

CHAPTER III

BACKGROUND IN ION EXCHANGE PROCESSES

3.1. Introduction

Most ion exchanger resins in use today are synthetic materials consisting of a net work of hydrocarbon radicals with attached soluble ionic functional groups. They are considered as large three dimensional macromolecules containing fixed charges distributed uniformly throughout the structure. The total number of functional groups in a resin determines the exchange capacity and ion selectivity while the hydrocarbon matrix provides insolubility and toughness to the resin. During the synthesis of resins, a combining agent will be added to adjoin monomer building blocks together to form a larger and denser three-dimensional polymer, which is used as a matrix on which functional groups are attached. The functional groups should be amply provided in order to ensure a high exchange capacity.

Ion exchanger resins may be widely classified as cation and anion exchange materials. Cation exchange resins may be defined as polymers which contain phenolic, sulfonic, carboxylic or phosphoric anionic groups as an integral portion of the resin, and an equivalent number of cations. They may be sub-classified

into strong acid and weak acid types, depending on the functional groups. Anion exchange resins are similarly defined as polymers containing amine groups as integral parts of the polymer lattices, and an equivalent number of anions such as hydroxyl, chloride, and sulfate. They may also be sub-divided into strong base and weak base exchangers, again depending on the functional groups. Those resins in between are referred to as intermediate type resins. (7)

3.2 General Characteristics of Ion Exchange Resins.

3.2.1 Crosslinking

Crosslinking is one of the important characteristics of ion exchange resins. It influences not only the solubility but the mechanical stability, exchange capacity, water uptake and swelling behavior, volume changes in different forms of loading, selectivity, and chemical as well as oxidation resistance of ion exchangers. (8) A low degree of crosslinking is associated with high porosity and low resin density, as well as a high level of resin swelling in an aqueous media. Lowering the degree of crosslinking thereby results in a higher rate of exchange, a lower selectivity, and smaller volumetric capacity. Resins with low levels of crosslinking are also softer and less resistant to deformation and oxidation. In addition, this type of resin undergoes large contractions and expansions during the regeneration or exhaustion step. (7)

In contrast, highly cross-linked products are hard and brittle with an increased sensitivity to osmotic influence.⁽⁸⁾ They have better stability, more resistance to deformation and particle breakage, greater volume capacity and higher density. However, the degree of crosslinking above an optimum level (usually 8% DVB) are not recommended because the resins will tend to be too tightly bonded to permit the entrance of functional groups, thereby limiting the total exchange capacity.⁽⁷⁾

3.2.2 Ion Exchange Kinetics and Reaction Rate

When an ion in solution approaches an ion exchange resin, it encounters a stagnant film (the Nernst film) at the interface. It must pass through this film before diffusing into the pores or mesh openings to active exchange site, the ion will react to replace an ion of similar charge and the displaced ion will then diffuse out of the resin into the bulk solution. Transport of ion through a surface film to and from the exterior of resin particle is called film diffusion while diffusion of ion within pores of resin is called pore or intraparticle diffusion. The rate of ion exchange is determined by the diffusion rate within the resin (particle diffusion) or in the stagnant film (film diffusion). If the solution to be treated is very diluted, film diffusion may be the rate determining step. On the other hand, particle

diffusion tend to control in system with ample agitation, highly crosslinked resins, and/or large exchanging particle size. Generally, the net exchange rate of the ion exchange process is also affected by several other factor: a) concentration of the solution in contact with the resin, b) the degree of agitation, c) particle diameter, d) the degree of crosslinking, e) the degree of saturation of exchange capacity, f) pH of the system, g) acidity and basicity of resins, and h) temperature of the system. (7,9,10)

3.2.3 Affinity and Selectivity

The selectivity of ion exchangers is defined as the property of certain ion exchangers to exhibit a preferential activity for different ions.⁽⁸⁾ In dilute solutions under normal temperatures, the relative affinity has generally been shown to follow a certain pattern: the extent of exchange increases with increasing valence of the exchanging ion and with increasing atomic number (or decreasing hydrated ionic radius) of the exchanging ion if the valence is constant. The affinity of cation exchangers in dilute solution has been reported to be in the order of $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{+2} < \text{Ca}^{+2} < \text{Sr}^{+2} < \text{Ba}^{+2} < \text{Al}^{+3} < \text{Th}^{+4}$, while that of the anion exchangers is $\text{F}^- < \text{HCO}_3^- < \text{Cl}^- < \text{Br}^- < \text{CrO}_4^- < \text{NO}_3^- < \text{I}^- < \text{SO}_4^- < \text{PO}_4^{-3}$ ^(7,9) often referred to as Hofmeister or Lyotropic series. It is important to note that the above series are not followed in non-aqueous media, at high temperature, and of high concentrations.

