Chapter IV-A

Characterisation of residue after evaporation generated from Leather industry

4A.1. Introduction

According to the data received from the studies of several researchers, approximately 200 kg of finished leather is manufactured from 1 ton of wet-salted skin/hide [69]. More than 600 Kg of solid waste (which constitutes 30-40% of inorganic salt) is generated during the transformation of 1000 Kg of raw skin/hide into leather. Sodium chloride which was added to inhibit microbial attack during transportation/storage of hides/skins is removed by soaking them in water. However, the soaking process consists of removal of NaCl adhered to hides/skins besides dissolution of soluble proteins such as albumin & globulin, dung and blood. The soak wastewater is evaporated in solar evaporation pans to get residue for disposal.

The tannery wastewater after primary clarification was treated through one or two stages of biological treatment systems. The secondary biological treated wastewater was subjected to membrane separation process for the recovery of water and consequently the reject stream with high TDS concentration. Membrane separation process has become increasingly attractive for the treatment and recycling of wastewater. But, the efficiency of the process was limited only upto 70% and the rest 30% of feed stream was considered as reject stream. The salt laden streams soak liquor
and RO reject streams were evaporated in solar evaporation pans (for small volume of discharge) or in multiple effect evaporator (MEE) (for large volume of discharge as in Common Effluent Treatment Plant) leaving behind the evaporated residue (RAE). The residue left after evaporation lacks the reusable option as it contains high concentration of organic, biological and microbiological impurities. Hence, the soak liquor and RO reject streams after evaporation in solar pans are dumped onto land lined with protective polymers. The risk factor associated with the land fill sites is leachability of salts from the land fill sites leading to the ground water contamination. The pollution control agencies have banned RAE for land filling since it produces non treatable saline leachate. Moreover, investment and maintenance costs towards treatment of leachate generated from secure landfill are very expensive. At present, the RAE is being packed and stored in the storage yard in all ETPs and CETPs of leather sector. The conditions become worsen, that the requirement of new land space for storing the RAE in proportion with the production capacity of leather sector. As the land cost is increasing over the years, augmentation of new land space becomes a limiting factor. Hence, there has been a constant research by many researchers on the disposal of RAE. Even though, the researchers have been focusing on the development of alternative curing system for skins/hides such as mobile chiller for transporting raw hide/skin from slaughter houses to leather process industries and pickle free tanning to reduce the salt emission in leather processing [70]. However, the generation of inorganic salts in leather processes is inevitable as usage of alkalies and acids are still in practice. Several organic salts
added along with the inorganic salts are expected to be disposed off in an environmentally safe manner.

The complication on disposal of RAE is due to contamination of inorganic salts with organic salts. The characteristics of solid wastes generated from the leather industry are well documented; but reports on characteristics of residue after evaporation are very little or perhaps nil [13]. The disposal techniques for the inorganic salts mixed with high level of organic solid waste are very few or perhaps nil. The separation of alkali salts from the mixture becomes mandatory for the disposal onto secure landfill sites. Thus, an attempt was made in the present investigation to separate sodium chloride from RAE by chemical precipitation process. A detailed characterization of RAE generated from leather industry was carried out in this chapter IVA as a part of the present investigation.

4A.2. Materials and methods

4A.2.1. Source of residue after evaporation

The RAE of soak liquor and RAE of RO reject stream were collected from solar evaporation pan of effluent treatment plant in a commercial tannery, Tamil Nadu, India. In order to get wide range of characteristics, RAE samples were collected from various industries processing skin and hides as raw materials. The samples were labeled as S₁ & S₂ for RAE generated from skin and hide of soak liquor evaporated in solar
evaporation pan; R₁ & R₂ for RAE of RO reject stream (from wastewater generated while processing skin and hide) evaporated in solar evaporation pan.

4A.2.2. Characterization of RAE

The RAE samples were randomly collected from leather industries processing skins and hides. Inorganic salt laden solid waste was homogenized and dried and stored until further experiments.

The various process parameters such as moisture content, pH, Total Kjeldahl nitrogen, sodium, chloride, sulphate and soluble organic substances in dichloromethane were determined in accordance with APHA [69].

4A.2.2.1. Atomic absorption spectroscopy (AAS)

Na, Ca, Cr and Fe content in RAE of soak liquor and RO reject stream were determined as follows. A known weight of RAE samples were first pre-treated in acid digestion process and were made upto 100 mL with distilled water. The digested samples were analyzed using Atomic Absorption spectrophotometer (Perkin-Elmer 3110). Cr was measured at \( \lambda = 357.9 \) nm with 0.7 slit intervals by using air-acetylene mixture, Fe was measured at \( \lambda = 248.3 \)nm with 0.2 slit intervals by using air- acetylene mixture, Na was measured at \( \lambda = 589.6 \)nm with 0.2 slit intervals by using air-acetylene mixture and Ca was measured at \( \lambda = 422.7 \)nm with 0.7 slit intervals by using air-acetylene mixture.
4A.2.3. Preparation of saturated solution of RAE

The saturated solution of RAE was prepared by dissolving 600 g of RAE in 1 L of distilled water under agitation. The RAE was contaminated with sand, grit, suspended matter, soluble proteins and insoluble lime during evaporation in solar pans. Hence, the RAE was pre-treated through grit chamber and filtration using sand filter. The supernatant solution was transferred to another container to separate the grits settled at the bottom of the container. Then, the resulting solution was allowed to stand for 30 min to settle coarse suspended particles before it was filtered through sand filter. The design of sand filter consists of a layer of gravel (5 mm) to a depth equal to $1/12^{th}$ of height of the reactor from the bottom of the reactor. This was followed by a layer of gravel (3 mm) to a depth equal to $1/15^{th}$ of the height of reactor. This was followed by a layer of coarse sand (1 mm) to a depth of $2/3^{rd}$ of reactor height. The header and laterals positioned at the gravel packing medium to collect the filtered RAE saturated solution. The void space in the gravels at the bottom facilitates the filtration of saturated RAE solution. The filtered solution was collected through an assembly consisting of header of diameter 10 mm and laterals of diameter 5 mm. The laterals were perforated with holes of diameter 0.8 mm.
4A.3. Results and discussion

4A.3.1. Moisture content and loss on ignition

Table 4A.1a shows that the moisture content of RAE of soak liquor (derived from goat skin and buffalo hide) and RO reject stream was found to be 14.3 % and 15.3 % respectively. The loss on ignition of RAE of soak liquor and RO reject was found to be 16.3 % and 18.4%. The moisture content of RAE varied to a greater extent with the mode of collection, storage conditions and prevailing climate. The percentage moisture content of RAE is of greater significance during storage period. Due to high moisture content in leather wastes, or natural environment conditions like rain or snow, infusion of the soluble salts in RAE into soil and surface/ground water cause the deterioration of the receiver environment. The damage is very much accelerated in the case of solid wastes containing soluble inorganic salts.

Table 4A.1a Characteristics of RAE of soak liquor and RO reject stream generated in Leather industry

<table>
<thead>
<tr>
<th>Type of RAE</th>
<th>Moisture Content (%)</th>
<th>TS with grits (g/L)</th>
<th>TDS (g/L)</th>
<th>TSS (mg/L)</th>
<th>VDS (mg/g)</th>
<th>VSS (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>12.3±1.5</td>
<td>530±2.5</td>
<td>334±1.2</td>
<td>149±2.1</td>
<td>18.8±2.5</td>
<td>110±0.8</td>
</tr>
<tr>
<td>R1</td>
<td>12.8±2.3</td>
<td>572±3.2</td>
<td>328±0.5</td>
<td>192±2.0</td>
<td>15.3±2.0</td>
<td>144±1.3</td>
</tr>
<tr>
<td>S2</td>
<td>12.8±1.5</td>
<td>545±4.5</td>
<td>337±3.4</td>
<td>166±2.3</td>
<td>20.2±2.5</td>
<td>120±0.7</td>
</tr>
<tr>
<td>R2</td>
<td>13.0±2.3</td>
<td>589±2.3</td>
<td>334±1.1</td>
<td>211±1.5</td>
<td>15.1±2.0</td>
<td>156±1.2</td>
</tr>
</tbody>
</table>
4A.3.2. Volatile dissolved salts (VDS) of RAE

TS, TDS, TSS were evaluated for the RAE of soak and RO reject stream and presented in Table 4A.1a. VDS and VSS were determined in both RAE (soak liquor and RO reject stream) using muffle furnace at 550°C for 90 min. The saturated solution of, RAE of soak liquor and RAE of RO reject stream were prepared by dissolving 535 and 580 g/L respectively in deionised water and the corresponding average TDS was found to be 330 g/L for both RAE (soak liquor and RO reject stream). VDS and VSS were varied from 10 to 20 mg per gram of RAE and 100 to 160 mg per gram of RAE (S₁, S₂, R₁ and R₂).

4.3.3. Chemical oxygen demand (COD) of RAE

The moisture free RAE (S₁, S₂, R₁ and R₂) of weight 1g was dissolved in 100mL of deionised water. The pH of S₁ and S₂ solutions were observed to be in the neutral range, i.e. from 7.5 to 8.6. Generally, pH of the RO feed is maintained in the range of 6.8 to 7.5 to avoid precipitation of inorganic salts onto the membrane active surface. The pH of RAE (R₁ and R₂) generated from RO reject stream was in the range of 7.8 to 8.5 which could be due to the increase in concentration of divalent and multivalent ions in the RO reject.

