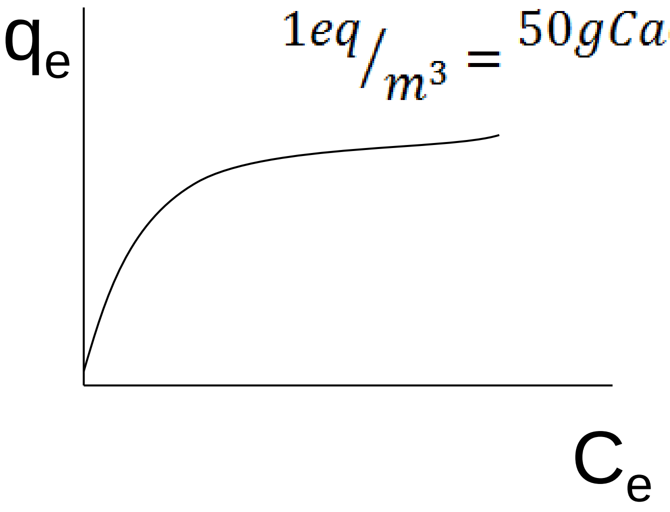
The cationic resins exchange **hydrogen** ions for **cations**, and the anionic resins exchange **hydroxyl** ions for **anions**.

2. Demineralization

Thus, the treated water has only hydronium and hydroxyl ions, which makes it essentially pure water. Industries using high- pressure boilers require demineralized water as boiler water. In addition, there are other industries that require demineralized water.

Thus synthetic resins are available that have both cation and anion exchange capabilities. Resin capacity is given by

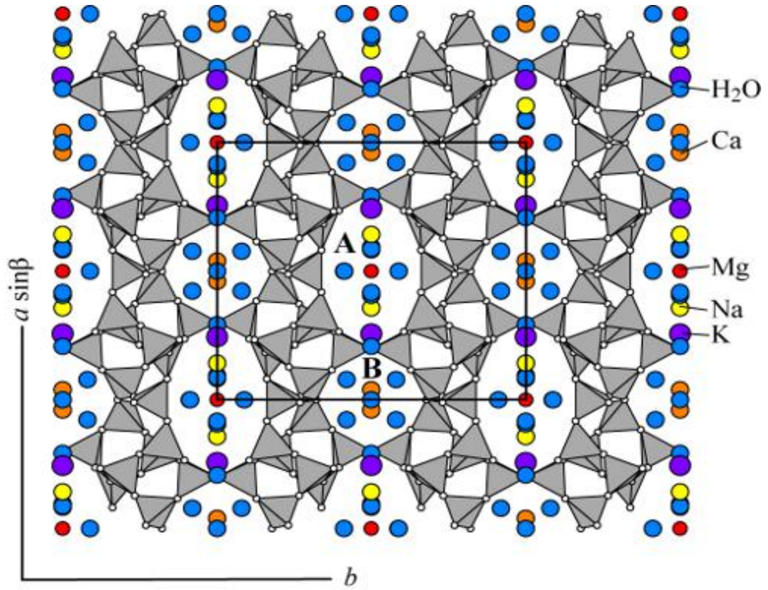
1. eq/m^3 of resin
2. gram as $CaCO_3$ / m^3