At high concentrations, the differences in the exchange 'potential' of ions of different valence diminish and in some cases are even reversed, thereby permitting the possibility of regeneration.⁽⁷⁾

3.2.4 Resin Capacity

The capacity of a given resin may be expressed in terms of its total activity (Total or ultimate capacity) or its actual performance under specified conditions (Breakthrough or operating capacity).

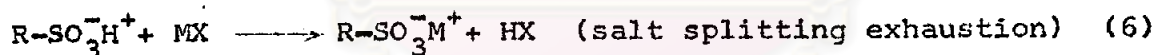
Ultimate or total capacity may be defined as the total quantity of ions which can be exchanged by a resin. It is equal to the number of chemical groups attached to the inert polymeric resin structure. It is also referred to as saturation-column capacity.

Breakthrough capacity is the capacity of the resin for exchanging ions from a solution flowing through a fixed bed of resin particles under specific conditions. It may be defined as the capacity of a resin bed when the solute being removed from the feed solution first begins to appear in the column effluent. It has been reported to depend upon the flowrate, bed depth, exchange particle size, the amount of regenerant used, the composition and concentration of the feed solutes, temperature, and desired quality or purity of the product water.⁽⁷⁾

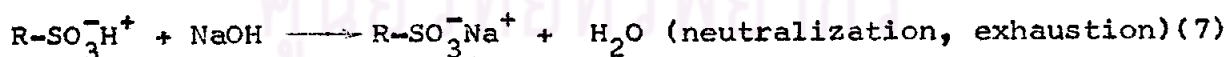
3.3 Characteristics of Strong Acid Cation, Weak Acid Cation, Strong Base Anion, and Weak Base Anion Resin

3.3.1 Strong Acid Cation Exchangers (SAC)

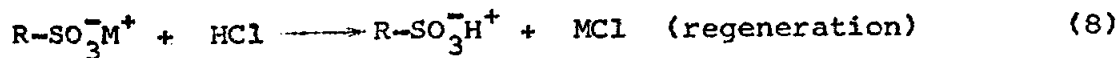
Strong acid cation exchangers are resins which contain functional groups derived from a strong acid, and owe the exchange properties to strongly acidic nuclear sulfonic acid groups ($\text{C}_6\text{H}_4\text{SO}_3^-\text{H}^+$). Their degree of ionization is analogous to that of mineral acids (low pK_a), which permits the hydrogen to be dissociated and ready for exchange over practically the entire pH range. They have fast reaction rates, and are the major cation exchangers used in deionization processes. In acid form, the SAC resins can split neutral salts, thereby converting the salts to their corresponding acids and the resins to salts.



They can also exchange with alkaline solution producing resin salt form and water:



Once exhausted, SAC resins can be regenerated with a strong mineral acid. However, because their affinity for H^+ ion is less than $\text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{+2} < \text{Ca}^{+2} < \text{Al}^{+3}$ and Fe^{+3} , all of which are common impurities removed by the resins, relatively high concentrations of strong acid must be added to upset the lyotropic series and to achieve the desired level of regeneration.



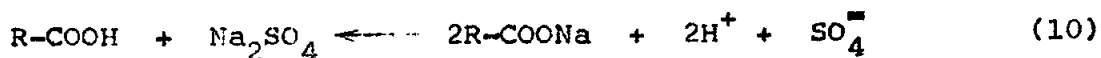
In addition, SAC resins may be used in the Na^+ form, as in water softening practice. The sodium ion exchange with calcium and/or magnesium (hardness) ions to yield a softened water with no reduction in total salt content.