The raw hides/skins contain high percentage of fats and proteins. During soaking the raw skins/hides in soaking pit/drum for 18 to 24 hr, the animal fats, tissues, stained blood and albumin & globulin are dissociated and dispersed in water. This
constitutes the organic content of soak wastewater. The results presented in Table 4A.1b show that the maximum amount of organic content in soak liquor RAE (S₁ and S₂) was 10.3 mg/g and in RO reject stream RAE (R₁ and R₂) was 13.8 mg/g. The excess organic content in RAE of soak liquor and RO reject stream may also be due to algae growth and contaminants in the surrounding environment during evaporation in solar pans.

Table 4A.1b Characteristics of RAE of soak liquor and RO reject stream generated in Leather industry

<table>
<thead>
<tr>
<th>Type of RAE</th>
<th>pH*</th>
<th>COD (mg/g)</th>
<th>Oils and grease (%)</th>
<th>TKN (mg/g)</th>
<th>Salt (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>7.4-8.6 (7.8)</td>
<td>67.1±0.8</td>
<td>0.06±0.02</td>
<td>0.25±0.1</td>
<td>59.2±2.0</td>
</tr>
<tr>
<td>R₁</td>
<td>6.8-8.8 (7.6)</td>
<td>48.0±0.5</td>
<td>0.01±0.01</td>
<td>0.05±0.02</td>
<td>55.2±2.2</td>
</tr>
<tr>
<td>S₂</td>
<td>7.5-8.3 (8.0)</td>
<td>64.3±0.6</td>
<td>0.04±0.05</td>
<td>0.23±0.1</td>
<td>58.5±2.2</td>
</tr>
<tr>
<td>R₂</td>
<td>7.0-8.4 (7.7)</td>
<td>42.4±0.4</td>
<td>0.01±0.01</td>
<td>0.04±0.02</td>
<td>53.4±2.2</td>
</tr>
</tbody>
</table>

* pH value is expressed as range and median value.

4A.3.4. Oils and grease of RAE

The fat in raw hides/skins affects leather processes by retarding the diffusion of chemicals into the raw materials, and also causes a strong odour emission due to enhanced microbial activities and consequently defects like spew on leathers are imparted. Thus, maximum amount of fat in hides/skins are removed before tanning by
degreasing process using organic solvents. Another source of fat in RAE is the natural oil or synthetic fat liquors used in the fat liquoring process in order to impart leather with characteristic properties such as softness, elasticity and resistance, and to facilitate the collagen fibrils to slide easily over one another according to the type of leather produced and end use. The dispersed fat in wastewater was removed as much as possible in the primary treatment steps and the rest was oxidized in biological treatment processes. The membrane separation processes retain the fatty substances either in the free forms or in the combined forms with divalent/multivalent salts and thereof they enter in the reject stream. Thus, the RAE of soak liquor and RO reject stream contain a considerable concentration of fatty substances. The percentage of fat content was 0.06% (Table 4A.1b) in RAE of soak liquor (S₁ and S₂) and 0.01 % in RAE of RO reject stream (R₁ and R₂).

4A.3.5. Nitrogen content of RAE

Determination of total Kjeldhal nitrogen (TKN) facilitates to calculate the amount of proteinaceous organic content of RAE. The TKN content of RAE soak liquor (S₁ and S₂) and RO reject stream (R₁ and R₂) was estimated to be in the range of 0.23-0.25 mg/g and 0.04-0.05 mg/g respectively (Table 4.1b). The TKN was found to be very less in RAE of R₁ & R₂ than in RAE of S₁ & S₂. A very less TKN content in R₁ & R₂ may be attributed to the maximum elimination of organic nitrogen during primary and secondary biological treatment of wastewater.
4A.3.6. Sodium Chloride Content of RAE

The salt contents in terms of sodium chloride were determined; it was found that salt content in both the sources of RAE (soak liquor and RO reject) samples varied between 50% (w/w) and 60% (w/w). The sodium chloride used in preservation of hides/skins during transportation and storage was desalted and removed in soaking process before it was considered for leather processing. The complete removal of sodium chloride was achieved in two to three times soaking the hides/skins. The soak wastewater was evaporated in solar pans and the dried residue was stored in the storage yard. The \( R_1 \) & \( R_2 \) generated by the thermal evaporation followed by solar evaporation. The RAE of soak liquor and RO reject stream lack reusable characteristics due to the presence of impurities. They have been dumped onto the secured landfills provided with polymeric protective liner along with in-situ monitoring devices for leachate detection. But, during the spring season dissolution of salts in leachate causes ground water contamination because the leachate severely affects the surrounding ecological systems. In addition, high salinity or total dissolved solids in wastewater causes high osmotic pressure, which results in reduced water availability to plants and retarded plant growth in salt intolerant crops [1]. The land co-disposal of RAE is associated with ground water contamination and thus recovery of specific major constituent from RAE may be an ideal approach. The recovery of constituents from RAE may reduce the impact of RAE onto ecology and further the recovered salt can be reused. The pollution control board enforces the leather industry to follow eco-friendly disposal or the better alternative process as such as recovery of value added products from RAE. Hence, there has been a
constant research to recover the value added products from RAE (RO reject and soak liquor).

4A.3.7. Determination of Na, Ca, Mg, Cr, Fe, Zn ions in RAE

The various categories of ions detected in RAE generated from the leather industry are presented in Table 4A.2. The sources of sodium in RAE can be attributed to sodium chloride, sodium sulphate, sodium carbonate, sodium formate or sodium sulfide used in leather processing. The amount of salts used may vary with the types of leather produced and volume of water used. For example, tanning processes carried out at low pH or strong acidic conditions such as pickling process requires more sodium chloride for buffering action to collagen matrix. Similarly, neutralization and basification processes employ various sodium based buffering salts and they are responsible for the Na$^+$ content in RO reject stream. The direct discharge of RO reject in irrigation water adversely affects the soil structure by causing dispersion of clay. Deterioration in soil permeability can occur depending on sodium, calcium and magnesium ion concentrations in the soil. The presence of calcium and magnesium ions in RAE ($S_1$ & $S_2$) may be due to the presence of alkaline salts in the waste water and lime used in the primary treatment of wastewater. The liming and deliming processes are also responsible for the presence of calcium ion in the tannery wastewater. The secondary treated waste water still contains some amount of calcium ions. Thus, the calcium ion was concentrated and accumulated in the RO reject stream from RO process. The chrome content was found to be less in all RAE ($S_1$, $S_2$, $R_1$ and $R_2$)
samples. The absence of chromium in RAE is due to the fact that chromium containing chemicals were not added during the soaking process and the RO pre-treatment process reduced or eliminated the chromium ions in the RO feed water. However, about 90% of hides/skins across the globe are tanned with basic chromium sulphate as tanning agent, because other tanning materials fail to give the leather a high hydrothermal stability and other selective properties that chrome provides. But, national and as well as international scenario presents that the soluble chromium salt was completely recovered and reused within the industry. Hence, the very trace amount of chromium (III) escaped during the chrome tanning was detected in the RAE of RO reject stream. Iron content of RAE was generally not very high, and is attributed to residual iron salts present in the process water and iron salts used in the primary treatment of wastewater. A trace amount of zinc was observed in RAE (S₁, S₂, R₁ and R₂).

Table 4A.2 Mean values of Na, Ca, Mg, Cr, Fe, Zn ions in RAE generated from Leather industry

<table>
<thead>
<tr>
<th>Type of RAE</th>
<th>Na (mg/g)</th>
<th>Ca (mg/g)</th>
<th>Mg (mg/g)</th>
<th>Cr (mg/g)</th>
<th>Fe (mg/g)</th>
<th>Zn (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>264</td>
<td>86</td>
<td>50</td>
<td>0.01</td>
<td>20</td>
<td>0.018</td>
</tr>
<tr>
<td>R₁</td>
<td>234</td>
<td>128</td>
<td>70</td>
<td>0.03</td>
<td>7</td>
<td>0.01</td>
</tr>
<tr>
<td>S₂</td>
<td>252</td>
<td>94</td>
<td>63</td>
<td>0.03</td>
<td>10</td>
<td>0.013</td>
</tr>
<tr>
<td>R₂</td>
<td>246</td>
<td>118</td>
<td>72</td>
<td>0.01</td>
<td>4</td>
<td>0.017</td>
</tr>
</tbody>
</table>
4A.3.8. Instrumental analyses

The surface morphology of S₁, S₂, R₁, and R₂ are shown in Fig. 4A.1. The RAE of soak liquor (S₁ & S₂) (Fig. 4A.1a & b) appeared to be crystalline, in nature, may be attributed to sodium chloride, because preservation of skins/hides is practiced with sodium chloride. The irregular rod shapes in the SEM image may be related to contamination of sodium chloride with fats, protein, blood tissues and other inorganic and organic salts of Ca, Mg etc. Fig. 4A.1 c & d show the surface morphology of RAE of RO reject stream (R₁ & R₂) with irregular masked image. Thus, it confirms that the RO reject salts are contaminated with the residual chemicals along with sodium and chloride ions.