$$1eq/_{m^3} = 50gCaCO_3/_{m^3}$$

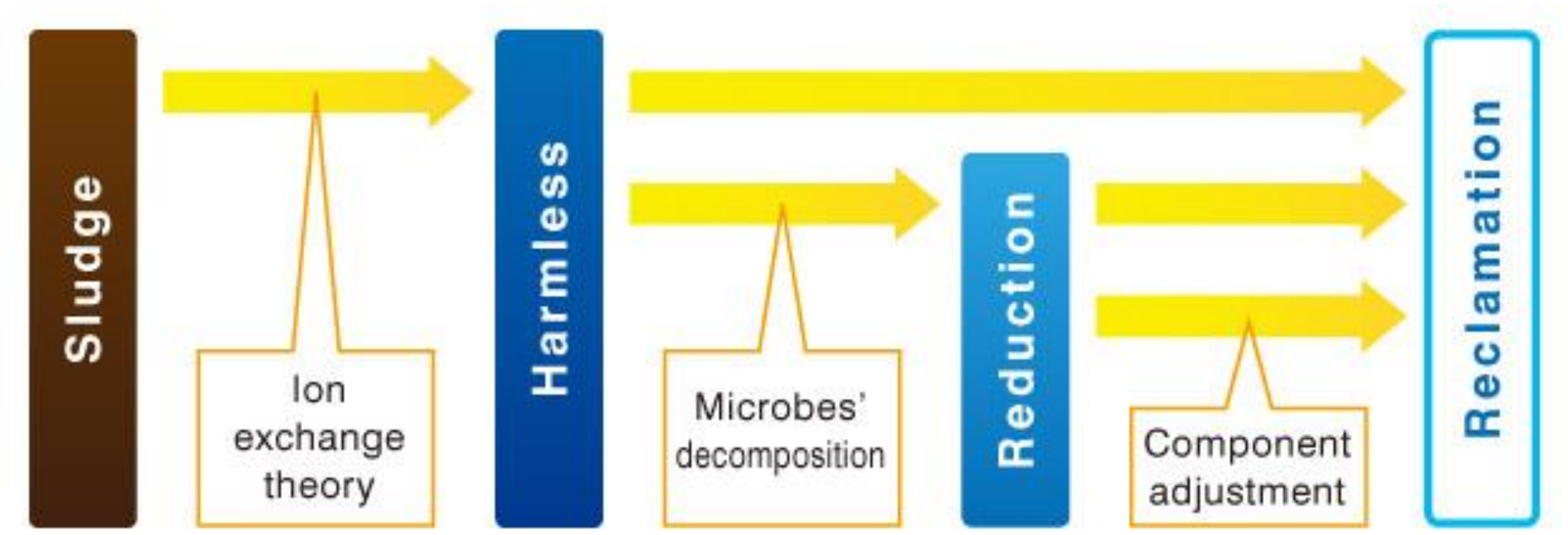
3. Ion exchange may be used for **partial demineralization** of wastewaters in tertiary treatment and of brackish waters for water supplies. Several ion exchange techniques may be employed, one of which is split-flow demineralization.

4. The natural zeolite, clinoptilolite may be used to remove ammonia in advanced waste treatment plants in lieu of or in addition to other methods of ammonia removal.



clinoptilolite

5. Ion exchangers may be used to remove heavy metallic ions from certain wastewaters. The heavy metallic ions are thus concentrated in the spent regenerate. An example is the treatment of wastewaters from a metal plating industry that contain zinc, cadmium, copper, nickel, and chromium.



http://www.giwgroup.com/en/system/sludge.html

Pollutants in the sludge caused by sewage treatment can be removed and the sludge can be turned into resources again.

The essence of sludge reclamation is to degrade heavy metal elements and reduce the quantity of sludge.

6. Clays and other minerals possessing ion exchange capacities are used to treat low- or moderate-level radioactive wastes to remove pre-ferentially such heavy metallic radionuclides as Cs^{137}.

Water Softening

Styrene based R – SO_3 – Na

$$Ca^{++} + 2R - Na \leftrightarrow R_2 - Ca + 2Na^{+}$$

$$Mg^{++} + 2R - Na \leftrightarrow R_2 - Ca + 2Na^{2}$$

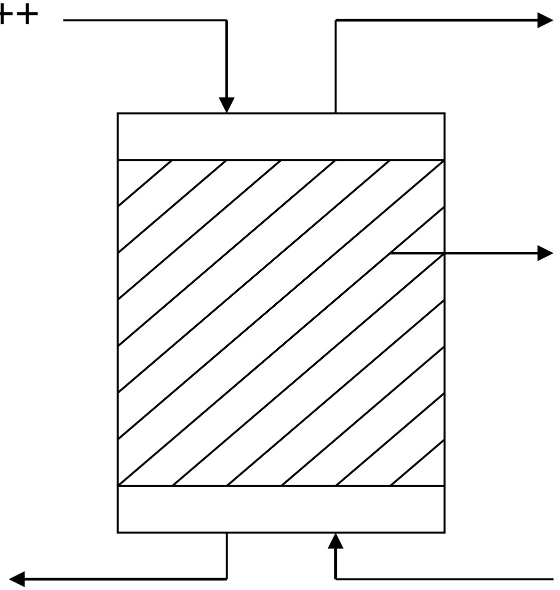
- R – SO3 – H
- R – OH
- R – COOH

After the solid is saturated with the Ca^{+2} and Mg^{+2}, it may be regenerated by a strong salt solution since the reactions are reversible. The regeneration reactions are

$$Ca.Ex_2 + 2Na^{+} \overset{\text{strong brine}}{\leftrightarrow} Ca^{+2} + 2Na.Ex$$

$$Mg.Ex_2 + 2Na^{+} \overset{\text{strong brine}}{\leftrightarrow} Mg^{+2} + 2Na.Ex$$

After regeneration, the exchanger solid is washed to remove the remaining brine and then is placed back on-line to soften more water.



