Recovery of Dilute Caustic Solution from the Desalination Plant Reverse Osmosis Discharge Brine Wastewater

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Abstract. In the Gulf region, the major source of drinking water is from sea water desalination with reverse osmosis process. It is a well-known fact that during desalination process highly concentrated brine wastewater is being discharged into the deep sea. As a result, the sea water ecosystem and aquatic life are disturbed. The coral reefs are diminishing in the vicinity of brine wastewater discharge point. The aim of this project is to convert the desalination plant wastewater (brine) into dilute caustic solution. An electrodialysis unit was fabricated with silver anode and graphite cathode. A cation membrane and an anion membrane fixed to separate anode and cathode compartments. The wastewater samples were collected from the Sur, desalination plant. A study was conducted by varying direct current voltage of the electrodialysis unit from 24 V to 48 V. It was observed that at 24 volts the pH was steadily increased to 13.8 in 10 hours. The dilute caustic concentration was reached to 1.2% in 12 hours. The results are encouraging.

1. Introduction

The reverse osmosis (RO) process to produce potable water from the sea water is economical when compared with other desalination processes. The major problem with R.O process is that it generates 50 to 55% of wastewater (brine). The wastewater contains highly concentrated dissolved solids. The brine with high total dissolved solids (TDS) is being discharged into the deep sea. The wastewater discharge point from desalination plants is fixed at inter-tidal zones so that the feed water to R.O. process will not be contaminated with outlet wastewater. However, there is a possibility of contamination. The marginal rise in the seawater quality affects the production rate of potable water. The high-density wastewater discharge reaches the bottom layers of receiving waters and may affect marine life (Tularam & Ilahee 2007). The production and growth of marine organisms are severely affected by the discharge of brine from the desalination process (Musfique Ahmed, 2012). In the Sultanate of Oman, fisheries are contributing for 1% of Gross Domestic Product (GDP). Desalination plant discharges are the important sources of marine pollution in the Red Sea and the Arabian Gulf (Abdul Aziz, 2010). It was observed in the Arabian Gulf the salinity was increased due to desalination plants brine discharge (Mohamed A.Dawoud, 2012). The recent studies had proved that the electrodialtsis is the most appropriate process to
treat desalination brine and to recover value added products. (Luigi Gurreri, 2020). The electrodialysis process is cost effective particularly energy rich Gulf countries. If the electrodialysis process coupled with solar energy further reduces the operating cost. Moreover the separation of ionic and nonionic compounds is much easier with electrodialysis process (James W. Blackburn, 1999).

1.1. Statement of problem:

It was found that the brine plumes are spreading downstream and heading towards the Oman coast. The increase in salinity of ground water in coastal area is due to highly concentrated seawater intrusion into groundwater aquifers. As a result, the growth and yield of agriculture is being affected.

The brine discharge from the desalination plants has an impact on coral reef, rocky beach or sandy surfaces on the marine environment. (Chrysi Laspidou 2010). To protect the marine ecosystem, the brine discharge into the coastal water may be arrested. Technology is available to use brine to produce magnesium hydroxide (A. Cipollina, 2015). The brine is effecting different marine species like benthic foraminifera (Kenigsberg C, 2020).

The aim of this project is to convert the high TDS concentrated desalination plant brine into dilute caustic (NaOH) solution.

The objectives are

- To fix the voltage of the electrodialysis unit.
- To fix the time to convert the brine into dilute caustic.

2. Methodology

The RO discharge brine sample was collected from the nearest desalination plant. Nearly 10 liters of brine transferred into the electrodialysis unit. The wastewater which contains 3-4% of brine, acts as an electrolyte. The electrodialysis unit is fitted with a graphite cathode and a silver anode at the two ends. The cathode area is fitted with a cathodic membrane and the anode area is fitted with an anodic membrane. The electrodialysis unit contains two ducts to collect hydrogen and chlorine gasses. Direct current is passed through the electrodialysis cell. The electrolyte dissociates into sodium hydroxide (caustic soda), hydrogen gas and chlorine gas. The cathode compartment releases hydrogen gas and the anode compartment releases chlorine gas. The leftover liquid in the electrodialysis cell is caustic soda. The electrodialysis cell reaction is as given below.

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 + \text{Cl}_2 \]

The general process of electrodialysis (ED) unit is as shown in fig 1.
Figure 1. Electrodialysis Unit

A laboratory scale experimental setup with DC power and continuous pH monitoring setup is shown in figure 2.

Figure 2. Electrodialysis Unit With DC Power And Ph Meter

The production cost of caustic soda can be reduced by using solar energy to generate required DC power (Babatope A.Olufemi, 2011). Further Concentrated Solar Power (CSP) can be used to increase the
concentration of dilute caustic. That is how the developed technology becomes technically feasible and economically viable.

3. Results and Discussion

If the pH is more than 8.3, it means hydroxide (OH-) alkalinity is present. Experiments were conducted by varying the voltage from 18 V to 48 V. The initial experiments were conducted without membrane separation. It was observed that the pH in the anode compartment was decreasing from 8.6 to 4.5. In the cathode compartment the pH was raised marginally from 8.6 to 9.0. The results were shown in table 1 and figure 1.

| Time       | Voltage Outside ED | Voltage Inside ED | pH Anode compartment | Cathode compartment |
|------------|--------------------|-------------------|----------------------|---------------------|
| 9:07 am    | 36                 | 33.9              | 8.6                  | 8.3                 |
| 9:15 am    | 36                 | 34.4              | 6.0                  | 8.9                 |
| 10:09 am   | 35.9               | 32.38             | 3.3                  | 8.5                 |
| 11:20 am   | 35.9               | 32                | 3.3                  | 8.5                 |
| 12:13 pm   | 35.5               | 31                | 3.3                  | 9.0                 |
| 2:15 pm    | 34.5               | 30.3              | 3.2                  | 8.4                 |
| 4:00 pm    | 33.5               | 30                | 3.5                  | 8.7                 |
| 4:40 pm    | 30                 | 27.3              | 4.5                  | 9.0                 |
Figure 3. The Ph Values Vs Voltage Of Electrodialysis Unit