Fig. 4A.2a shows the Energy Dispersive X-ray (EDX) spectrum of RAE. The spectrum has evidence for the presence of Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn and Pb along with Na and Cl ions. X-ray diffraction (XRD) spectra of RAE of soak liquor and RO reject stream are shown in Fig. 4A. 2b. The diffraction peak at 2θ of 26° attributed to the presence of calcium and sulfate ions and 28° may be attributed to the presence of silica in RAE. These ions may be sourced from leather processing chemicals or from process water. The other peaks at 2θ values of 27°, 29°, 31°, and 45° may correspond to many diffracting planes of sodium chloride crystal in RAE.
Fig. 4A.1 Surface morphology of RAE (a) RAE from Soak liquor of hide processing ($S_1$), RAE from Soak liquor salt of skin processing ($S_2$), (c) RAE from Reverse osmosis reject of hide processing ($R_1$), (d) RAE from Reverse osmosis reject of skin processing ($R_2$)
4A.4. Conclusions

The saline wastewater generated in soaking process and RO reject stream are evaporated in solar evaporation pans. The residue after evaporation is required to be managed in an environmentally sound manner. The residue after evaporation of soak liquor and RO reject stream were characterized for the selection of treatment process. The RAE generated in leather sector lack reusable characteristics and land co-disposal was also prevented due to the generation of leachate of high TDS. Hence, it is important to find an alternative technique to handle RAE. It has been attempted and proposed to recover sodium chloride from RAE by reactive precipitation process as illustrated in the next chapter.
Chapter IV-B

Separation, Purification and Characterisation of sodium chloride recovered from RAE solution

4B.1. Importance of salt recovery

Membrane separation process has become increasingly attractive for the treatment and recycling of wastewater. However, the efficiency of the process is limited only up to 70% and rest 30% of feed stream is considered as reject stream. The reject stream is evaporated in solar evaporation pans (for small volume of discharge) or in multiple effect evaporator (for large volume of discharge) leaving behind the residue. The residue after evaporation (RAE) lacks the reusable option as it contains high concentration of organic, biological and microbiological impurities. The disposal of RAE onto landfill has been banned by pollution control agencies as the leachate generated from the landfill sites failed to meet the discharging standards. Moreover, investment and maintenance costs towards treatment of leachate generated from secure landfill are very expensive. At present, RAE is being packed and stored in the storage yard in all ETPs and common effluent treatment plants (CETPs) of leather sector. The condition becomes worse as new land spaces are required to store the fresh generation of RAE in proportion with production capacity of leather sector. The recovery of salt and other minerals from RAE is the most obvious solution to resolve environmental issues concerned with direct disposal onto open land.
Recovery of salts from RO reject stream for reuse or commercial applications has been an attractive means for reducing the environmental and cost impacts on disposal of RO reject stream. Further, the development of technology for the recovery of commercial grade salt and other by-products from salt laden streams including RO reject has substantial advantages over the current management practice of direct land disposal which commonly require the disposal of RAE at high costs.

Reports are available on the recovery of salts from various sources such as salt lakes [71], sea water [72], textile effluent [73], industrial effluents [74, 75], and multistage flash distillation [76, 77]. However, no single report is available on the recovery of sodium chloride from RAE generated in leather sector.

Hence, this chapter was focused on the recovery of sodium chloride from RAE of RO reject stream by selective chemical precipitation technique using hydrogen chloride gas.

4B.2. Principle on precipitation of sodium chloride from RAE

The sodium chloride is highly soluble in water and it reaches the saturation at 35% (w/v) and super saturation at 36% (w/v). The mathematical expression for equilibrium constant for NaCl in water is given by:

\[
K_e = \frac{[Na^+][Cl^-]}{[NaCl_{(s)}]} 
\]

(4B.1)
\[ K_e[NaCl]_s = [Na^+][Cl^-] \]  \quad (4B.1a)

\[ K_{sp} = [Na^+][Cl^-] \]  \quad (4B.1b)

Where, \( K_{sp} \) is the solubility product of sodium chloride, 36.0 (mol/L)^2. The magnitude of solubility product \( (K_{sp}) \) measures the highest concentration of dissolved ionic species in aqueous solution. Thus, in a saturated solution, the solubility product is equal to the product of all the ions, i.e., \( K_{sp} = [Na^+][Cl^-] \). This dynamic equilibrium can be disturbed by changing the concentration of either \([Na^+]\) or \([Cl^-]\). According to Le chatelier’s principle the sodium chloride is precipitated out from the aqueous solution when the ionic product of \([Na^+]\) and \([Cl^-]\) is greater than \( K_{sp} \) of NaCl.

4B.3. Preparation of saturated RAE solution

In order to favour the reactive precipitation of RAE solution, the RAE saturation profile was evaluated and found to be saturated with the dissolution of RAE at 60 % (w/w). The saturated RAE solution was characterised and the characteristics are presented in Table 4B.1.
Table 4B.1 Characteristics of saturated RAE solution

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.67</td>
</tr>
<tr>
<td>Chloride</td>
<td>205.94</td>
</tr>
<tr>
<td>Sulphate</td>
<td>35.17</td>
</tr>
<tr>
<td>Sodium</td>
<td>125.92</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.44</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.51</td>
</tr>
</tbody>
</table>

* All the values are expressed in g/L except pH.

4B.4. Generation of Hydrogen chloride gas

The sources of HCl gas for the precipitation of sodium chloride was attempted from sodium chloride (99.9 %) and Conc. sulphuric acid (98% purity, sp. gr, 1.84); hydrochloric acid (37 % (v/v), sp. gr, 1.18) and Conc. sulphuric acid (98% purity, sp. gr, 1.84). The chemical system for the generation of HCl gas was selected based on the quantity HCl gas generation and amount of reagent consumed instantly. The table 4B.2 shows that 10 g of sodium chloride-50 mL of Conc. Sulphuric acid were required for the generation of 6.18 g of HCl gas to cause the reactive precipitation of 33 g of NaCl from the saturated NaCl solution, while the theoretical requirement of Conc. Sulphuric acid is 4.55 mL (98% purity, sp.gr 1.84) only. The increase in consumption ratio (actual/theoretical) of conc. Sulphuric acid was found to be 11.1 fold. Similarly, in the
case of hydrochloric acid (37 % (v/v), sp. gr, 1.18)-Conc. sulphuric acid (98% purity, sp. gr, 1.84) system, the theoretical requirement of conc. hydrochloric acid for the generation of HCl gas and thereof for the precipitation of 33 g of NaCl is 18 mL, but the experimental results revealed that 30 mL of conc. HCl acid was needed for the precipitation of 28 g of NaCl. The observed consumption ratio of HCl acid was found to be increased to 1.9 fold than the theoretical requirement. These results revealed that the consumption of chemicals for HCl gas generation was very less with dehydration of HCl acid than with sodium chloride dissociation by conc. sulphuric acid. Hence, the generation of HCl gas was carried out using conc. HCl acid for the reactive precipitation of NaCl from the saturated RAE solution.

**Table 4B.2 Mass balance on HCl gas generation**

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Theoretical</th>
<th>Experimental</th>
<th>Consumption Ratio (Actual/theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Using NaCl</td>
<td>10 g of NaCl with 4.55 mL of conc. H₂SO₄</td>
<td>10 g of NaCl with 50 mL conc. H₂SO₄</td>
<td>11.1/1</td>
</tr>
<tr>
<td>Using HCl acid</td>
<td>18 mL of HCl acid with 50 mL conc. H₂SO₄</td>
<td>30 mL of HCl acid with 50 mL conc. H₂SO₄</td>
<td>1.9/1</td>
</tr>
</tbody>
</table>
4B.5. Experimental setup for precipitation of sodium chloride from RAE solution

A known volume of saturated solution of RAE (100 mL) was transferred to a reactor for selective precipitation of NaCl. The hydrogen chloride gas was injected at the rate of 2.06 g/min into the solution through a distributor provided at the bottom of the reactor. The temperature of the reactor was thermostatically controlled using external water circulation system. The reactor was equipped with an agitator for uniform mixing. The reactor was fitted with a scraper mechanism at its bottom to remove the precipitated and settled salt. The precipitated NaCl was washed with pure brine solution to get a high purity salt. The detailed flow sheet for the batch precipitation of NaCl from RAE is shown in Fig. 4B.1. The optimum conditions for the effective precipitation of sodium chloride from the RAE solution were determined by varying the parameters: HCl purging time (1, 2 and 3 min), pH (1, 3, 5, 6, 7, 8 and 9), temperature (10, 20, 30, 40, 50, 60, 70 and 80°C), concentration of RAE (40, 45, 50, 55, 60 and 65 %, w/v) at constant HCl gas injection rate.
4B.6. Precipitation of Sodium chloride from the saturated solution of RAE

The movement of ions during precipitation are expressed in the form of chemical equations as given below:

RAE + H₂O → Na⁺, Cl⁻, Ca²⁺, SO₄²⁻, Mg²⁺, Org⁻/Org⁺, H₂O      (4B.2a)

(Na⁺, Cl⁻, Ca²⁺, SO₄²⁻, Mg²⁺, Org⁻/Org⁺, H₂O) + HCl(g)

→ NaCl(s) + [H₃O]⁺ + Na⁺ + Cl⁻ + Ca²⁺, SO₄²⁻, Mg²⁺, Org⁻/Org⁺    (4B.2b)
All the constituents of RAE saturated solution are in the ionised state as shown in Eqn (4B.2a). The increase in concentration of either \( \text{Na}^+ \) or \( \text{Cl}^- \) in the saturated solution shifts the reaction to backward direction by the common ion effect. In this study, hydrogen chloride gas was injected to increase the concentration of \( \text{Cl}^- \) ions in the RAE solution. The incremental increase in \( \text{Cl}^- \) ion concentration disturbed the dynamic equilibrium by increasing the ionic product of \( \text{Na}^+ \) and \( \text{Cl}^- \). The ionic product of \( \text{Na}^+ \) and \( \text{Cl}^- \) exceeded the solubility product of sodium chloride [solubility product of \( \text{NaCl} \), \( (K_{sp}) \) is 36 (mol/L)\(^2\)] and thus the precipitation of sodium chloride was achieved from the saturated solution of RAE as illustrated in Eqn (4B.2b).

