8.1. Introduction

Chemical neutralization of residual acidified supernatant solution (RAS) solution needed high amount of neutralizing chemicals and thus significantly increased the total dissolved solid content in the nRAS solution. The problem encountered in handling high TDS containing waste water was high working cost for thermal evaporation and/or crystallization processes. Moreover, the hydrogen ions in the RAS solution are also lost during chemical neutralization with alkali agents. If hydrogen ions are separated as hydrogen gas and chloride ions are separated as chlorine gas, there is a scope for converting them back into hydrogen chloride gas. The recovered HCl gas can be reused again in the salt recovery system to achieve sustainable technology and also to avoid the consumption of HCl gas significantly. Hence, this chapter was devoted to study the feasibility of electro neutralization of RAS solution using graphite/graphite electrode system under batch experiment.

In general, net balance in water electrolysis is expressed as:

$$2H_2O \rightarrow (4e^-) \rightarrow O_2 + 2H_2 \quad (8.1)$$
The minimum necessary cell voltage needed to initiate electrolysis process, $E^0_{cell}$, under standard conditions (Pressure, Temperature are held constant) can be obtained from the Eqn (8.2)

$$E^0_{cell} = \frac{-\Delta G^0}{nF}$$

where $\Delta G^0$ is the change in Gibbs free energy under standard conditions and $n$ is the number of electrons transferred.

In general sulphuric acid is used in water electrolysis to increase the electrical conductivity. In the present investigation, the RAS solution itself contains high concentration of hydrogen ion ($H^+$ concentration, 4.2 g/L). It is expected that in the electrolysis of RAS solution the products could be hydrogen and chlorine gases and therefore the RAS solution would reach neutral pH. Hence, the RAS solution was considered for electrolysis process to neutralize the solution.

### 8.2. Materials and methods

#### 8.2.1. Experimental set-up for electro neutralization of RAS solution

A rectangular shaped electrochemical cell (length, 15; width, 3.5 and height, 15cm) with triangular hopper bottom was fabricated using acrylic plastic material. Two copper coated cylindrical graphite (diameter, 1 cm, and length, 15 cm) rods were used as electrodes (Preparation of Cu-coated graphite is presented in Chapter VI). The electrodes were positioned horizontally with inter electrode spacing of 2 cm as shown in
RAS solution of volume 500 mL at pH, 3.0 was taken in electrochemical cell (Fig. 7.1) and peristaltic pump (Watson Marlow, Switzerland) was used to maintain uniform concentration operate at a flow rate of 3 cm$^3$/min by re-circulating the solution. The solution pH was monitored at regular interval of time to check the completion of electro neutralization of RAS solution.

**8.2.2. Electro neutralization of RAS solution**

Residual acidified solution after neutralized upto pH, 3.0 was considered for the electro neutralization process using electron as a further neutralizing agent. Thus, by passing electrical energy into the RAS solution the hydrogen ions are converted into hydrogen gas and the half cell (cathode) reaction as represented in Eqn. 8.3.

Reduction at cathode is 

\[ 2H^+ + 2e^- \rightarrow H_2(g) \]  
(8.3)

In order to maintain the counter ionic balance, the chloride ions are converted into chlorine gas at the anode as,

Oxidation at the anode 

\[ 2Cl^- \rightarrow Cl_2(g) + 2e^- \]  
(8.4)

The overall reaction in the RAS solution is represented by Eqn. 8.5

\[ 2H^+ + 2Cl^- \rightarrow H_2(g) + Cl_2(g) \]  
(8.5)

The electro neutralization of RAS solution was carried out using graphite/graphite electrode system as per the above electro chemical reaction. The RAS solution was rich in H$^+$ ion concentration (pH, -0.62; equivalent mass, 4.2 g/L) and the concentration of chloride ion was calculated to be 157.5 g/L (chloride ion from HCl gas,
148.6 g/L; chloride ion from remaining NaCl, 8.83 g/L). The high concentrations of hydrogen and chloride ions are due to the addition of hydrogen chloride gas for NaCl recovery. In this investigation excess hydrogen and chloride ions are expelled from the RAS solution by electrolysis.

Assume that, all the chloride ion concentrations are being converted into chlorine gas then the concentration of chloride ion was calculated to be 4.19 gmol/L. Then, the theoretical amount of equivalent chemical charge required for the conversion of chloride ion to chlorine gas was $4.19 \times 98487 = 404456$ coulombs. The amount of current required per hour was calculated by,

$$\text{Current required per hour} = \frac{\text{equivalent of chemical charge}}{24 \times 60 \times 60}.$$

The calculated amount of electrical energy required for the present conversion of chloride ion to chlorine gas per litre of RAS solution per hour was calculated as 4.6A.