3.3.2 Weak Acid Cation Exchangers (WAC)

Weak acid cation exchangers are those having carboxylic acid ($-COOH$) or phenolic hydroxyl ($-C_6H_4OH$) functional groups. Because their affinity for H^+ ion is greater than $Fe^{+3} > Al^{+3} > Ca^{+2} > Mg^{+2} > K^+ > Na^+ > Li^+$, they need only slightly more than the stoichiometric requirement to completely convert the resin to H^+ form. WAC resins can be regenerated by using the spent regenerant from a SAC resin. This practice makes better use of the regenerant and increases the regeneration efficiency. Because of its low dissociation constant ($pK_a \approx 6$ for carboxylic acid and ≈ 10 for phenol), the reaction employed by the WAC resins is rather slow. Consequently, operations involving these resins are more sensitive to flowrate and are effective only when the feed is high, or at least neutral, in pH.

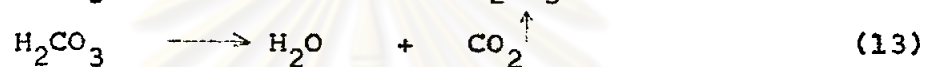
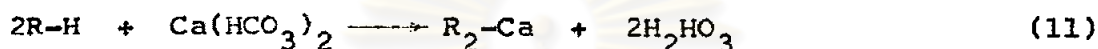


In solution of pH lower than 7.0 or, if only a neutral salt is present in a neutral pH influent, no exchange can be expected because the reaction will not be in favorable equilibrium:



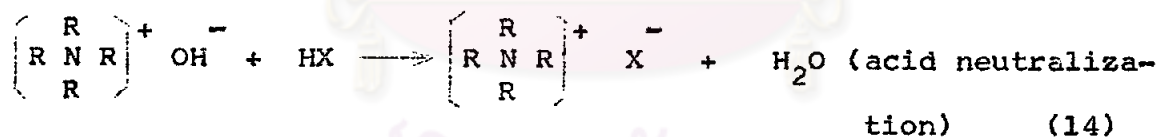
The affinity for H^+ ion will keep the dissociated H^+ ions attached to the resin and no exchange will occur.

When the feed pH is favorable, WAC resins can simultaneously remove alkalinity and hardness. The mechanism of the process may be demonstrated by the following equations.



3.3.3 Strong Base Anion Exchangers (SBA)

Strong base anion exchangers contain either type I or type II quaternary ammonium groups ($-NR_3OH$) as their functional groups. Their exchange mechanism is shown by the following equations:

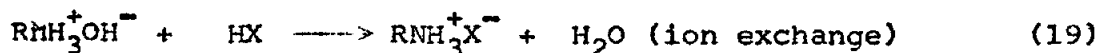
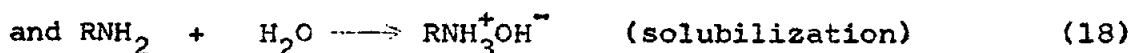


The hydration and the extent of swelling, which have a direct effect on exchange rate, increase extensively with degree of dissociation. Therefore, the SBA resins which are highly dissociated can employ a fast rate of exchange. Based on this high dissociation, the resins are in protonated form and hence are effective in exchanging over the entire pH practical range.

The OH^- form SBA resins can split neutral salts in the same manner as the SAC resins, and they also have the capability of removing very weak acids with the exchange behavior governed by mass action. The affinity of SBA resin for different ions increases with valence, mass, and degree of ionization in the order of $\text{SO}_4^{2-} > \text{CrO}_4^{2-} > \text{COOH}^- > \text{NO}_3^- > \text{CH}_3\text{COO}^- = \text{I}^- = \text{Br}^- > \text{Cl}^- > \text{F}^- > \text{OH}^-$. It is noted that the OH^- ion exhibits the lowest selectivity, making it the weakest replacing ion in this series. As a result, high concentration of NaOH at the level of 150 to 200% of the stoichiometric requirements are frequently necessary to achieve complete regeneration.

3.3.4 Weak Base Anion Exchangers (WBA)

The functional groups of WBA resins are primary ($-\text{NH}_2$), secondary ($-\text{NHR}$), and/or tertiary amine ($-\text{NR}_2$), with the more common resins containing mixtures of secondary and tertiary amine groups. The exchange reaction in the WBA systems can be explained either by the acid adsorption mechanisms or by the real exchange mechanisms as shown by the following equations:



At low pH, the resins are in protonated form which makes them capable of sharing an electron with mineral anions such as Cl^- , SO_4^{2-} and PO_4^{3-} . The carbonate species, however, are in non-dissociated H_2CO_3 form and sharing of electron will not result. This concept accounts for the behavior of WBA resins in not being able to remove weak acid. At high pH, the WBA resins are non-protonated or in inert form and no ion exchange reaction will occur. The feed to the WBA system has to be low in pH, ranging usually from 0 to 7 depending upon the dissociation constants of the WBA exchangers.