4B.7. Optimization of process parameters for separation of NaCl from RAE

4B.7.1. Effect of HCl gas injection time on sodium chloride precipitation

The influence of injection time on precipitation of sodium chloride from RAE solution was carried out by varying hydrogen chloride gas injection time from 0.5 to 3 min at pH 8.0 and temperature, 40°C. The precipitation of NaCl could be achieved by the optimum injection time for the maximum NaCl precipitation at the selected flow rate of HCl gas. Figure 4B.2 shows that the mass of precipitated NaCl was increased with increase in HCl gas injection time up to 3 min and leveled off with 81 % salt recovery. The plateau region resulted may be due to dynamic equilibrium was established i.e. the rate of precipitation of NaCl becomes equal to the rate of dissolution of NaCl in the solution. The dissolution may be due to the decrease in ionic strength of the solution as the time of precipitation progressed. Hence, the optimum time required
for the precipitation of NaCl from RAE solution was fixed at 3 min. The mass of precipitated NaCl at the optimum time was 26.7 g with 81 % recovery with respect to the dissolved salt concentration (solubility of NaCl is 35g in 100 mL of water). The residual supernatant solution after precipitation was highly acidic (pH -0.62, H\(^+\) concentration, 4.2 g/L) in nature.

The acidified RAE solution was tested for reuse in the subsequent cycles. It was observed that the solubility of fresh RAE in acidified RAE solution was nearly zero. The high acidity of the solution might be the reason for resisting further dissolution of RAE.

Similarly, syn-RAE solution, syn-RAE-cat and syn-RAE-pyr were prepared and considered for the recovery of NaCl to understand the influence of organic compound in the precipitation of NaCl. Fig. 4B.2 shows the recovery of NaCl from the syn-RAE solution (25.5 g/100 mL solution) was found to be less than the NaCl recovery from RAE (RO reject stream) solution (27.2 g/100 mL solution). But in the case of syn-cat and syn-RAE-pyr solutions showed an increase in mass of NaCl recovery than the syn-RAE solution. This clearly confirmed that the presence of organic molecules affects the solubility rule in the solution and thus increased NaCl recovery. This may be due to protonation of catechol and pyrogallol molecules strengthen the inter-molecular hydrogen bond [78] and thus the forward chemical reaction was favored to precipitate out more NaCl crystals by suppressing its re-dissolution in to bulk solution.
Fig. 4B.2 Effect of HCl gas injection time on NaCl recovery from saturated RAE solution (RAE Concentration, 60 % (w/v)), syn-RAE-Cat solution (Concentration, 10 mmol/L), syn-RAE-pyr solution (Concentration, 10 mmol/L) and syn-RAE solution. (Conditions: Temperature, 40ºC and HCl injection time, 3min)

4B.7.2. Effect of pH on sodium chloride precipitation

The effect of initial pH (Fig. 4B.3) on precipitation of NaCl from RAE solution was studied by varying the pH such as 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 for a fixed HCl gas injection time of 3 min, temperature 40ºC and at constant HCl gas flow rate 2.06 g/min. The magnitude of NaCl precipitation was observed to be less in the pH range from 1 to 6 and the mass of precipitation was increased with rise in pH and it continued upto pH 8.0. The maximum amount of NaCl precipitation (26.9 g) was
observed at pH 8.0 (native pH of the RAE solution). There was no increase in mass of sodium chloride crystal in the pH range between 7 and 8 [79]. Mohameed and Ulrich (1996) [80] explained the effect of pH on salting out of crystalline substances in solution based on hydration theory. Most cations and anions are hydrated in aqueous solution. The $H^+$ ion, being smaller in size, is characterised by the highest enthalpy of hydration and thus it has a stronger tendency to interact with water molecules in the presence of other cations, so that a competition occurs among other ions to acquire water molecules. Sodium ions have low probability to acquire the critical hydration number and, they tend to orient towards the crystalline solid surface rather than to remain in the solution. On the another hand, in alkaline solution the hydroxide ions have low tendency to hydrate themselves, so that sodium ions have more probability to acquire the critical hydration number leading to drive into the solution. At high hydroxide ion concentration, the tendency of hydration prevails and the sodium ions are transferred into the solution again [80]. It is known that NaCl in water establishes ionic equilibrium with sodium ion, hydroxide ion, chloride ion and hydronium ion (formed from water). Hence, the presence of high concentration of hydrogen ion at low pH favours the rate of dissolution of NaCl. Moreover, at acidic pH range the consumption of hydrogen chloride gas was also increased and the solution was under saturated. Hence, the precipitation of NaCl was retarded with respect to the dissolved ion concentration. The residual supernatant solution after precipitation was highly acidic (pH =0.62, $H^+$ concentration, 4.2 g/L) in nature. The hydrogen ion concentration of the residual solution was determined by volumetric analysis, g equivalence per litre, and the
pH was calculated using Debye-Huckel ionic equation. The drop in pH was due to the replacement of sodium ions by hydrogen ion in the solution, which is due to supply of HCl gas. Similarly, the NaCl recovery from Syn-RAE-cat, syn-RAE-pyr and syn-RAE solutions were yielded the maximum in the pH range 6-8.

Fig. 4B.3 Effect of solution pH on NaCl recovery from saturated RAE solution (RAE Concentration, 60% (w/v)), syn-RAE-cat solution (Concentration, 10 mmol/L), Syn-RAE-pyr solution (Concentration, 10 mmol/L) and syn-RAE (Conditions: temperature, 40ºC and HCl injection time, 3min)
4B.7.3. Effect of temperature on precipitation of sodium chloride

Sodium chloride was precipitated from saturated RAE solution at different temperatures viz., 10, 20, 30, 40, 50, 60, 70 and 80°C. The pH of the initial solution was maintained at optimum pH (8.0) and time of precipitation was 3 min. Fig. 4B.4 shows that the mass of NaCl precipitation increased with increase in initial temperature of RAE solution from 10°C to 40°C. The maximum amount of NaCl precipitation (27 g) was achieved at 40°C. Beyond this temperature and up to 80°C, NaCl precipitation decreased with increase in temperature drastically. The observed result suggests that increase in temperature beyond the optimum temperature 40°C favoured the reverse reaction, i.e., dissolution of the precipitated NaCl back into the bulk solution. The presence of organic impurities in RAE solution affected the precipitation of NaCl from RAE solution. Fig. 4B.4 shows that the maximum recovery of NaCl from syn-RAE-cat, syn-RAE-pyr and syn-RAE solutions were observed in the temperature range from 30°C to 40°C.
Fig. 4B.4 Effect of solution temperature on NaCl recovery from saturated RAE solution (RAE Concentration, 60 % (w/v)), syn-RAE-cat solution (Concentration, 10 mmol/L), Syn-RAE-pyr solution (Concentration, 10 mmol/L) and syn-RAE. (Condition: HCl injection time, 3min)

4B.7.4. Effect of concentration of RAE solution on precipitation of sodium chloride

The concentration of RAE [40, 45, 50, 55, 60 and 65 % (w/v)] was varied to determine its effect on precipitation of NaCl while the other conditions were initial solution pH, 8.0; temperature, 40°C and time, 3 min respectively. The results are presented in Fig. 4B.5a and the Fig. 4B.5a illustrates show that the mass of salt recovery increased with increase in concentration of RAE solution. In general, precipitation depends on the concentration of dissolved ions in solution. As the initial concentration of RAE was increased, the dissolved ions concentration was also increased in the
solution and reached the saturation limit (concentration 60% (w/v)). The maximum amount of NaCl was recovered (27 g with 81% recovery) from saturated RAE solution (60%, w/v). Hence, the optimum concentration of RAE for the precipitation of NaCl was fixed at 60 % (w/v) (60 g of RAE in 100mL of distilled water). Fig. 4B.5b shows the increase in organic concentration of either catechol or Pyrogallol in synthetic RAE solution increased the recovery of NaCl significantly. This may be explained as increase in organic concentration shifts the reaction to forward direction by reducing re-dissolution of NaCl owing to suppression of H⁺ activity through interaction with organic molecules. Thus, the syn-RAE-cat and syn-RAE-pyr were yielded high recovery of NaCl with increase in organic concentration than the saturated RAE solution.

![Graph](image)

**Fig. 4B.5** Effect of concentration on NaCl recovery from (a) RAE solution (b) Syn-RAE-cat and syn-RAE-pyr solutions (Conditions: temperature, 40°C and HCl injection time, 3 min).
4B.8. Evaporative crystallization of sodium chloride from acidified RAE solution

The precipitation of sodium chloride attains equilibrium after the precipitation of 27g NaCl per 100 mL from saturated RAE solution. This may be due to the increase in H\(^+\) ions (equivalent concentration, 4.2 g/L) in the solution suppressed the precipitation of NaCl. Also, the decrease in NaCl precipitation may be due to the decrease in Na\(^+\) ion concentration in the bulk solution and became under saturated solution. In order to increase the sodium ion concentration in the solution to facilitate the precipitation of NaCl, the acidified RAE solution was evaporated to drive away water molecules at 120°C. Fig. 4B.6 shows that, the crystallization of NaCl was increased with mass of water removed from acidified RAE solution by thermal evaporation. The increase in evaporation upto 10 % (v/v) increased Na\(^+\) ion concentration and reached near zero concentration at evaporation of water by 12 % (v/v) from acidified RAE solution. The decrease in concentration of Na\(^+\) ion was equated to precipitation of sodium chloride called evaporative crystallization. However, evaporation of water beyond 10 % (v/v), calcium and sulphate ions were also precipitated along with NaCl. Hence, the optimum evaporation of water molecules was fixed at 10 % (v/v) for the recovery of pure NaCl crystals. The maximum amount of NaCl was crystallized at 10 % (v/v) water evaporation yielded 5.5 g of NaCl for the working volume of 100 mL. This was due to the evaporation of water molecules from the acidified RAE solution which resumed the super saturation of NaCl in the acidified RAE solution. Thus, by solubility rule the sodium chloride was crystallized first and settled at the bottom of the reactor. Thus, the cumulative yield of NaCl from reactive precipitation and evaporative crystallization was
32.5 g per 100 mL of RAE solution, i.e. the overall percentage recovery of NaCl from RAE solution was 98.7%. Fig. 4B.6 illustrates that the removal of water from the acidified RAE solution in evaporative crystallization also increased the sulphate ion concentration from 12.05 g to 12.3 g per 100 mL of solution.