water Ca^{++}, Mg^{++}

Ca^{2+}, Mg^{2+}

Regeneration of resins

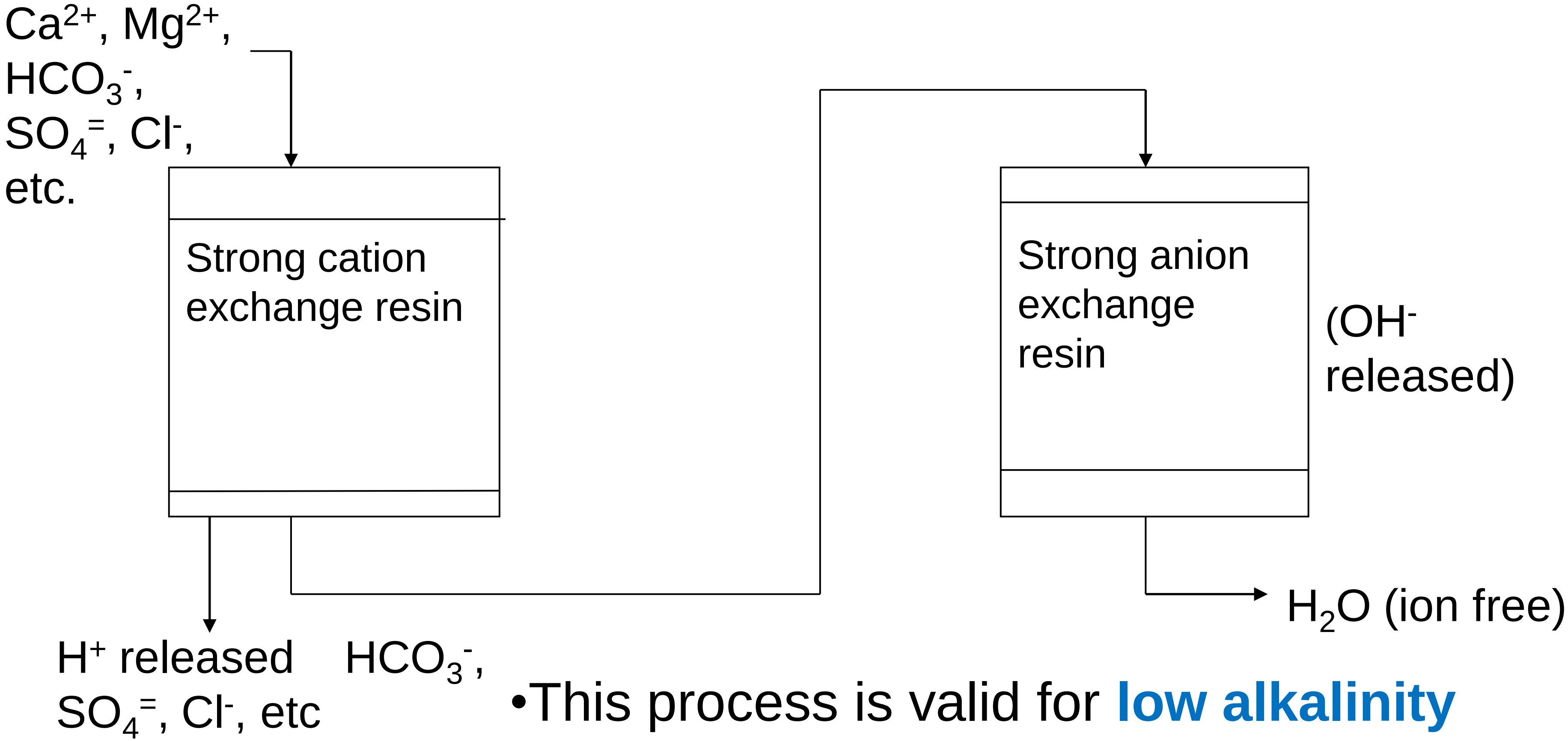
Na^{+}

Regenerant Na^{+} (strong brine)

This process does not have any limits.

Water Demineralization

The purpose is to remove all of the ions. The water will have only H_2O ions, pure water.



Ca^{2+}, Mg^{2+}, HCO_3^-, $SO_4^=$, Cl^-, etc.

Strong cation exchange resin

Strong anion exchange resin

(OH^- released)

H_2O (ion free)