The affinity of the WBA resins for different anions is similar to that of SBA resins except that the OH^- ion has the highest priority in selectivity. Consequently, they need less regenerant and can be regenerated at higher flowrates, resulting in lower regeneration cost and less time. Some aspects of WBA system are of note. First, the capacity of the WBA resins for strong acids increases with the valence of ions. Secondly, the effectiveness of the WBA resins generally improves with a decrease in influent pH. (7)

3.4 Typical Operation Cycle of Ion Exchange

3.4.1 Exhaustion or Operating Cycle of Ion Exchange Process

In the treatment by means of ion exchange, the downflow fixed-bed techniques predominates. It is so called because the

exchanger material is not moved during exhaustion and stays compact (unexpanded) as a bed or column, through which the water or solution percolates during the exhaustion phase of the cycle. The percolation allows time for the ions in the solution to make contact with the exchange particles. The top of the column captures most of the ions during the downward flow, and the bottom receives the leftovers; therefore it is the bottom part that accomplishes the final purification and determines the purity of the effluent. (11)

Figure 2 shows the concentrations of Ca^{+2} ion in the influent and effluent of an exchange column as a function of the volume treated. The effluent concentration curve is normally referred to as a Breakthrough or Concentration History curve, and is a well-known characteristic of fixed-bed operation. This break-through curve is very sharp with the leakage line perpendicular to the time or volume axis (abscissa) if the system is operated under an ideal equilibrium condition (100% exchange) as shown in Figure 3. Under non-equilibrium conditions, however, leakage occurs earlier and the history curve is not as sharp. The result is that the curve tends to take on a S-shaped appearance. Deviation from the vertical line also increases with increases in flowrate, particle size, and any other factor that may decrease the rate of exchange. Ion concentration, system temperature and affinity of the resin for the exchanging ions are examples of