The experiments were conducted by separating the cathode and anode compartments. A cation membrane was fixed in the graphite cathode compartment and an anionic membrane was fixed in the silver anode compartment. The results were shown in Table 2 and Fig 2.

| Time     | Voltage Outside | Voltage Inside | pH          |
|----------|-----------------|----------------|-------------|
|          |                 |                | +ve (Chlorine) | In between the Membranes | -ve (Hydrogen) |
| 10:15 am | 24              | 24             | 5.2         | 8                        | 7.5            |
| 11:18 am | 24              | 24             | 5           | 7.7                      | 8              |
| 12:05 pm | 24              | 23.5           | 5.7         | 7.5                      | 8.7            |
| 1:06 pm  | 24              | 23.5           | 7.5         | 7                        | 9.4            |
| 3:56 pm  | 24              | 22.5           | 9           | 7                        | 12             |
The experiments were repeated with increasing the hydraulic retention time from 8.30 am to 6.20 pm. The results were shown in Table 3 and Fig 3. The required pH was reached at 6.20 pm.

**Table 3. pH verses ED voltage  [With Cation & Anion Separation Membranes]**

| Time    | Voltage Outside | Voltage Inside | pH      |
|---------|----------------|----------------|---------|
|         | +ve (Chlorine) | In between the Membranes | -ve (Hydrogen) |
| 8:30 am | 24             | 5.2            | 10.9    |
| 9:30 am | 24             | 5              | 11      |
| 12:05 pm| 24             | 5.7            | 12      |
| 2:00 pm | 24             | 8.5            | 12.8    |
| 3:30 pm | 24             | 9.5            | 13.3    |
| 4:15 pm | 24             | 12             | 13.5    |
| 6:20 pm | 24             | 13.3           | 13.8    |
The dilute caustic concentration calculations
The dilute caustic 33 grams was transferred quantitatively into a 250 ml conical flask and a few drops of phenolphthalein was added and titrated with 0.5 N sulfuric acid. 19 ml consumed.

The percentage of caustic is as given below.
$$\frac{19 \times 0.5 \times 40 \times 100}{1000 \times 33} = 1.15\%$$

The dilute caustic 10 grams was transferred quantitatively into a 250 ml conical flask and a few drops of phenolphthalein was added and titrated with 0.5 N sulfuric acid. 6 ml consumed.

The percentage of caustic is as given below.
$$\frac{6 \times 0.5 \times 40 \times 100}{1000 \times 10} = 1.20\%$$

4. Conclusions
The electrodialysis performance was analyzed by varying the duration and voltage of electrolysis process. It was observed that for an electrodialysis unit of 5 liters capacity 24 volts are sufficient to get the dilute caustic solution. The chlorine gas completely released from the salt solution. It was observed that 10 hours duration is sufficient to get the required pH value.
5. REFERENCES

[1] A. Cipollina, M. Bevacqua, P. Dolcimascolo, A. Tamburini, A. Brucato, H. Glade, L. Buether, G. Micale. (2015) Reactive crystallisation process for magnesium recovery from concentrated brines. *Desalination and Water Treatment* 55:9, pages 2377-2388.

[2] Babatope A. Olufemi, Williams O. Ozowe (2011) “Studies on the Production of Caustic Soda Using Solar Powered Diaphragm Cells”, ARPN Journal of Engineering and Applied Sciences, 2011, vol 6, no 3, March(2011), pp. 49-54.

[3] Cipollina, A; Brucato, A & Micale, G. (2009).”A mathematical tool for describing the behavior of a dense effluent discharge”. Journal of Desalination and Water Treatment,(2009), vol 2, pp. 295-309

[4] James W. Blackburn (1999) Electrodiyalis Applications for Pollution Prevention in the Chemical Processing Industry, Journal of the Air & Waste Management Association, 49:8, 934-942, DOI: 10.1080/10473289.1999.10463870

[5] Kenigsberg C, Abramovich S, Hyams-Kaphzan O (2020) The effect of long-term brine discharge from desalination plants on benthic foraminifera. PLoS ONE 15(1): e0227589. https://doi.org/10.1371/journal.pone.0227589

[6] Laspidon, C, Hadjibiros, K, & Gialis, S, 2010,” Impact of Sea Brine Disposal by Coupling Desalination Plants with Solar Salt Works-A case study for Greece. Water, Vol 2, pp 75-84.

[7] Luigi Gurreri, Alessandro Tamburini, Andrea Cipollina and Giorgio Micale, (2020). Electrodiyalis Applications in Wastewater Treatment for Environmental Protection and Resources Recovery: A Systematic Review on Progress and Perspectives. Journal of membranes (MDPI).10(146), pp.1-93.

8. Mohamed A. Dawoud and Mohamed M. Al Mulla, 2012,” Environmental Impacts of Seawater Desalination: Arabian Gulf Case Study”. International Journal of Environment and Sustainability”, 1(3), pp.22-37

9. Musfique Ahmed and Rifat Anwar (2012),” An Assessment of Environmental Impact of Brine Disposal in Marine Environment” J.J.of Modern Engineering Research,(2012)vol 2(4),Aug 2012, pp. 2756-2761.

10. Tularam G.A and Ilahee. (2007), “Environmental Concerns of Desalinating Seawater Using Reverse Osmosis” Journal of Environmental Monitoring, 9(10), pp. 805-813.