The solution after cumulative recovery of NaCl was named as residual acidified supernatant (RAS) solution. The RAS solution was rich in H\(^+\) ion concentration (equivalent concentration, 4.2 g/L) and the concentration of chloride ion was calculated to be 157.5 g/L. This was correlated to the addition of HCl gas which increased the chloride ion concentration in the RAS solution.

![Fig. 4B.6 Effect of water evaporation on NaCl recovery from acidified RAE solution by evaporative crystallization](image)

Fig. 4B.6 Effect of water evaporation on NaCl recovery from acidified RAE solution by evaporative crystallization
4B.9. Sequential stages of sodium chloride precipitation from saturated RAE solution

It was observed that during sodium chloride precipitation a considerable volume of hydrogen chloride gas escaped without being utilized in the system. To conserve the escaped HCl gas from the reactor, a sequential three stage batch precipitation experimental setup was fabricated and they were connected in series. In this sequence, hydrogen chloride gas escaped from the first precipitation reactor was collected and injected into the second precipitation reactor. Similarly, the hydrogen gas escaped from the second precipitation reactor was injected into the third stage precipitation reactor. The results (Table 4B.3) revealed that the sequential stages of injecting HCl gas considerably reduced the consumption of HCl gas in the second and third stage precipitation reactors. The consumption of hydrogen chloride gas was less by 1.31 g in second stage precipitation and 2.18 g less in the third stage than the first stage precipitation reactor. The sequential reactor configuration significantly reduced the consumption of hydrogen chloride gas by 8 and 21 % for second and third stage respectively. But investment cost towards the fabrication of reactors is to be considered for large scale applications.
Table 4B.3 Precipitation of sodium chloride from saturated RAE solution by sequential batch mode

<table>
<thead>
<tr>
<th>S.No</th>
<th>Reactor stage</th>
<th>Hydrochloric acid consumption (g)</th>
<th>Recovered Sodium Chloride (g)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>One</td>
<td>16.6</td>
<td>26.8</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>Two</td>
<td>15.2</td>
<td>26.8</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>Three</td>
<td>13.1</td>
<td>26.8</td>
<td>81</td>
</tr>
</tbody>
</table>

4B.10. Two stage HCl gas injection process for recovery of NaCl from saturated RAE solution

In order to increase the overall recovery of NaCl from saturated RAE solution, the acidified RAE solution after first stage NaCl precipitation was transferred to stage two precipitation reactor and HCl gas was injected at the same flow rate. It was observed (Table 4B.4) that, the cumulative recovery of NaCl from both stages was 29.7g (i.e. 90 % recovery) as against 26.8 g per 100 mL of RAE solution. But, HCl gas consumption was doubled i.e 33.2 g. Hence, the two stage NaCl precipitation is not economically viable.

Table 4B.4 Mass balance in single stage and two stage precipitation of acidified RAE solution

<table>
<thead>
<tr>
<th>S.No</th>
<th>Condition</th>
<th>Consumption of HCl acid (g)</th>
<th>Cumulative mass of sodium Chloride Recovered (g)</th>
<th>Percentage Recovery of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single stage precipitation</td>
<td>16.6</td>
<td>26.8</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>Two stage precipitation</td>
<td>33.2</td>
<td>29.7</td>
<td>90</td>
</tr>
</tbody>
</table>
4B.11. Effect of compressed air agitation during sodium chloride precipitation

The precipitation of sodium chloride from saturated RAE solution can be enhanced by effective distribution of HCl gas into the bulk solution. This was achieved by maintaining uniform concentration in the precipitation reactor by providing proper agitation. Hence, compressed air at pressure 2 kg/cm$^2$ was passed into the RAE solution along with HCl gas. The results (Table 4B.5) revealed that, the percentage of sodium chloride recovery was decreased on injecting HCl gas along with compressed air. The percentage of NaCl precipitation was decreased from 81% to 71%.

Table 4B.5 Influence of compressed air agitation on sodium chloride precipitation

<table>
<thead>
<tr>
<th>S.No</th>
<th>Mixing conditions</th>
<th>Recovery of Sodium Chloride (g/100 mL)</th>
<th>% Recovery of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without air agitation</td>
<td>26.7</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>HCl injection With compressed air</td>
<td>23.4</td>
<td>71</td>
</tr>
</tbody>
</table>

4B.12. Effect of salt seeding on sodium chloride precipitation

The commercial sodium chloride (0.5%) was added to the saturated RAE solution to induce crystallization. This study was carried out to determine the influence of salt crystals on to recovery of sodium chloride from RAE solution. The time and mass of precipitation of sodium chloride from saturated RAE solution were not affected by seeding the saturated RAE solution (Table 4B.6). The observation showed that the
recovery of NaCl was achieved only by reactive precipitation and not by crystal growth mechanism. The high concentration of H⁺ concentration after HCl gas purging maintains the equilibrium of the solution. Thus, no increase in crystal growth was observed after the addition of NaCl seeded into the acidified RAE solution. Hence, the salt seeding was not practiced in further experiments on recovery of sodium chloride.

Table 4B.6 Effect of salt seeding on sodium chloride precipitation

<table>
<thead>
<tr>
<th>S.No</th>
<th>Conditions</th>
<th>Recovery of NaCl (g/100 mL)</th>
<th>% Recovery of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without salt seeding</td>
<td>26.7</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>With salt seeding</td>
<td>26.7+0.5 (Recovered NaCl+ Seeded crystal)</td>
<td>81</td>
</tr>
</tbody>
</table>

4B.13. Effect of reactor dimension (H/D ratio) on sodium chloride precipitation

The dimension of precipitation reactor, height to diameter (H/D) ratio was varied from 0.39 to 6.98 for the recovery of NaCl from saturated RAE solution. The percentage sodium chloride recovery was increased with increase in H/D ratio from 0.39 to 2.23 and decreased with further increase in H/D ratio beyond 2.23 (Table 4B.7). Hence, the optimum H/D ratio for the precipitation of NaCl (81 %) was 2.23.
### Table 4B.7 Effect of reactor dimension (H/D ratio) on sodium chloride precipitation

<table>
<thead>
<tr>
<th>S. No</th>
<th>H/D ratio</th>
<th>Recovery of NaCl (g/100 mL)</th>
<th>Percentage recovery of NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.39</td>
<td>14.8</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
<td>19.6</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>1.13</td>
<td>20.4</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>2.23</td>
<td>26.7</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>3.78</td>
<td>24.3</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>6.98</td>
<td>22.6</td>
<td>68</td>
</tr>
</tbody>
</table>

### 4B.14. Analysis of thermodynamic parameters for the recovery of NaCl from saturated RAE solution

The thermodynamic parameters such as change in Gibbs-free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS) were calculated for the precipitation of NaCl from saturated RAE solution using classical Van’t Hoff equation and the values are presented in Table 4B.8. The ΔH and ΔS values were obtained from the slope and intercept of the plot between lnK_e versus 1/T.

The thermodynamic parameters presented in Table 4B.8 are consistent with the results obtained from Fig. 4B.2. The ΔG value decreased from +1097 kJ/mol at 283°K and it attained the minimum value (+522.11 KJ/mol) at 313°K and again increased to
+2217.66 KJ/mol at 353°K. This indicates that, the precipitation of NaCl was non spontaneous and the non spontaneity was decreased at 313°K. The positive value of enthalpy suggests that the NaCl precipitation process was endothermic in nature in the lower temperature range (283, 293, 303 and 313°K) and was exothermic in the higher temperature range (323, 333, 343 and 353°K).

Table 4B.8 Thermodynamic parameters for sodium chloride precipitation from saturated RAE solution (Conditions: HCl injection time, 3 min; pH, 8.0 and Concentration of RAE, 60 % (w/v))

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Pseudo first order rate constant, k₁ (min⁻¹)</th>
<th>ΔG (kJ/mol)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (kJ/K.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>1.12</td>
<td>+1097.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>1.16</td>
<td>+943.73</td>
<td>+74.27</td>
<td>+0.336</td>
</tr>
<tr>
<td>303</td>
<td>1.18</td>
<td>+524.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.19</td>
<td>+522.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>1.11</td>
<td>+1064.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>1.06</td>
<td>+1386.33</td>
<td>-1173.9</td>
<td>-2.57</td>
</tr>
<tr>
<td>343</td>
<td>0.96</td>
<td>+1681.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>0.93</td>
<td>+2217.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4B.15. Non-linear kinetic model study for the precipitation of NaCl from RAE solution

To investigate the order of reaction and the rate-controlling step for the precipitation of NaCl from saturated RAE solution, the following kinetic rate equations were used to validate the experimental data. The kinetic data obtained in batch studies were evaluated using first order, second order reaction kinetics, pseudo first and pseudo second order equations. The pseudo first-order and pseudo second-order rate equations are expressed, respectively as:

\[ \text{NaCl}_t = \text{NaCl}_e (1 - e^{-k_1 t}) \]  
\[ \frac{1}{\text{NaCl}_e} - \frac{1}{\text{NaCl}_t} = k_2 m_e t \]

Where \( \text{NaCl}_e \) (g) and \( \text{NaCl}_t \) (g) are the quantities of NaCl precipitated at equilibrium and at time “t” respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g min\(^{-1}\)) are the rate constants of pseudo first-order and second-order reactions respectively.