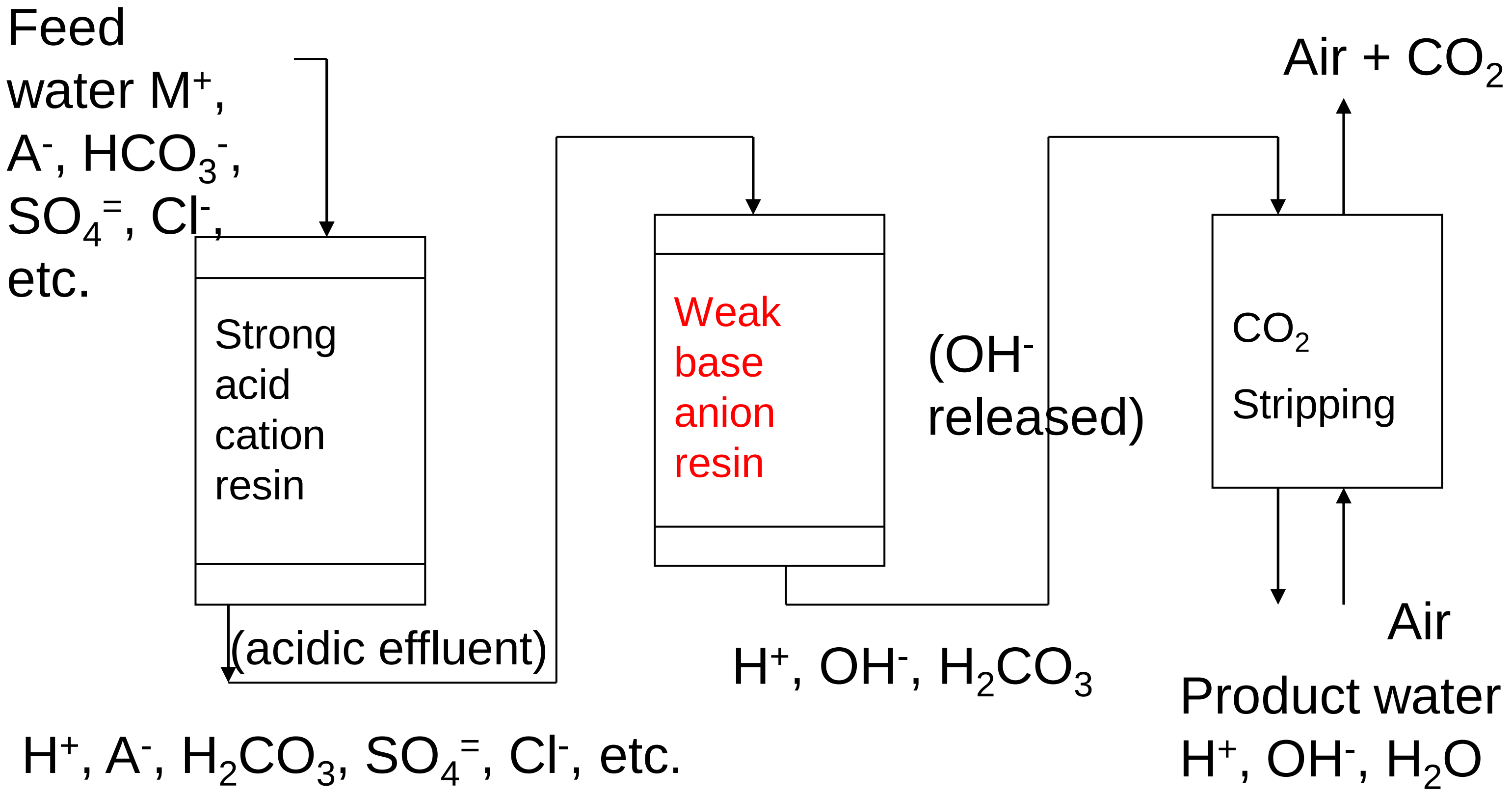
H^+ released HCO_3^-, $SO_4^=$, Cl^-, etc

- This process is valid for **low alkalinity** water, and **no silicate** (SiO_4^{4-}) in water.

Applied for water treatment in

- Beverage industry
- Pharmaceutical industry
- Boilers, cooling towers, etc.

From Reynold's, (page 383) :



Feed water M^+, A^-, HCO_3^-, $SO_4^=$, Cl^-, etc.

Strong acid cation resin

(acidic effluent)

H^+, A^-, H_2CO_3, $SO_4^=$, Cl^-, etc.

Weak base anion resin

(OH^- released)