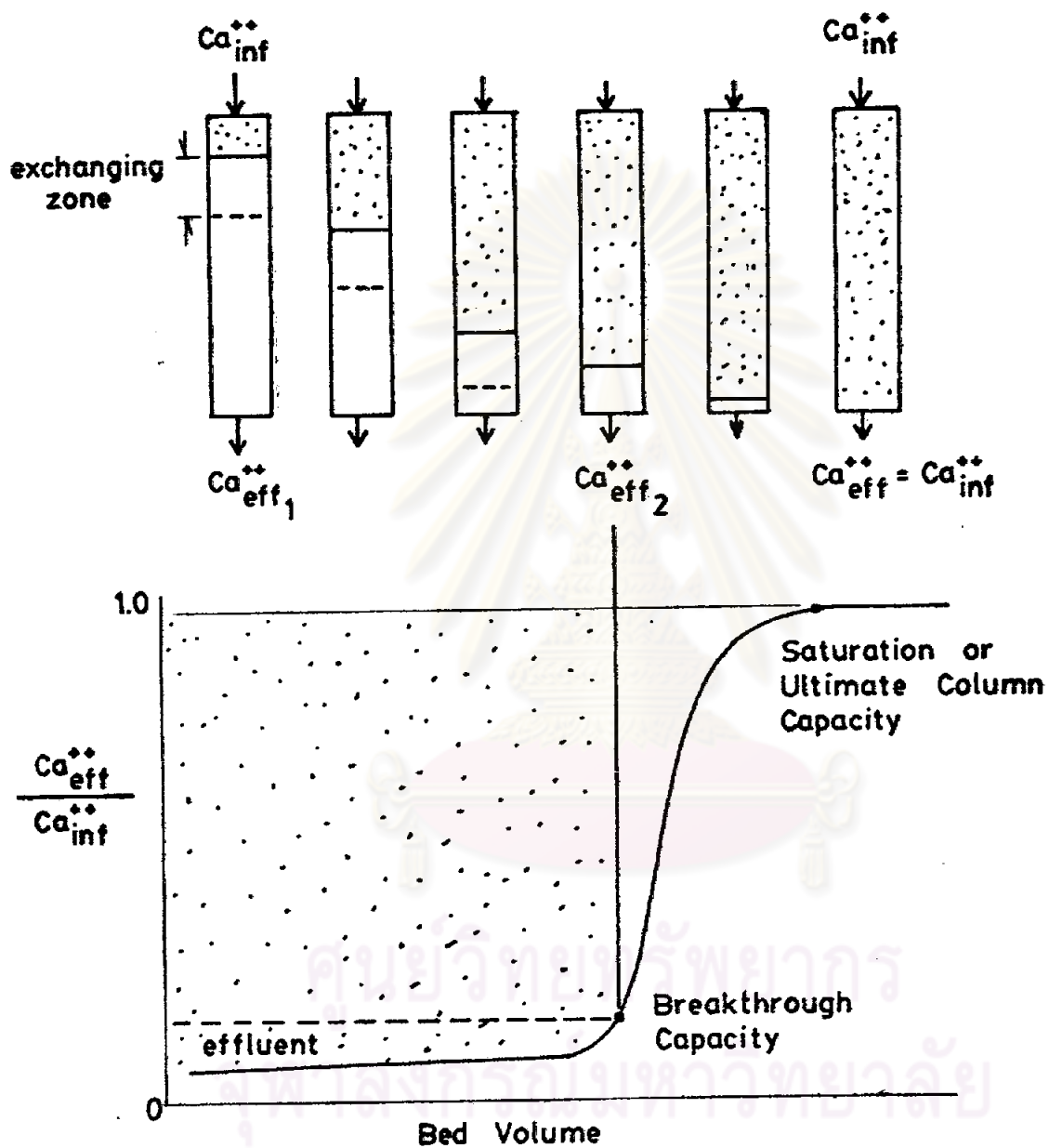


Fig.2 Concentration History for Exhaustion of a Cation Exchange Bed

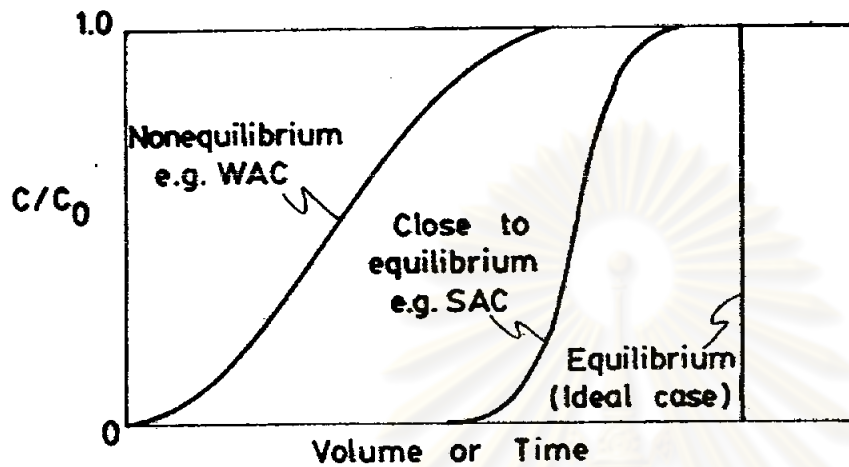


Fig. 3 Typical Concentration History Curves

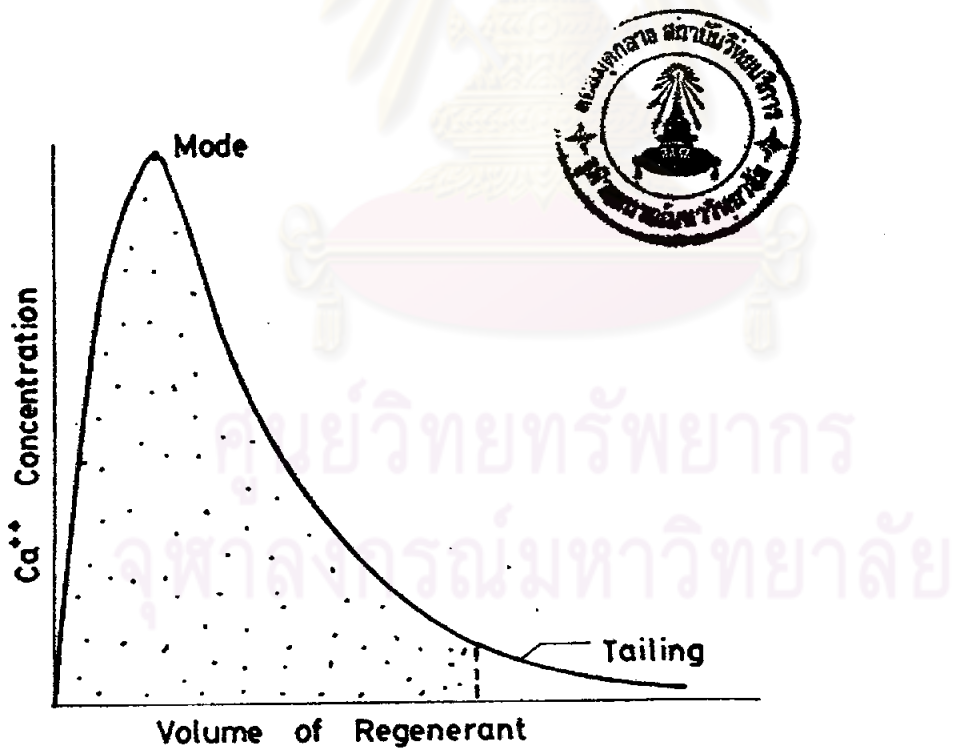


Fig. 4 Concentration History for Regeneration of Cation Exchange Bed

such factors. Increases in the regeneration level (the quantity of electrolyte used to regenerate the column) and bed depth have been suggested to reduce of leakage and steepen the S-shaped curve.

The demineralization process is usually performed at a flowrate of 8 to 32 BV/hr., with 16 BV/hr. being a common rate. Early breakthrough and more gradual concentration history curves generally occur with higher flowrates and increases in the influent concentration.

3.4.2 Backwash of Ion Exchange Columns.

Backwashing is practiced after an ion exchanger has completed an operating or exhaustion cycle. It is an upflow process which is used to loosen, expand, and re-stratify the resin bed so that flow will be uniformly distributed during subsequent downflow operations. It is also employed to remove dirt and other foreign matter which become entrapped in the resin media by filtration. In addition, exchanged ions which tend to be distributed in the bed in bands will be uniformly mixed over the entire length of the column by backwashing so that more effective regeneration can occur. Failure to expand a resin bed properly during backwash may permit the accumulation of dirt, silt, colloids etc., and cause a reduction in resin effectiveness, increment in the headloss across the bed and short circuiting. Three to six gpm/ft² has been reported as the range of optimum backwashing rates, with an accompanying 50 to 80 % bed expansion.

3.4.3 Regeneration of Ion Exchange Resin

The reverse of the exchanging reactions takes place in the regeneration phase. In the process the resins are restored to their initial capacities or to any other desired level. Numerous factors affect the degree of regeneration: 1) the type of resin and its crosslinking; 2) composition of the exhausted bed; 3) flow-rate; 