The values of \( \text{NaCl}_e \), \( k_1 \) and \( k_2 \) were determined by non-linear regression models using solver in MS-excel as shown in Table 4B.9. The validity of the kinetic model was verified based on two criteria, regression coefficient \( R^2 \) and chi-square error \( \chi^2 \) analysis. The correlation coefficients of first order (0.97), second order (0.92), pseudo first order (0.99) and pseudo second order (0.95) rate kinetics indicated that the experimental data were more accurately obeyed by the pseudo first-order kinetic model (Fig. 4B.7). Furthermore, the minimum \( \chi^2 \) value was observed in the pseudo first order
(0.21) kinetic model than the other kinetic models (first order, 3.4; second order, 0.72 and pseudo second order, 0.47). This indicates that the precipitation of NaCl followed the pseudo first order rate kinetics. This implies that the precipitation of NaCl was controlled by the concentration of NaCl rather than HCl gas; the mass of sodium chloride recovered was not increased irrespective increase in HCl addition (mass of HCl gas was selected such that excess HCl gas was allowed to dissolve in the solution).

Table 4B.9 Non-linear kinetic model for the precipitation of sodium chloride from saturated RAE solution (Conditions: HCl injection time, 3 min; pH, 8.0; temperature, 40°C; Concentration of RAE, 60 % (w/v))

<table>
<thead>
<tr>
<th></th>
<th>First order reaction</th>
<th>Second order reaction</th>
<th>Pseudo first order reaction</th>
<th>Pseudo second order reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant, k</td>
<td>0.517 min⁻¹</td>
<td>0.04 g min⁻¹</td>
<td>1.01 min⁻¹</td>
<td>0.074 g min⁻¹</td>
</tr>
<tr>
<td>Regression coefficient (R²)</td>
<td>0.97</td>
<td>0.96</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>Chi-square (χ²)</td>
<td>3.40</td>
<td>0.722</td>
<td>0.21</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Pseudo first order rate constant for the precipitation of NaCl was determined at different temperatures (Table 4B.9) and the rate constant was used to calculate activation energy of reaction. The activation energies for the precipitation of sodium chloride in the temperature range 10 - 40°C and 50 - 80°C were found to be 21.37 kJ/mol and 85.5 kJ/mol respectively (the standard activation energy for NaCl crystal formation at ambient condition is 60 kJ/mol). The activation energy observed in the present investigation was much lower at the lower temperature range. The higher
activation energy at the higher temperature range suggests that precipitation of NaCl from saturated RAE solution required higher energy than the reported value for sodium chloride crystallization at the standard conditions. This indicates that the formation of NaCl crystal from the constituent ions in this present condition was more favoured at the lower temperature range.

![Kinetic models for precipitation of sodium chloride from saturated RAE solution](image)

Fig. 4B.7 Kinetic models for precipitation of sodium chloride from saturated RAE solution (Conditions: reaction time, 3 min; pH, 8.0; temperature, 40°C and concentration of RAE, 60 % (w/v)).
4B.16. Mathematical modeling of sodium chloride precipitation from synthetic NaCl saturated solution

4B.16.1. Reactive crystallization theory

The development of semi-batch reactive crystallization model is much more complex than non-reactive crystallization. This complexity is due to the chemical reaction kinetics and the nature of crystallization. There has been extensive research on the modeling and analysis of reactive crystallization through simulation and experimentation. The majority of the studies focused on understanding the interplay between mixing and crystallization kinetics. Very little research has been directed towards coupling mathematical optimization with reactive crystallization. Reactive crystallization is a very complex process and extensive effort has been directed towards understanding and interpreting the interplay between the reaction, crystallization and mixing kinetics. However, further exploitation of the interplay between these kinetic processes for the optimal operation of reactive crystallizers remains a scarcely researched area. The lack of mathematical optimization studies on reactive crystallization could also be attributed to the difficulty in modeling the mixing kinetics.

The super saturation that is the main driving force for crystallization, in reactive crystallization the potential super saturation is created by chemical reaction. However, the definition of super saturation is dependent on the system. According to Klein and David theory, there are generally two categories of reactive precipitation, Categories I and II [81]. Category I refers to chemical reaction that leads to a more or less soluble
product molecule, which then crystallizes. The super saturation is simply expressed as \( \Delta C = C_A - C^* \). Where, \( C_s \) is concentration of solute at saturation and \( C^* \) is concentration of solute at equilibrium. Category II refers to chemical reaction that does not lead to an intermediate soluble species. The solid crystallizes directly from the reaction. This is normally the case for ionic reactions. In this case, the thermodynamics of super saturation is commonly used to describe the driving force for the crystallization process. The mathematical model developed will include systems of both the categories.

Moreover, a comprehensive optimization of the model can also serve as convenient and robust starting conditions for more rigorous simulation and experimentation. The interplay between mixing and crystallization kinetics will not be studied here since there have been many studies in this area. Therefore, the mathematical model formulated will be based on the assumption of perfect mixing.

In this investigation, HCl gas was purged through a syn-RAE solution contained in a semi batch type reactor where the salt started precipitating after the concentration of salt exceeded solubility of the salt due to common ion effect. Precipitation refers to composite phenomena of nucleation and subsequent growth. Growth can take place at concentration lower than those needed for nucleation (as long as concentration of salt in solution is more than solubility of salt at that temperature). The mathematical models formulated here are based on lumped parameter model.
4B.16.2. Lumped parameter model

As per the first approach, the following section is described. According to the law of thermodynamics, it consists of two elementary processes: (1) Formation of nuclei or crystallization centre and (2) Growth of crystals on or around the nuclei. Reactant B (HCl gas) is injected in solution of NaCl (reactant A). Let \( G \) denote the linear growth rate of crystals in mm/s. There are two steps involved in deposition of mass or growth of crystals in salt solution namely; (1) Reaction: by which the solute molecules arrange themselves into the crystal lattice which are influenced by concentration gradient in bulk solution and (2) Diffusion: by which solute molecules are transported from the bulk of the fluid phase to the solid nuclei/crystal surface. Let \( C \) be the concentration of sodium solute (A) in the bulk solution, \( C_i \) be the concentration of sodium ion (A) at the interface of crystal and solution and \( C^* \) be the concentration of sodium ion (A) at equilibrium in the bulk solution. Also, \( V \) is the volume of solution in reactor and \( V_0 \) is volumetric flow rate of reactant B. Hence, the precipitation reaction,

\[ A + B \rightarrow C \]

and the general solute balance on NaCl precipitation is given by,

\[
0 + r_A V = \frac{dN_A}{dt} \quad (4B.5)
\]

in terms of concentration of A,

\[
r_A = v_0 C_A + V \frac{dC_A}{dt} \quad \text{or} \quad \frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \quad (4B.6)
\]

Similarly, for species B,

\[
r_B V + F_{B0} = \frac{dN_B}{dt} \quad \text{or} \quad \frac{dC_B}{dt} = r_B + \frac{v_0}{V} (C_{B0} - C_B) \quad (4B.7)
\]

During the reaction phase, the rate of mass of NaCl precipitation \((m = \rho V)\) is
\[ \frac{dm}{dt} = K_r A (C_i - C^*) + \frac{C_i - C^*}{\tau} \quad \text{where} \quad r_B = K_r A (C_i - C^*) \quad \text{and} \quad \tau = \frac{v}{V_0} \quad (4B.8) \]

where \( K_r \) represents the rate constant for the surface reaction or diffusion of solute molecules from bulk solution to crystal surface through stationary film, ‘t’ be the time of passing gas and during diffusion phase, A is area of crystals.

Rate of mass transport through diffusion is

\[ \frac{dm}{dt} = K_d A (C - C_i) + \frac{C_i - C}{\tau} \quad (4B.9) \]

where \( K_d \) is coefficient of diffusion.

Thus, on comparing Eqn (4B.8) and (4B.9), one gets an overall expression for mass transport under concentration gradient as

\[ \frac{dm}{dt} = K_g A (C - C^*)_g + \frac{C - C^*}{\tau} \quad (4B.10) \]

It can be seen that \( C_i \) has been eliminated in Eqn (4B.8 & 4B.9) while it incorporates a constant specific for a particular system, \( g \), the order of growth process that varies from 1 to 2 for solutions. \( K_G \) is overall crystal growth coefficient.