H^+, OH^-, H_2CO_3

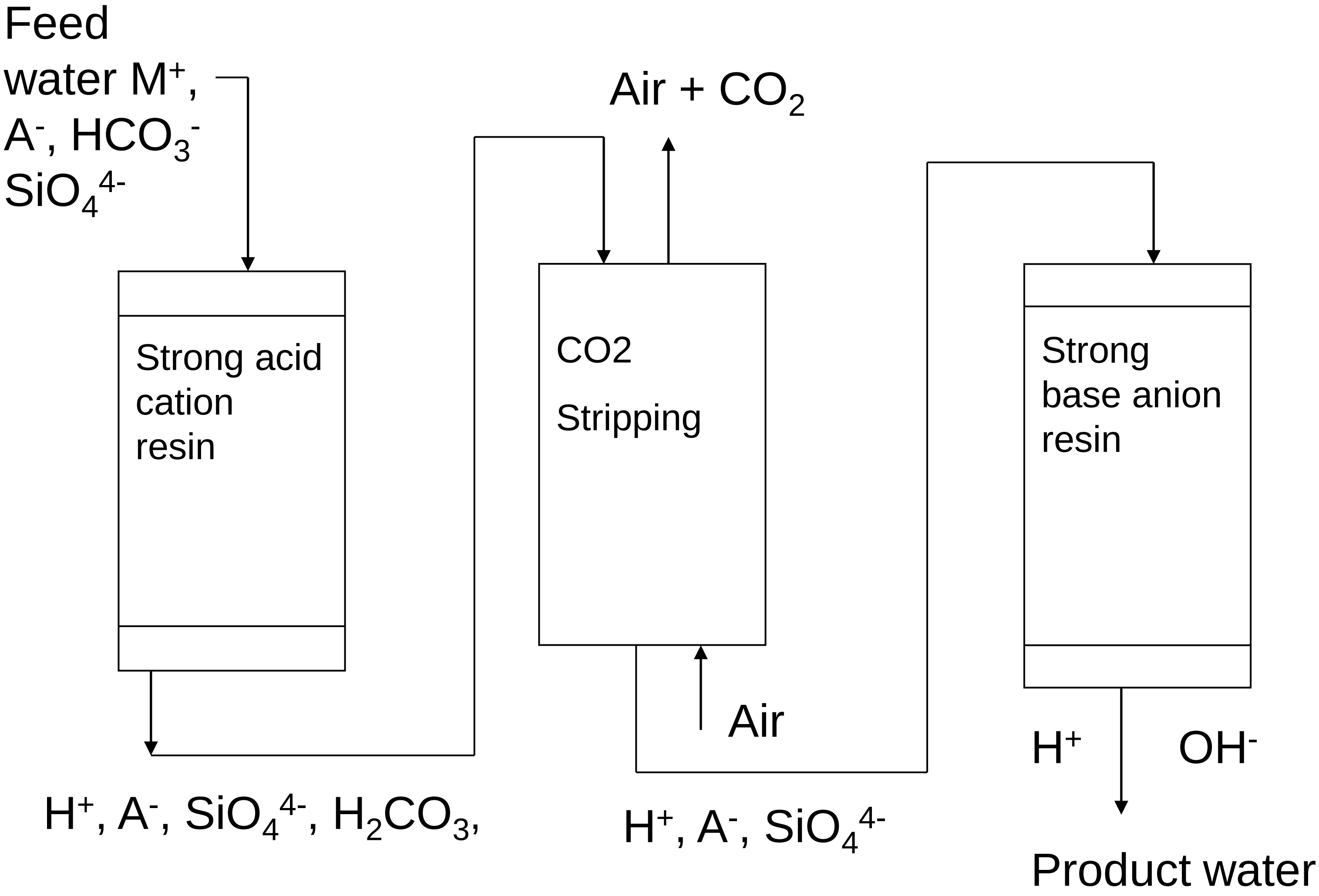
Air + CO_2

CO_2 Stripping

Air

Product water H^+, OH^-, H_2O

Figure 13.3 Demineralization where alkalinity is high but silicate reduction is not required.



Feed
water M^+,
A^-, HCO_3^-
SiO_4^{4-}

Strong acid
cation
resin

H^+, A^-, SiO_4^{4-}, H_2CO_3,

Air + CO_2

CO2

Stripping

Air

H^+, A^-, SiO_4^{4-}

Strong
base anion
resin

H^+ OH^-

Product water

Figure 13.4 Demineralization where alkalinity is high and silicate removal is required.

In the demineralization of water, the water is first passed through cation exchange resins charged with the hydrogen ion. The cation removal may be represented by the reaction

$$M^{+x} + xH.Re \leftrightarrow M.Re_x + xH^+$$

where M^+ represents the cationic species present and x is the valence number. After passing through the cation exchange resins, the water passes through anion exchange resins charged with the hydroxyl ion.

The anion removal may be represented by the reaction :

$$A^{-z} + zRe.OH \leftrightarrow Re_z.A + zOH^-$$

where A^- represents the anion species present and *z* is the valence number. After the resins become exhausted, the cation exchange resins are regenerated using a strong mineral acid such as sulfuric or hydrochloric acid. In a similar manner, the anion exchange resins are regenerated using a strong base such as sodium hydroxide.

Exchange resins are usually bead- or granular-shaped, having a size of about 0.1 to 1.0mm. The ion exchange ability of resins may be as "strong" or "weak" according to the characteristics of the capability (Dorfner, 1971).

