A Review of Brine Sludge Management practises in Caustic Soda Industries

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Abstract–
Industries producing caustic soda and chlorine generates huge quantity of solid waste known asbrine sludge. By conducting site visits in major chlor alkali units and analysing the obtaineddata, present work aims to review existing practises of brine sludge generation, handling and disposal in chlor alkali units across India and deducegaps in existing practises.

Keywords: Chlor-alkali, Brine sludge, membrane cell, liner, Landfill

1. INTRODUCTION:

Chlor Alkali is the term used for the industrial sector which produces chlorine and Alkalies. Caustic Soda is the major product of Chlor Alkali Sector. There are around 30 major industrial units in India manufacturing Caustic Soda as per the database of Alkali Manufacturers Association of India (AMAI). Growth of chlor alkali sector in India is projected at the CAG rate of 8% annually.

Caustic soda is one of the important chemicals which have contributed significantly to the growth of chemical and other allied industries. An ever increasing demand pattern for this important chemical in India is primarily due to its increasing use in major industries such as the textile, pulp & paper, aluminium, pharmaceutical, dye stuffs, soap and detergents, and fertilizers etc. to name a few.

1.1 Statistics of Chlor alkali sector in India:

- Chlor-alkali sector forms around 74 % of basic chemical industries in India.
- The Installed Capacity of Caustic Soda in India as on 31 March 2019 was 42.78 Lakh MTPA.
- The Production of Chlorine during the year 2018-19 was 31.8 Lakh MT.
- For production of every Ton of Caustic soda, approx.0.9 MT of Chlorine and 0.03 MT Hydrogen and 0.1 MT brine sludge is produced.
- During manufacturing of Caustic Soda through electrolysis process, huge amount of Chlorine and hydrogen gas is generated from the membrane cell process.

2. Material And Methodology of study:

For study of manufacturingprocess,site visit was conductedin 5 major caustic soda producing units located inindustrial area of Bharuch district.Also, process description givenbytechnology suppliers, waste data given by process owners and interaction with process experts is the basis of this study.References have been taken from standard literarysources of Alkali Manufacturers Association of India (AMAI) and web sources of various caustic chlorine industries.

2.1 Manufacturing Process of Caustic Soda:

Common Salt (NaCl) is the raw material for production of Caustic soda (NaOH) which is brought from salt panes and stored in silos within the site.

Caustic Soda is produced by Electrolytic Process of SodiumChloride(Brine) usingIon-Exchange Membrane Process.This process also produces Chlorine & Hydrogen as Co-products. Modern Electrolytic process uses membrane cell which is sensitive to impurities hence, before electrolysis of brine solution (NaCl) it is necessary to purify the brine to the required degree to achieve high concentration.Manufacturing process consists of following stages:

a. Brine Saturation
b. Primary Brine Purification
c. Secondary Brine Purification
d. Membrane Electrolysis

a. Brine Saturation

The starting step is to prepare a saturated brine solution and for this a vertical saturator is used. The saturator is designed for a hold up of 12 hrs. of salt. Salt is charged into the Saturator by means of a conveyor. Depleted brine (Lean Brine) from the process having a concentration of approximately 225-230 mgpl of NaCl is fed into the Saturator by means of a dip pipe. The brine rises through the Salt bed, getting saturated in the process and overflows with a concentration of approximately 305-310 gpl NaCl.
Demineralized water is also added to the Saturator along with the learn brine to provide the requisite quantity of water which diffuses through the membrane from the anode chamber to the cathode chamber of the cells. Part of the

insoluble present in the salt accumulate at the Saturator bottom from where it is periodically drained out into the sludge pit. After setting, the clear liquid from the sludge pit is pumped back to the saturator and the sludge is disposed of by shovelling into a trolley

b. Primary Brine Purification:

Primary brine purification involves following steps:

Chemical Precipitation

Saturated brine overflows from the saturator into the precipitation tanks, where it is treated chemically to precipitate the impurities which are primarily Calcium, Magnesium and Sulphate. There are two precipitation tanks arranged in series and the outlet from the first tank overflows into the second tank. A 10% slurry of Barium Carbonate and Sodium Carbonate prepared in lean brine is added to the first tank.

The Sulphate react with Barium Carbonate to form Barium Sulphate, and the Calcium is precipitated as Calcium is precipitated as Calcium Carbonate by reaction with Sodium Carbonate. 33% NaOH solution is added to the second tank to precipitate out the Magnesium as Magnesium Hydroxide. Strontium, which is precipitated mainly as strontium carbonate. Mild air agitation is provided in both these tanks.