For \( g=1 \), combining Eqn (4B.9) and (4B.10) we get,

\[ \frac{dm}{dt} = \frac{A (C - C^*)}{K_d + \frac{1}{K_r}} + \frac{C - C^*}{\tau} \quad (4B.11) \]

\[ K_G = \frac{K_d K_r}{K_d + K_r} + \frac{1}{A \tau} \quad (4B.12) \]
Thus, the growth of mass is given by

\[ R_g = \frac{1}{A} \frac{dm}{dt} = K_g (\Delta C)^g \]  

(4B.13)

where \( \Delta C = C - C^* \). But, as it is difficult to measure \( C^* \), the solute equilibrium concentration, Eqn (4B.11) needs to be reformed to a practical one. Let us consider a specific crystal lattice with volume shape factor \( \alpha \) and surface shape factor \( \beta \). The mass of single crystal can be expressed as

\[ m = \alpha \rho_c L^3 \]

(4B.14)

(4B.15) Where \( \alpha \), characteristic shape factor; \( L \), Characteristic size (length) of crystals and \( \rho_c \) be crystal density.

The growth rate becomes

\[ G = \frac{dL}{dt} \]  

(4B.16)

From Eqn (4B.15) and (4B.13), we get

\[ R_g = K_g \Delta C^g = \frac{3\alpha}{\beta} \rho_c G \]  

(4B.17)

as \( A = \beta L^2 \)

or, in other words, Eqn (4B.14) can be expressed in terms of the rate of changes in solution concentration that is dependent on rate of change in crystal mass.
\[ \frac{dc}{dt} = \frac{3\alpha}{MV} \rho_c \frac{dL}{dt} \]  \hspace{1cm} (4B.18)

Crystal size distribution is described by the moment equations (Randolph and Larson, 1988). The minimum number of differential equations required is 4 (\(\mu_0\), \(\mu_1\), \(\mu_2\) and \(\mu_3\)) in order to complete the mathematical modeling.

\[ \frac{dc}{dt} = \frac{3\alpha}{MV} \rho_c \frac{d\mu_3}{dt} \]  \hspace{1cm} (4B.19)

Where \(M\) is molecular weight of NaCl, 58.45 Kmol and \(V\) is volume of solute, m\(^3\).

The rate of change of zeroth moment is expressed by

\[ \frac{d(\mu_0)}{dt} = B_p \]  \hspace{1cm} (4B.20)

\[ \frac{d(\mu_j)}{dt} = jm_{j-1}GV \]  \hspace{1cm} (4B.21)

Where \(B_p\), primary nucleation

In precipitation processes, normally the predominant mode of nucleation is through a primary mechanism. There are various expressions for primary nucleation. The most common descriptions of primary nucleation are expressed by the following equations:

\[ B_p = k_p \Delta C_p \]  \hspace{1cm} (4B.22)

\[ B_p = B_0 \exp\left(-\frac{A_p}{ln^2S_a}\right) \]  \hspace{1cm} (4B.23)
Eqn (4B.22) was an empirical equation that was commonly used in non-reactive crystallization. However, Eqn (4B.22) has been used to describe primary nucleation of reactive crystallization in numerous literature studies [82]. Eqn (4B.23) was based on the theoretical derivation of the primary nucleation expression. This theoretical expression of the primary nucleation has found relatively widespread use in reactive crystallization. 

**Sa** was the thermodynamic super saturation ratio, which commonly used, in ionic reactive crystallization. The thermodynamic super saturation was defined as follows [83, 84]

\[ S_a = \left[ \frac{Na_+^\theta + Cl^-}{K_{sp}} \right]^{1/\theta} \]  

(4B.24)

The variable \( u \) refers to the number of mole of ions in 1 mol of solute. Variables \( u^+ \) and \( u^- \) are the number of moles of cations and anions in 1 mol of solute. \( K_{sp} \), is solubility product of NaCl, 36 (mol/L)^2.

The overall linear crystal growth rate can be described by several forms of expression. Two of the most common forms are the semi-empirical power law equations:

\[ G = k_g (1 - S_a)^\theta \]  

(4B.25)

The occurrence of secondary nucleation in reactive precipitation is generally considered insignificant. In this present investigation, the reaction time was quite low. Hence, the growth of crystals in the precipitation reaction was not measurable. This was confirmed by finding the particle size distribution of precipitated sodium chloride by HCl gas purging. The particle size distribution showed a particle size data with high
standard deviation. Thus, the result confirmed the growth of crystals was not achieved at the time of HCl purging time in syn-RAE solution. Hence, the Eqn (4B.25) may not be the valid mathematical equation to validate the response. Hence, modeling of NaCl crystal growth was needed more complex mathematical expression to explain the precipitation of sodium chloride by the addition of HCl gas. The development of mathematical valid expression is in progress in our research group.

4B.16.3. Development of a transient growth rate model

Here, we develop sodium ion solute balanced equation for semi batch system where evaporated residue salt solution was taken in the reactor and HCl gas (reactant B) flow was added in continuous mode. Let, F be particle count distribution function, G be growth rate and L be characteristic length and $R_N$ be rate of nucleation. From classical population balance we get $F(L,t)$

$$\frac{\partial F}{\partial t} + \frac{\partial (GF)}{\partial L} = B_p$$

(4B.26)

or

$$\frac{\partial F}{\partial t} + G \frac{\partial F}{\partial L} = B_p$$

(4B.27)

Subjected to following conditions

Initial condition $F(L,0) = F_0$

Boundary condition $F(0,t) = \frac{B(t)}{G(t)}$

For simplicity one can take $B(t) = B_p = K_b \mu \left(\frac{C-C^*}{C^*}\right)^b$
and \( G(t) = K_G \left( \frac{C - C^*}{C} \right)^g \), where \( b=0.33 \), for the present system \hspace{1cm} (4B.29)

Here, \( C \) is concentration of sodium ion solute in the bulk solution \( C^* \) was equilibrium concentration of sodium ion in bulk solution. The concentration ‘\( C \)’ of sodium ions are measured in the bulk solution at regular interval of time and compared with theoretical value.

4B.16.4. Method of computation

In order to evaluate the performance of the reactive precipitation of sodium chloride the above set of equations is solved using specific parameters as listed in Table. 4B.10. Lumped parameter model was solved using Runge-Kutta method for first order ordinary differential equation (ODE) with initial conditions.

<table>
<thead>
<tr>
<th>S. No:</th>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equilibrium concentration, ( C^* ) (kmol/kg)</td>
<td>( 7.66 \times 10^{-4} )</td>
</tr>
<tr>
<td>2</td>
<td>Bulk solution concentration, ( C ) (kmol/kg)</td>
<td>( 4.25 \times 10^{-3} )</td>
</tr>
<tr>
<td>3</td>
<td>Density, ( \rho_c ) (kg/m(^3))</td>
<td>2165</td>
</tr>
<tr>
<td>4</td>
<td>Nucleation rate constant, ( k_p ) (no ( \text{s}^{-1} ) ( \text{kg}^{-1} ) ( \text{mol/kg} )(^{-4.5} ))</td>
<td>( 3.1 \times 10^{10} )</td>
</tr>
<tr>
<td>5</td>
<td>Growth rate constant, ( K_G ) (m ( \text{s}^{-1} ) ( \text{mol/kg} )(^{-1.5} ))</td>
<td>( 2.98 \times 10^{-5} )</td>
</tr>
<tr>
<td>6</td>
<td>Nucleation order, ( b )</td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td>Growth order, ( g )</td>
<td>1.5</td>
</tr>
</tbody>
</table>
4B.16.5. Sodium ion concentration profile in NaCl precipitation reactor

The change in sodium ion concentration during the precipitation of sodium chloride by HCl gas injection was simulated by Eqn (4B.13) with initial conditions and the results (bulk concentration) were compared with the experimental conditions and are shown in Fig. 4B.8. The Fig. 4B.8 shows that the observed and simulated concentrations are close to change in concentration of sodium ion with respect to reaction time. The concentration of sodium ion in the solution decreased drastically with increase in the contact time for purged gas. The sodium chloride salt was precipitated and settled down at the bottom of the reactor. The decrease in concentration of Na\(^+\) in the bulk liquid phase was a driving force to increase H\(^+\) ion in order to maintain the charge balance. The hydrogen ion in solution has a stronger tendency to interact with water molecules than Na\(^+\) in aqueous phase. The NaCl precipitation continued for 180 sec and thereafter the rate of precipitation was reduced with increase in HCl gas injection time upto 240 sec. Thus, the optimum equilibrium contact time for the precipitation of sodium chloride was fixed as 180 sec. The rate of precipitation of sodium chloride depends on the temperature of the process. In general, the reactive precipitation of sodium chloride is exothermic in nature and the precipitated sodium chloride re-dissolved them back into the solvent medium. This was overcome by circulating cold water through the external jacket. During the reactive precipitation of sodium chloride the process temperature was maintained at 40\(^\circ\)C to reduce the solubility product for maximizing the precipitation of sodium chloride.
4B.16.6. Sodium chloride precipitation profile across the radial direction of the reactor

The rate of precipitation of sodium chloride across the radial direction inside the reactor was examined by counting the number of particles. The eqn. 4B.27 with initial conditions was considered to calculate no of particles by nucleation. The reactor conditions were maintained at constant HCl gas supply and by maintaining the solution temperature at 40°C. Fig. 4B.9 shows that the particle count along radial direction in the reactor was parabolic shaped trend. It was evident that more precipitation of sodium chloride was observed at the HCl injection point of the reactor and decreased gradually towards the centre to the wall of the reactor. This may be due to steric hindrance of precipitated sodium chloride back into the centre of the reactor and also the formation of NaCl crystal was more at the centre by the nucleation than at the wall of the reactor.
Fig. 4B.9 Population density curve for sodium chloride precipitation in saturated RAE solution (HCl gas injection time, 3 min and temperature, 40ºC)

4B.17. Separation of precipitated NaCl by filtration

The precipitated sodium chloride was filtered through vacuum filtration to separate out precipitated NaCl from residual acidified RAE solution. Filtration using applied vacuum was desirable than ordinary cloth filtration to ensure low volume of occluded residual solution in the voids of precipitated NaCl crystalline matrix. The application of vacuum will reduce the concentration of impurities adhered onto the precipitated NaCl crystals and thereof to reduce the degree of purification.
4B.18. Purification of recovered sodium chloride

The precipitated and filtered sodium chloride was washed with pure brine solution to increase the purity of recovered NaCl. The washed recovered NaCl was dried in hot air oven at 110°C to get free flowable granular NaCl crystals. The recovered salt was confirmed as NaCl through instrumental evidences such as EDX spectroscopy and cyclic voltammetry.