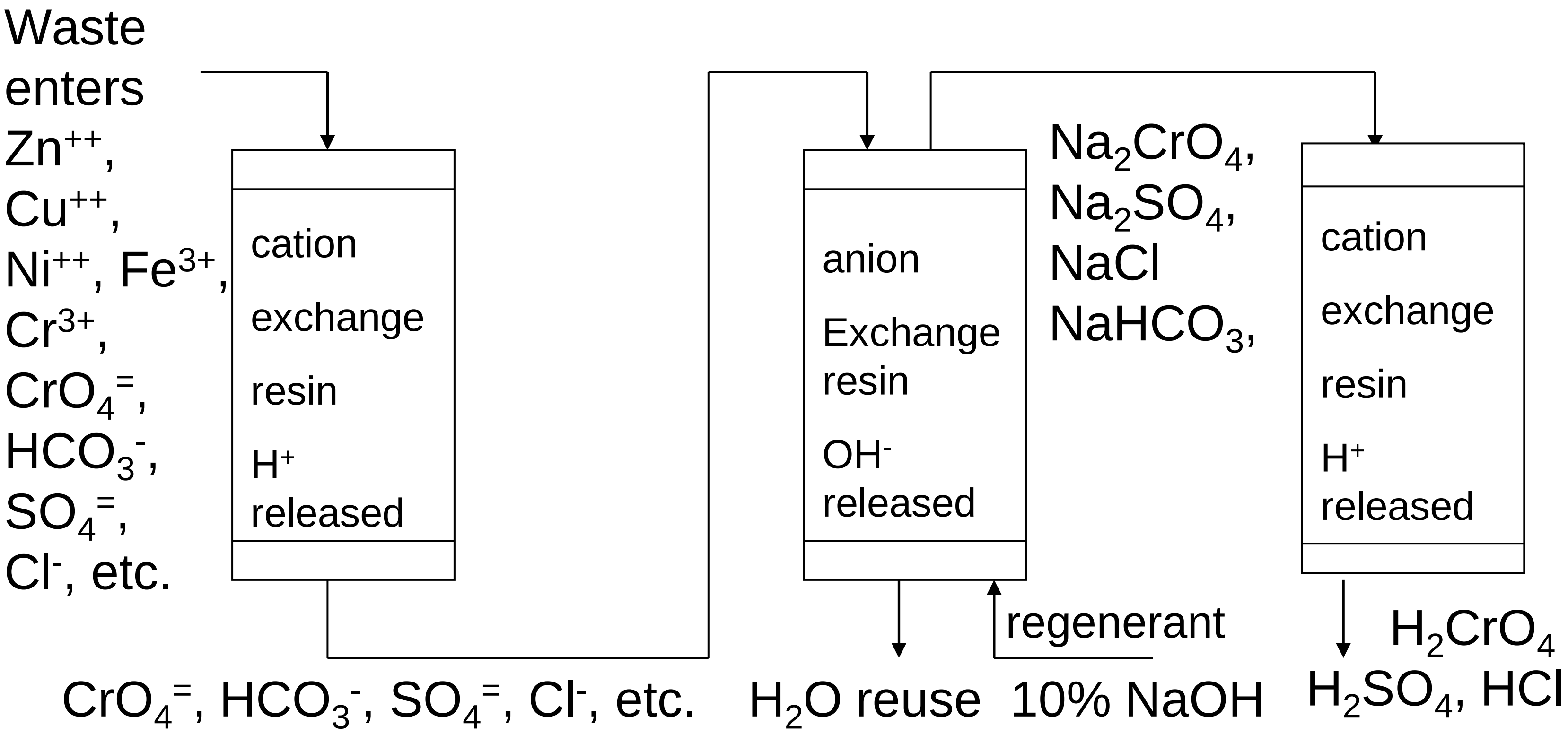
The strong acid cation resins have strong reactive sites such as the sulfonic group ($-S0_3H$), and the resins readily remove all cations. Conversely, the weak acid cation exchange resins have weak reactive sites such as the carboxylic group (-COOH), and these resins readily remove cations from the weaker bases such as Ca^{+2} and Mg^{+2} but have limited ability to remove cations from strong bases such as Na^+ and K^+.

The strong base anion exchange resins have reactive sites such as the quaternary ammonium group, and these resins readily remove all anions.

The weak base anion exchange resins have reactive sites such as the amine group, and these resins remove mainly anions from strong acids such as $S0_4^{-2}$, CI^-, and $N0_3^-$, with limited removal for $HC0_3^-$, $C0_3^{-2}$, or SiO_4^{-4}.

Recovery of Valuable Metals

Recovery of valuable metals, e.g. Cr (VI) in the form of $CrO_4^=$, Zn, Ni, Cd, etc.