4) temperature; 5) type of regenerants; 6) purity of regenerant; 7) concentration of regenerant; 8) amount of regenerant applied; and 9) contact time. A good regenerant solution should contain; 1) ions which are innocuous in water; 2) an ion which is held less strongly to the resin than ions which are to be removed from water in order to permit exchange in the exhaustion cycle; and 3) effective regenerant ions in a low-cost solution. Also, it should be a type that creates the maximum peak eluate concentration and minimizes 'tailing' of the eluate so that less time and regenerant will be required (see Figure 4). Concentration of regenerants normally varies from 2 to 30% with 5 to 10% being used most widely. The regeneration flowrate range is between 4 to 12 bed volume/hr. Sulfuric acid or hydrochloric acid are usually used for the regeneration of cation exchange resin. With sulfuric acid, the regeneration must be done carefully because the precipitate of CaSO_4 may form and tend to clog the resin bed. Hydrochloric acid can be used in place of sulfuric acid to avoid CaSO_4 formation, but the cost of hydrochloric acid is high and because of its corrosive characteristics a specialized container is required. Anion

exchange resins are normally regenerated with sodium hydroxide. The regeneration with lime may cause CaCO_3 precipitation if the influent contains a high concentration of carbonate alkalinity. (7,9)

Usually, the regeneration step is carried out with downflow direction which makes the top of the bed more completely converted to its original form than the bottom, but unless uneconomical amounts of excess regenerant are employed, the bottom usually contains a band of impure ions at the end of the regeneration. As the next service run starts, the impure ions in the influent are exchanged for the hydrogen or hydroxyl ions on the top of the bed. The hydrogen or hydroxyl ions are then exchanged for the impure ions in the bottom of the bed, releasing the ion leakage into the effluent. As the run progresses, this ion leakage decreases, because the impurity band at the bottom is gradually consumed.