4B.19. Material balance

The material balance on the preparation of saturated RAE solution of volume one litre and precipitation of sodium chloride was calculated as shown below;

4B.19.1. Mass balance on preparation of saturated RAE solution

Mass of RAE + Deionised water → Saturated RAE solution + Grit

\[0.6 \text{ kg} + 1\text{ kg} \rightarrow 1.32 \text{ kg} + 0.28\text{ kg} \quad (4B.30)\]

The mass of saturated solution of RAE was 1.32 Kg, obtained by dissolving 0.6 Kg of RAE in one litre of deionised water. The undissolved grit (0.28 Kg) mainly consists of sand, lime and clay being non hazardous in nature, that can be disposed off onto secured landfill.
4B.19.2. Mass balance on precipitation of sodium chloride

Saturated RAE solution + HCl(g) → Precipitated sodium chloride + Residual solution

\[ 1.32 \text{ kg} \quad + \quad 0.105 \text{ kg} \quad \rightarrow \quad 0.268 \text{ kg} \quad + \quad 1.157 \text{ kg}. \quad (4B.31) \]

The saturated RAE solution of 1 Litre volume yielded 0.268 Kg of NaCl under the optimized conditions.

4B.20. Instrumental analyses

4B.20.1. Scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses of RAE and recovered NaCl

The surface morphology of RAE and recovered NaCl was captured and analyzed. Fig. 4B.10a suggests that the RAE was aggregated in nature, due to the presence of inorganic and organic compounds. Fig. 4B.10b shows the cubic morphology of the recovered salt crystal from RAE solution. Fig. 4B.10c shows the EDX spectrum of RAE. The spectrum has the evidence for the presence of Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Pb elements along with sodium and chloride. Fig. 4B.10d shows the EDX spectrum of recovered sodium chloride, indicating that Na\(^+\) and Cl\(^-\) were only present in the recovered salt; hence the precipitated mass was confirmed to be NaCl. The spectral results proved that the recovered sodium chloride was of high purity. This was further confirmed using XRD analysis.
Fig. 4B.10 Scanning Electron microscopy images of (a) RAE (b) recovered NaCl from RAE and Energy dispersive X-ray spectra of (c) RAE (d) recovered NaCl from RAE

Fig. 4B.11 a & b show the surface morphology of syn-RAE-cat and syn-RAE-pyr. The aggregated images confirmed that the organic compounds are mixed together with the inorganic salts in synthetic RAE solutions. Fig. 4B.11 c & d show the recovered salt was confirmed as sodium chloride by its cubic morphology.
Fig. 4B.11 Scanning electron microscopy images of (a & b) syn-RAE-cat and syn-RAE-pyr (c & d) recovered NaCl from syn-RAE-cat and syn-RAE-pyr.

4B.20.2. XRD analysis of RAE and recovered NaCl

XRD spectra of RAE and precipitated NaCl salt shown in Fig. 4B.12. The peak at 2θ of 26° in Fig 4B.12a may be correlated to the presence of calcium sulphate (JCPDS No: 72-0916) and 28° may be attributed to the presence of silica in RAE. These ions might be sourced from leather processing chemicals or from process water. The
peaks at other $2\theta$ values $27^\circ, 29^\circ, 31^\circ$ and $45^\circ$ may be attributed to many diffracting planes [111], [200], [220], [222] and [400] in sodium chloride crystal in RAE. Fig. 4B.12b shows the peaks corresponding to $2\theta$ value at $27^\circ$, $31^\circ$, $45^\circ$, $56^\circ$ and $66^\circ$ of recovered crystalline sodium chloride (JCPDS No: 78-0751). The XRD spectra obtained for recovered sodium chloride and analar grade NaCl [SD fine chemicals, India] were identical, which confirms the recovered sodium chloride was equivalently pure with analar grade NaCl. The syn-RAE-cat and syn-RAE-pyr were also recorded and presented in Fig. 4B.12 c & e. The Fig. 4B.12 c & e show the multiple peaks corresponds to the organic compounds along with the inorganic salt in the syn-RAE-cat and syn-RAE-pyr. The Fig. 4B.12 d & f show the recovered salt was found to be NaCl with respect to the $2\theta$ value at $27^\circ$, $31^\circ$, $45^\circ$, $56^\circ$, $66^\circ$ and $75^\circ$. The recovered NaCl from the syn-RAE-cat solution and syn-RAE-pyr solution were found to be free from the spiked organic compounds. Thus, the results confirmed the precipitation reaction using HCl gas was selective for NaCl crystal.
Fig. 4B.12 X-ray diffraction spectra of (a) RAE (b) recovered NaCl from RAE (c) syn-RAE-cat (d) recovered NaCl from syn-RAE-cat solution (e) syn-RAE-pyr (f) recovered NaCl from syn-RAE-pyr solution

4B.20.3. Cyclic Voltametric (CV) analysis of RAE and recovered NaCl

In order to verify the purity of the recovered sodium chloride a cyclic voltammogram using sweep techniques at a scan rate of 10 mV/s was recorded for recovered salt and analar grade sodium chloride (SD fine chemicals, India) as a reference salt. Cyclic voltagramm is used to understand the rate of electron transfer step of electro active species to the plane of electrode surface. This means that the rate of
electron transfer step is considered to be fast compared to the diffusion of molecules from the bulk solution phase to the electrode surface. The electron sensitive CV curve was used to detect the presence of organic molecules entrapped in the precipitated NaCl. The precipitated salt (0.5M) was dissolved and recorded at a scan rate of 100 mV/s. The same experiment was repeated with analar grade salt (0.5M), as reference. If the peak potential difference is less than \((58/n)\) mV at all scan rates, as per Nernst electrochemical equation, then the process is said to be quasi-reversible. Fig 4B.13 shows the cathodic and anodic peak values for the standard NaCl and recovered salt (0.5 M) were 1.33 V and 0.91 V respectively. Similar peak potential was obtained for NaCl (0.5 M) recovered from syn-RAE-cat and syn-RAE-pyr solutions. This confirmed that the recovered NaCl was not occluded with spiked organic compounds.
Fig. 4B.13 Cyclic voltammogram of (a) reference NaCl and (b) recovered NaCl from RAE, (c) recovered NaCl from syn-RAE-cat solution (d) recovered NaCl from syn-RAE-pyr solution (conditions: Concentration of reference and recovered NaCl, 0.5 M)

4B.21. Cost analysis on NaCl recovery from RAE

The cost towards the consumption of chemicals and the electrical energy was calculated for precipitation of sodium chloride from RAE and compared it with the cost towards disposal onto secure land fill (Table 4B.11). The proposed process recovered 0.203 Kg of NaCl from 1 Kg of RAE. The cost of the recovered NaCl was 0.088 USD per Kg of RAE and cost towards the consumables used in recovery of NaCl such as chemicals and electrical energy was 0.058 USD per Kg of RAE. Thus, net expenditure on processing one kg of RAE was 0.04 USD. The cost towards disposal onto secure
landfill (inclusive of transportation cost and handling cost at secure landfill) is 0.11USD per Kg of RAE. Hence, the proposed process on the management of residue after evaporation indicates that there is a scope for the cost saving compared to dumping onto secured landfill. Moreover, the dumping onto secure landfill can be considered as a short term measure. Elimination of green house gas emission and generation of saline leachate normally encountered in dumping onto secured landfill are eliminated in this new process, and they may be considered as indirect benefits.

Table 4B.11 Comparison of costs (in USD per Kg of RAE) of the present process with disposal onto secure landfill

<table>
<thead>
<tr>
<th>Mode of disposal</th>
<th>Nature of consumables</th>
<th>Cost on consumables (USD)</th>
<th>Cost on recovery of NaCl (USD)</th>
<th>Total cost on treatment (USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disposal onto secure landfill</td>
<td>Landfill maintenance cost</td>
<td>0.11</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>Present process</td>
<td>Hydrogen chloride gas</td>
<td>0.049&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.017&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.040 ((a+b)-c)</td>
</tr>
<tr>
<td></td>
<td>Electrical energy</td>
<td>0.0087&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4B.22. Conclusions

The separation of sodium chloride from the residue after evaporation of RO reject stream was achieved by selective precipitation under batch mode. The optimum conditions were: HCl gas injection time, 3 min; pH, 8.0; temperature, 40°C, and initial concentration of RAE, 60% (w/v). The precipitation of crystals was modeled using physical laws behind reactive precipitation cum crystallization process and using population balance mechanism. The surface morphology and elemental analysis of RAE and the recovered NaCl were processed through SEM and EDX analyzer. The EDX analysis and X-ray diffraction pattern confirmed the purity of the recovered NaCl. The proposed process for the management of RAE was relatively lower in cost than the other disposal methods, and also the process has the scope to recover sodium chloride. The resulted acidified supernatant solution (RAS) was considered for separation of sulphahte ions as calcium sulphate in the next chapter.