Waste enters Zn^{++}, Cu^{++}, Ni^{++}, Fe^{3+}, Cr^{3+}, $CrO_4^=$, HCO_3^-, $SO_4^=$, Cl^-, etc.

cation exchange resin H^+ released

$CrO_4^=$, HCO_3^-, $SO_4^=$, Cl^-, etc.

anion Exchange resin OH^- released

H_2O reuse

regenerant 10% NaOH

Na_2CrO_4, Na_2SO_4, NaCl $NaHCO_3$,

cation exchange resin H^+ released

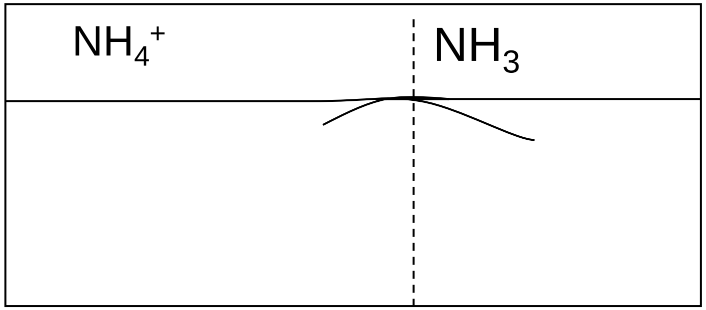
H_2CrO_4 H_2SO_4, HCl

NH_3 Removal

Clinoptilolite is particularly suitable for ammonium ion removal.

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

$pK_a = 9.3$



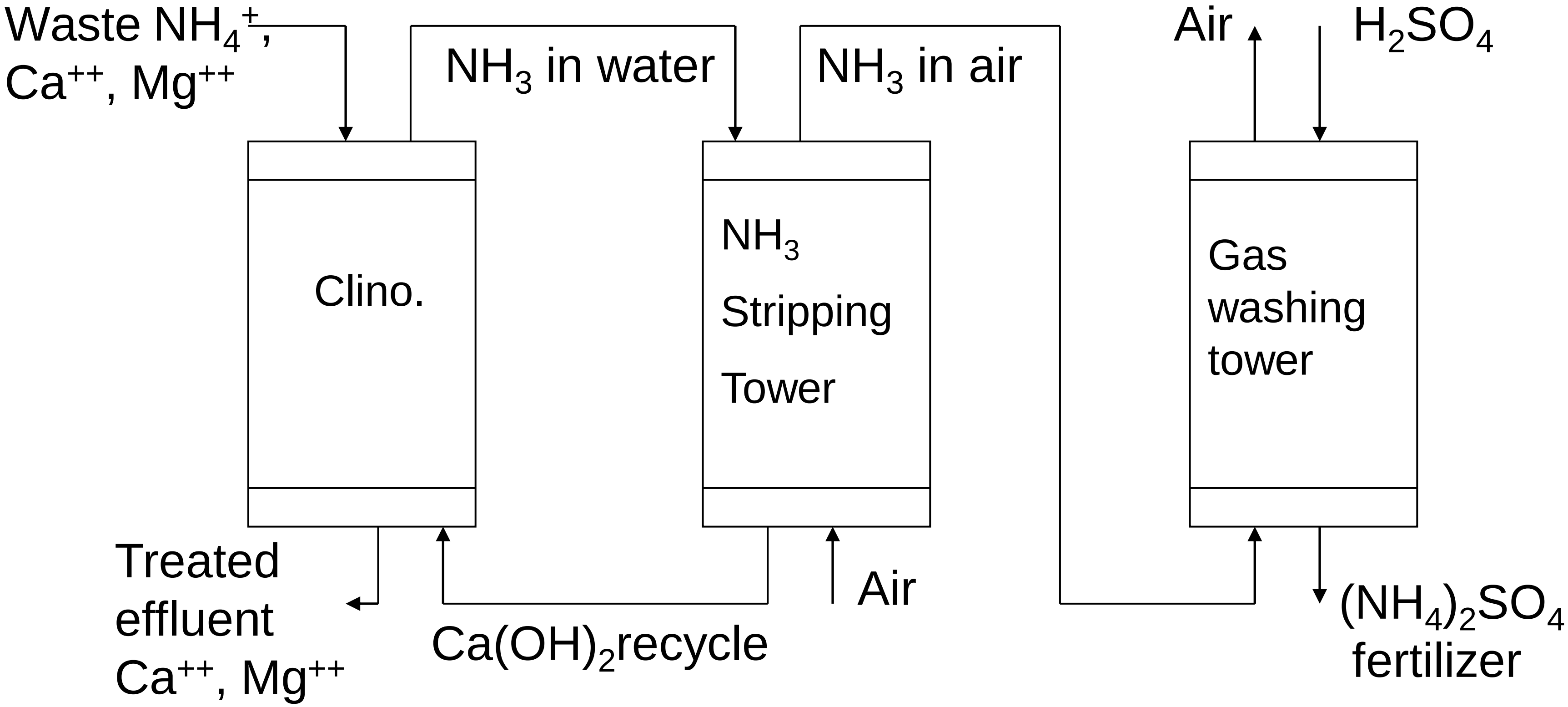
Below pH 9.3 NH_4^+ is the dominant form.

$pK_a = 9.3$

Regeneration :

a) Using $Ca(OH)_2$ as regenerant ;

Clinoptilolite has high selectivity for NH4+ over other higher charged ions.

