Hardness Removal from Brine

(Extracted from the Diaion Manuals pages 229 to 231)

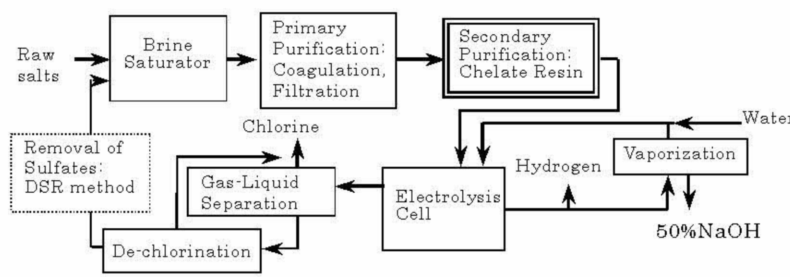
Chapter VII Purification of Chemicals

1. Removal of Hardness from Concentrated Brine

The removal of Ca, Mg and Sr from concentrated brines in chlor-alkali electrolysis factories, manufacturing factories of NaOH and Cl_2 by electrolysis of NaCl, is a typical example of removals of hardness form dense brines. Regarding manufacturing method of NaOH, the traditional mercury-cell process had been converted into the diaphragm process and the ion-exchange membrane process with "Minamata disease" that broke out early 1970's as a turning point. Then, the diaphragm process that needs asbestos membranes has been also converted into the ion-exchange membrane process, because of the malignant mesothelioma caused by asbestos.

Both solar salts and rock salts, raw salts, contain hardness such as Ca, Mg and Sr. In the ion-exchange membrane process, ions of these hardness move through membranes as well as sodium ion but sometimes they precipitate as their hydroxides within membranes due to strongly basic atmosphere. Such precipitates may cause interference of ions penetration, increase of operation voltages and damages onto membranes in the worst case. Accordingly, the concentrations of such materials in raw brines should be specified; e.g. Ca + Mg $\leq$ 20 μg-Ca/L and Sr $\leq$ 20 μg-Sr/L.

Fig.VII-1-1 illustrates a typical flow of the ion-exchange membrane process. Raw brines are usually treated as follows: a) dissolution, b) coagulation and filtration to remove hardness as carbonates or hydroxides with the addition of NaOH, soda ash and coagulants: primary purification, c) adsorption by chelate resin, CR11 etc.: secondary purification.



[Fig.VII-1-1] Typical Flow of Ion-Exchange Membrane Process of Electrolysis

Ca and Mg are considered to be the important impurities to be eliminated so far. Sr is also important from the point of "TTD" (time-to-degradation); the elapsed time until the operation voltage begins to rise and the membranes begin to deteriorate caused by impurities (44). The qualities of the treated brine after the primary purification should be controlled, e.g. Ca + Mg ≤ 10 mg-Ca/L, Sr ≤ 3 mg-Ca/L and temperature 60 ~ 80°C, though they vary in accordance with its own operation conditions, the total heat balance and other factors.

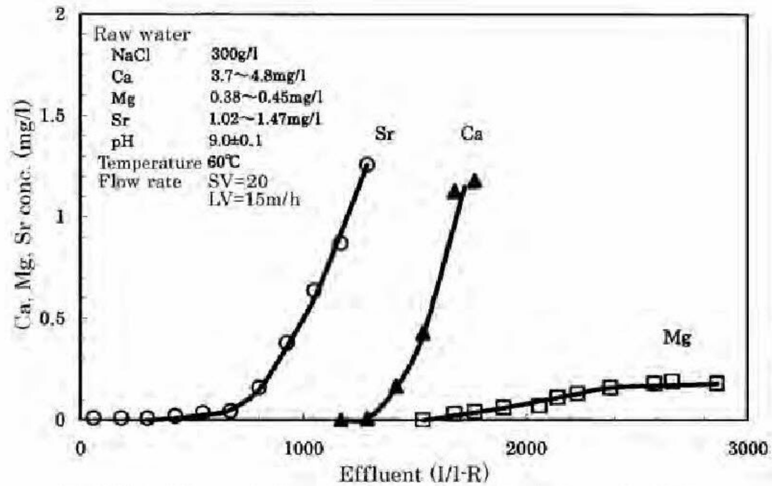
Chelate resin DIAION® CR11 has both very strong affinity with multi-valence metals and porous structures to accelerate reaction-rates. Thus, it can remove alkaline earth metal ions from saturate brines below the lower limit to analyze. Chelate resins applied in the secondary purification of brines should have enough heat resistance and physical strength to bear swelling or shrinkage caused by the changes of counter ions and outer solutions.

To remove perfectly the free chorine, derived from the return brines from the electrolysis cell, in the primary purification and to maintain the pH around 9, where the adsorption ratio is high and colloids such as $Mg(OH)_2$ never generate, are other important operation points in the secondary purification. Fig.VII-1-2 is an operation example. (45)

The resins that adsorb alkaline earth metal ions are regenerated; a) desorbed with HCl solution of around 1 mol/L, b) changed into Na-form with NaOH solution of around 1 mol/L. Points to notice in regeneration are a) to remove brines with sufficient washing with water, b) not to cause rapid volume change and c) to keep resin layers uniformly.

Two-tower alternate and series configuration is generally applied in the secondary purification. Three-tower system, two towers for serial feed and one tower for regeneration, or two-tower two-serial system are such examples with two advantages: one is to utilize the adsorption capacity effectively and the other is to use the second tower as a polisher. These two systems are best from all the evaluation points; stability of alkaline earth metals leakages, utilization rate of exchange capacity and resin volume needed.

The brines of KCl, raw materials for KOH, are secondary-purified as well as brines of NaCl.



[Fig.VII-1-2] Removal of hardness from concentrated brines with CR11(45)