On the other hand, with downflow exhaustion the regenerant may be passed upflow, or counterflow. This eliminates the impurity band at the bottom of the bed, because the excess pure regenerant passing upward through the bottom of the bed, converts it to the original form. Upflow, however, presents the problem of an expanding bed (if the rate of flow is high) and channeling (improper contact regenerant and resin). Counterflow regeneration is justified if the influent is high in solids and in sodium, because in such waters the sodium leakage is excessive, but for the usual

influent, which is not high in these, downflow regeneration give the same effluent quality and usually preferred. (11)

If sufficient regenerant is used, all exchangeable ions will be eluted from the resin and the exchanger will be restored to full capacity. Since this is a very costly practice, regeneration is usually carried out to an extent that only a portion of the available exchanger capacity is activated. This extent of regeneration is referred to as Regeneration Level (RL) which is represented by the quantity of regenerant used per unit volume of resin. (7,9)

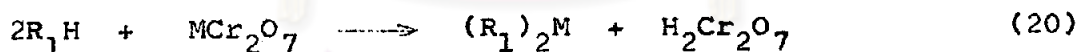
3.4.4 Rinsing of Ion Exchange Resins

After the regeneration step, the ion exchanger bed must be rinsed free of excess regenerant before being put into operation. The initial period is slow rinsing of which the flow is in the same direction as the regeneration flow. It is considered to be an extension of the regeneration step since any unused regenerant will be forced through the resin to produce further regeneration. The slow rinsing flowrate should be the same as or greater than the regeneration flowrate and desalted water volume of twice as large as the resin's volume should be used for this purpose. Once the slow rinsing is finished, the fast rinsing will be done at the same flowrate as in exhaustion step. The completeness of the rinsing operation may be checked by determining the pH or conductivity of the rinse effluent. Both of these parameters should be

close to the values in the original rinse water when rinsing is completed. (7)

3.5 Application of Ion Exchange to Chromium Containing Wastewater

In the attempt to recover chromic acid from an electroplating waste by using the ion exchange system, at least three exchange columns are required, see Figure 5. The first one shall be a H-form strong acid cation exchanger (SAC) while the second one is a OH-form strong base anion (SBA) bed. The last one is also a SAC column and is used as the recovery column. All the cations in the raw wastewater when fed to the system will exchange with the hydrogen ions attached to the SAC resins in the first column. This results in a release of hydrogen ions which, in turn, combine with the dichromate anions to become chromic acid. The reaction may be shown as follows:



when R_1 is the skeleton framework of the SAC resin,

H is the positive charged of functional group attached to the framework of the SAC resin,

R_1H is the hydrogen-form SAC resin,

MCr_2O_7 is the chromate salts present in the wastewater,

$(R_1)_2M$ is the exchanged SAC resin, and

$H_2Cr_2O_7$ is the produced chromic acid.