Chemical reaction of chemical precipitation process are as

BaCo3 (Barium Carbonate) + Na2SO4 (Sodium Sulphate) ⟶ Na2CO3 (Sodium Carbonate) + BaSO4 (Barium Sulphate)

Ca^{2+} (Calcium) + Na2CO3 (Sodium Carbonate) ⟶ CaCO3 (calcium carbonate) + $2Na^{+}$ (Sodium)

Mg^{++} (Magnesium) + 2NaOH (caustic soda) ⟶ $Mg(OH)_2$ (Magnesium hydroxide) + $2Na^{+}$ (Sodium)

Sr^{++} (Strontium) + CO_3 (Carbonate) ⟶ $SrCO_3$ (Strontium carbonate)

follows:

The precipitants are added in excess so as to maintain a level of 150 mgpl NaOH and 400 mgpl Na_2CO_3 in the brine. The brine containing the precipitates overflows from the second precipitation tank to the clarifier

Clarification

The impurities precipitated out in the earlier stage are removed in the clarified under gravity settling which is a large tank providing adequate settling time. A small quantity of flocculants is dosed at the inlet to aid the settling.The clarified brineoverflowing from the clarifier contains suspended solids to the extent of approximately 50 ppm and is fed in to the clarified brine tank.

The clarifier is equipped with a rake mechanism which pushes the settled sludge into the bottom discharge. The underflow from the clarifier contains approximately 10% solids and is pumped to the sludge filtration system. The cake containing 40% to 50% solids falls down a chute into a trolley for disposal as landfill. The filtrate is routed to the brine recovery tank and recycled to the precipitation tank.

Filtration

Clarified brine contains approximately 50 ppm suspended solids and this is removed by pumping through a bed of anthracite. Special quality anthracite is employed to avoid any contamination of brine. The suspended solids level is reduced to approximately 5 ppm in the filtered brine, which is collected in the filtered brine tank.

The same filtered brine acts as the backwashing medium for the Anthracite filter, which is normally backwashed after every 24 hours. The backwashing time is approximately 20 minutes and after a backwashed filter is again taken in line, there is a preparation step lasting approximately 5 minutes. The standby filter is backwashed and kept ready, to be taken in line when another filter becomes due for backwash.

The back wash flow from the filter is recovered back into the brine system.

c. Secondary Brine Purification

The Secondary Brine Purification Stage comprises two steps – Polishing filtration and Ion Exchange – and achieves the objective of producing the ultra-pure brine required for Membrane Cell operation.

Polishing Filtration

Precoat type cloth filters are used to render the brine totally free of suspended solids. Alpha cellulose is used as the precoating material on the cloth.

Filteredbrine containing approximately 5 ppmsuspended solids is passed through the polishing filters at a controlled rate. The brine flows through the precoat layer deposited on the surface and thus suspended solids are removed. The brine coming out of the polishing filters is termed as polished brine and is collected in the Polished brine tank.

The Polishing filters have to be backwashed normally once in 72 hours or earlier if the pressure drop across it exceeds 2 kg/cm^2. Backwashing is done by filling up the filter with Polished brine 3 times and draining it out each time by applying air agitation. The backwash flow is taken to a sludge tank from where it is pumped to the sludge filtration system to be filtered along with the clarifier underflow.

Ion Exchange:

Before the Polished Brine is passed through Ion Exchange columns, it is sent through Chlorine Recuperation, to recover the heat content of Chlorine and depleted brine leaving the electrolysers. By passing through these recuperators, the temperature of polished Brine increases by 8 to 12 Deg. C.

Polished brine at a temperature of 80 Deg. C. passes through two ion exchange columns connected in series. The columns are filled with a special cation exchange resin, which provides active sites for an adsorption of residual Calcium and Magnesium still present in brine. The Calcium and Magnesium level in the brine leaving the ion exchange columns is less than 30 ppb.

The first ion exchange column is designed for 100% duty and the second column plays polishing role, taking over the active role when the first column is taken out for regeneration.

The ion exchange resin is regenerated once in 3-4 days and the regeneration process takes about 5-6 hours. The regeneration is 7% HCL solution and the regenerated resin is conditioned in to Na+ from with 4% NaOH solution. The wastes resulting from regeneration are led into the effluent treatment pit for neutralization and dilution.

Pure brine from Ion Exchange columns is sent to the Pure brine head tank.

d. <u>Electrolysis:</u>

Heart of the entire process is the electrolysis. Electrolysis of purified brine is ensured by arrangement of numbers of electrolysers (electrolysis cells) arranged together called as rack. Number of such racks are arranged under a large roof called as cell house.

After treatment in above steps, the brine meets the requirements and is fed into the anode chamber of electrolyser cells. The anode and cathode chambers of the cell are isolated from each other by membrane which is selective to the migration of sodium ions. Water to some extent also diffuses through the membrane from the anode chamber.

Cl_2 is liberated at the anode surface and the brine in the anode chamber is depleted to about 200 – 220 gpl.The two phase mixture of depleted brine and chlorine overflows from the anode chamber via an insert pipe into the anolyte header.

As a result of the electrochemical reactions taking place in the cathode chamber, H_2 is generated at the cathode surface and OH- ions combine with the Na+ ions diffusing through the membrane. A two phase mixture of 33% NaOH and Hydrogen overflows from the cathode chambers into the catholyte header.