8.3. Results and Discussion

8.3.1. Selection of anode to cathode area ratio

In order to optimize the anode to cathode working area for better efficiency, the working area exposed to the solution was varied as 1:1, 2:1 and 1:2. Fig. 8.1 shows the electro neutralization was achieved at minimum electrolysis time with the ratio of 1:1 than with other ratios 2:1 and 1:2. Thus, confirmed the effective anode to cathode area
was found to be 1:1. Hence, the same anode to cathode ratio was considered in further experiments.

Fig. 8.1 Effect of Anode to cathode area on electro neutralization of RAS solution

(Conditions: Potential, 4.5 V, current, 1A and temperature, 25ºC)

8.3.2. Effect of working potential on electro neutralization of RAS solution

The applied potential from 4V to 5V was varied for electro neutralization of RAS solution by graphite/graphite electrode system. Fig.8.2 shows the increase in applied potential decreased the time of electrolysis from 10 hr to 4 hr. Synthetic RAS solution with model organic compounds such as catechol and Pyrogallol was also carried out to determine the effect of organic compounds on electro neutralization by electrolysis. The observed time for electro neutralization was found to be the same for both RAS solution and synthetic RAS solution. Thus, it is confirmed that the electro
neutralization was based only on the concentration of hydrogen ions in RAS solution and not on organic concentration.

Fig. 8.2 Effect of applied potential on electro neutralization of RAS solution
(Conditions: current, 1A and temperature, 25°C)

8.3.3. Effect of applied constant current on electro neutralization of RAS solution

The applied current for the electro neutralization of RAS was carried out by varying current from 1 A to 2 A. Fig.8.3 shows the increase in applied current decreased the time of electrolysis of RAS solution from 6 hr to 3 hr. The observed electrical energy required for electro neutralization was higher than the theoretically calculated one (4.3A per hour). The increase in actual electrical energy consumption was 1.4 times higher than the theoretical energy requirement. This may be explained by power losses
due to resistance by electrical wires and material resistance of electrodes in the electrolysis setup.

![Graph showing pH vs. Electro neutralization Time, h for 1 A and 2 A applied currents.](image)

**Fig. 8.3 Effect of applied current on electro neutralization of RAS solution**

*(Conditions: Potential, 4.5 V and temperature, 25°C)*

**8.3.4. Effect of inter electrode spacing on electro neutralization of RAS solution**

It is important to evaluate the inter electrode space on the time required for electro neutralization. In this study the inter electrode spacing was varied from 0.5 cm to 2 cm. Fig. 8.4 shows the decrease in inner electrode space from 2 cm to 0.5 cm decreased time of electro neutralization of RAS solution significantly. This may be explained that, the decrease in inter electrode space reduced the ohmic resistance in electrolysis of RAS solution significantly.
Fig. 8.4 Effect of inter electrode space on electro neutralization of RAS solution

(Conditions: Potential, 4.5 V, current, 1A and temperature, 25ºC)

8.4. Comparison of cost of electro neutralization with chemical neutralization

Cost towards electrical energy consumption in electro neutralization of RAS solution was compared with the chemical neutralization process as shown in Table 8.1. The cost on chemicals used in chemical neutralization was calculated to be 0.0088 USD per litre of RAS solution and the overall recovery of calcium sulphate was 0.17 Kg from 1 litre of RAS solution. The commercial price for the recovered calcium sulphate was calculated as 0.056 USD per Kg of calcium sulphate. But, the only consumable item in electro neutralization of RAS solution was electric power, and the consumption of electric power was found to be 0.068 kWh/L of RAS solution. The cost on electrical power supply was evaluated to be 0.0068 USD per litre of RAS solution.
Table 8.1 Comparison of cost of chemical and electro neutralizations of acidified RAS solution (per litre)

<table>
<thead>
<tr>
<th>Mode of neutralization</th>
<th>Nature of consumables</th>
<th>Cost on consumables (USD)</th>
<th>Cost on recovery of products (USD)</th>
<th>Total cost on treatment (USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical neutralization</td>
<td>Electrical energy</td>
<td>0.00024</td>
<td>0.056 (by calcium sulphate)</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>Chemicals</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electro neutralization</td>
<td>Electrical energy</td>
<td>0.0068</td>
<td>-</td>
<td>0.0068</td>
</tr>
</tbody>
</table>

8.5. Conclusions

Electro neutralization of RAS solution was studied by graphite/graphite electrode system. Process parameters such as applied potential, applied current and inter electrode spacing on the efficiency of the process was determined. The optimum conditions were found to be: applied potential, 4.5 V, current, 2 A and inter electrode spacing, 0.5 cm. However, the optimum conditions may vary with electro chemical oxidation time and nature of electrolyte system. The cost towards the electrical energy in electro neutralization (0.0068 US $) was found to be significantly lower than the expenditure on chemical neutralisation (0.047 US $). Also, there is a scope for the conversion of hydrogen and chlorine gas (if separated) back into hydrogen chloride gas and thus can be reused in the Sodium chloride recovery process.