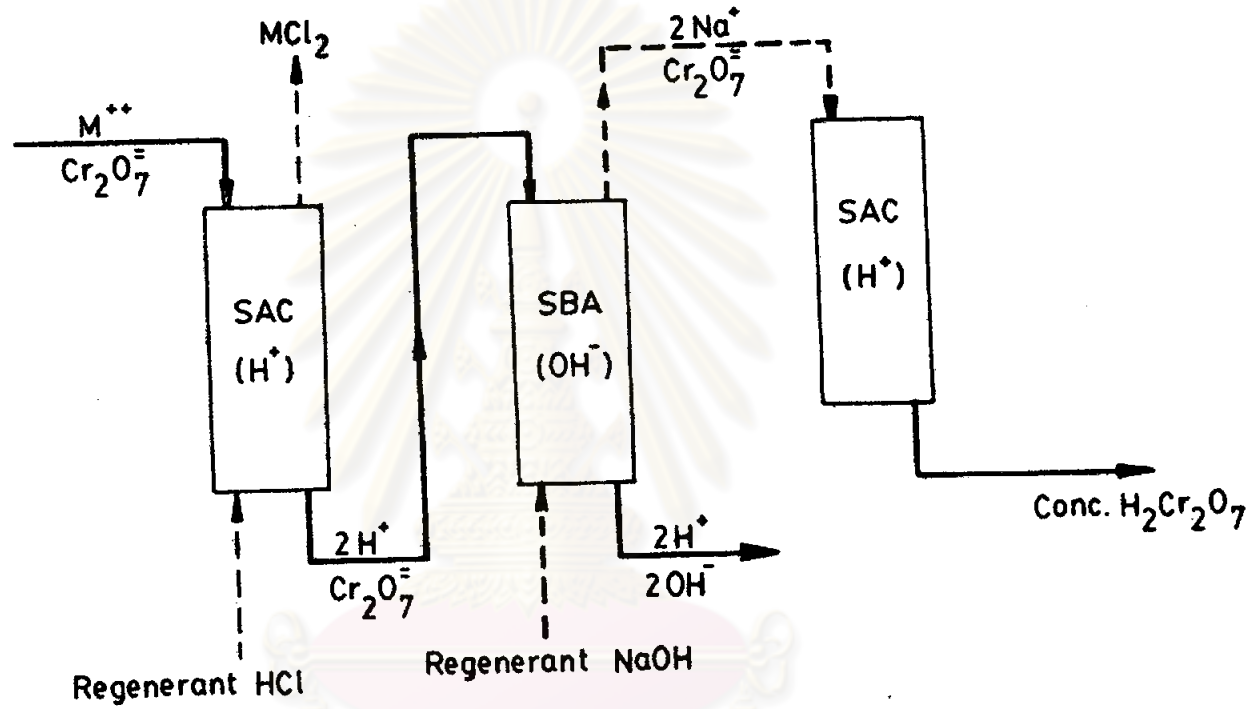
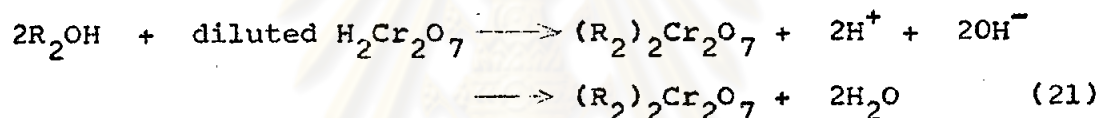


Fig. 5 Basic Diagram of Chromium Reclamation by Ion Exchange

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However, the chromic acid produced at this stage is too dilute for direct reuse. Its concentration relies upon the concentration of the dichromate salts ($M\text{Cr}_2\text{O}_7$) entering the first SAC bed. This is, generally, very low due to the fact that the process rinsed water contains small content of dichromate ions. This dilute wastewater, once passed through the SBA column, will contain theoretically nothing else but hydrogen ions and hydroxyl ions which combine together to become pure water. Equation (21) indicates the chemical reaction or exchange occurred.



when R_2 is the skelton framework of the SBA resin,

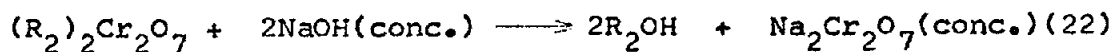
OH is the negative-charged of functional group present in the SBA resin,

$R_2\text{OH}$ is the hydroxyl-form SBA resin, and

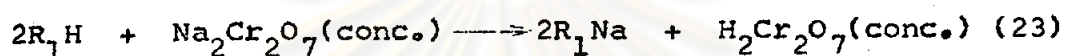
$(R_2)_2\text{Cr}_2\text{O}_7$ is the exchanged SBA resin

It is shown, therefore, that the chrome wastewater can be effectively treated by the ion exchange system.

The exhausted SBA resins which now have dichromate ions attached to their framework can be regenerated with sodium hydroxide solution, resulting in concentrated sodium dichromate solution as the eluate, see equation (22)



The concentration of sodium dichromate should vary as that of sodium hydroxide regenerant.^(8,11,12) If the concentrated sodium dichromate solution is sent to the recovery column which contains SAC resins, the concentrated chromic acid can be reclaimed as shown in the reaction in equation (23). The recovered chromic acid concentration is relating to the concentration of the



feed sodium dichromate solution and; as a result, depends, to a certain extent, upon the sodium hydroxide regenerant concentration.

On the other hand, the exhausted SAC column may be regenerated with hydrochloric acid. This process will result in a release of the chloride salt of the cation M which must be disposed away in the form of brine. Equation (24) shows the reaction of the SAC regeneration.