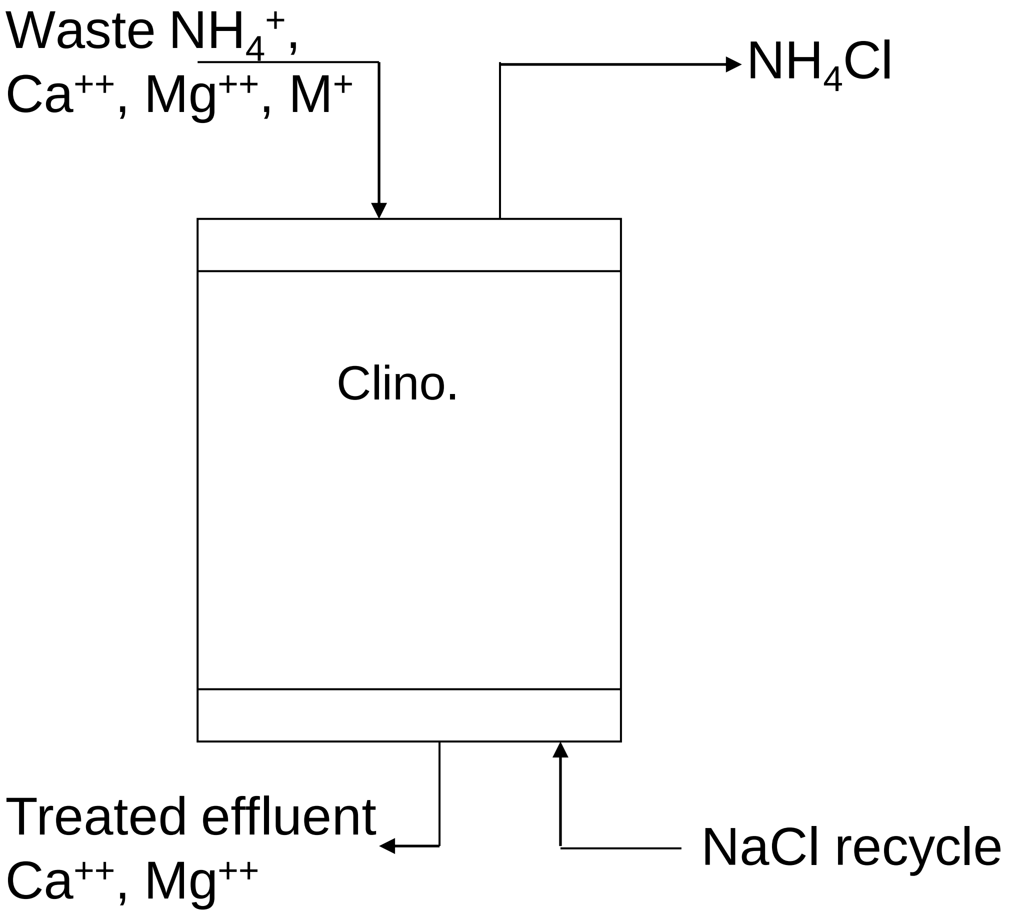


This system is very expensive. However, you can recover NH_4^+ as $(NH_4)_2SO_4$.
During regeneration ;

→high Ca^{++} concentration replaces NH_4^+
→high pH derives NH_4^+ to NH_3

Compared to direct NH_3 stripping, smaller tower is needed due to concentrated smaller volume to be treated, biogrowth is eliminated.
$CaCO_3$ and $Mg(OH)_2$ precipitation causes clogging requiring frequent backwashing.
High pH can affect the clino. structure.

b) Regeneration with NaCl ;



Waste NH_4^+,
Ca^{++}, Mg^{++}, M^+

NH_4Cl

Clino.

Treated effluent
Ca^{++}, Mg^{++}

NaCl recycle

Exchange of Na^+ is faster than Ca^{++}, less water is required.

$$NaCl + R - NH_4^+ \leftrightarrow NH_4Cl + R - Na$$

$$NH_4Cl \xrightarrow[\text{Chlorination}]{\text{Breakpoint}} N_2 + NaCl$$

- Ion exchange resins or zeolites have a limited number of ex available, and the total solid-phase concentration, q_o, is termed the **ion exchange capacity.** For cation exchange resins, it is usually between 200 to 500meq per 100 gms. Since a cation exchanger must remain electrically neutral during the exchange reaction, all of the exchange sites must be occupied by sufficient cations to balance the negative charge of the exchanger.

Thus, for a system involving Ca^{+2}, Mg^{+2}, and Na^{+}, the sum of the solid-phase concentrations of these ions must, at any time be equal to the cation exchange capacity, q_o. Electroneutrality applies to anion exchangers as well as to cation exchangers.