Reaction involved in electrolysis is as follows:

Anode Reaction : 2 NaCl → 2 Na+ + Cl2 + 2 e -

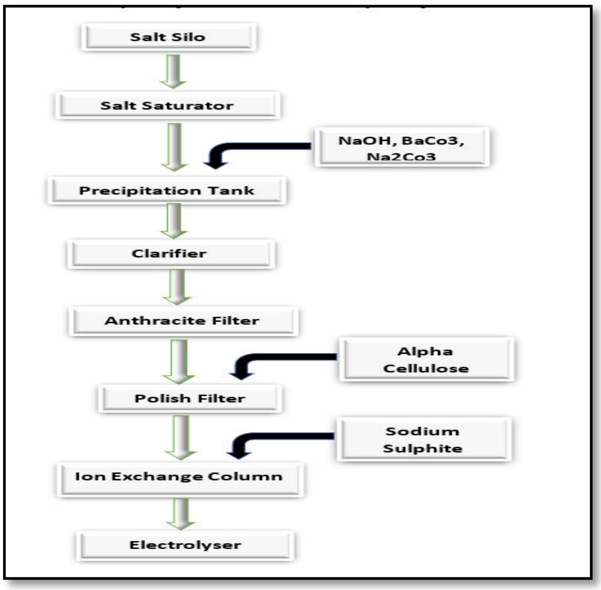
Cathode Reaction : 2 H2O + 2 e - → H2 + 2 OH

Overall Reaction :

2 NaCl + 2 H2O → 2 NaOH + Cl2 + H2

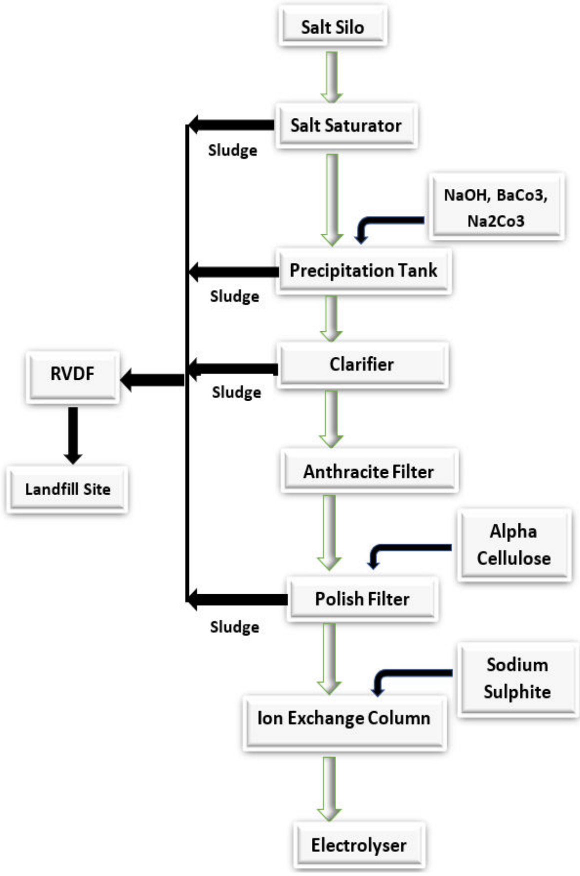
Schematic diagram of modern membrane based Electrolytic cell is depicted in fig.2.1

Fig: 2.1 membrane based Electrolytic cell (image: Euro Chlor)



A general Process Flow diagram showing all the stages in manufacturing process is shown in Fig.2.2

Fig.2.2 stages in Manufacturing process



Comparative review of manufacturing process adopted in all units under study.

It is noted that, all the units have adopted membrane cell process of electrolysis unlike previous mercury cell technology.Present technology i.e. membrane cell technology is more environment friendly compared to previous one as it avoids use of mercury and thus, mercury emission is avoided.It is highly energy intensive; around60 % of production cost is accounted to energy cost.

2.2 Sources of Brine sludge generation in caustic soda units.

a. Brine Saturator:

At the first step of manufacturing process, Salt is saturated with D.M water in vertical saturators. Part of the insoluble present in the salt accumulate at the Saturator bottom from where it is periodically drained out into the sludge pit. After setting, the clear liquid from the sludge pit is pumped back to the saturator and the sludge is disposed of by shovelling into a trolley.

b. Brine Precipitation tank:

Salt is raw material for the manufacturing of Caustic Soda and is obtained from sea shores in large salt pan areas. These salt contains impurities in the form of sand, grit, organic and inorganic impurities like Sulphates,CalciumandMagnesium.During Saturation of salt, common Salt is fed into the saturators. The impurities are removed by addition of chemicals like Barium Carbonate, Soda Ash and 32 % Caustic Soda Lye. This precipitation takes place in large precipitation tanks. Gradual deposition of impurities especially grits takes place in the base of the precipitation tank. During cleaning of tanks, such solid waste is generated.

c. Sludge from Clarifier:

After chemicals are added in precipitation tank, brine solution is transferred to clarifiers to provide sufficient retention time so that impurities are settled at the bottom. The under flow of the clarifier is the brine sludge. This sludge constitutes the major part of waste in entire caustic soda premises.

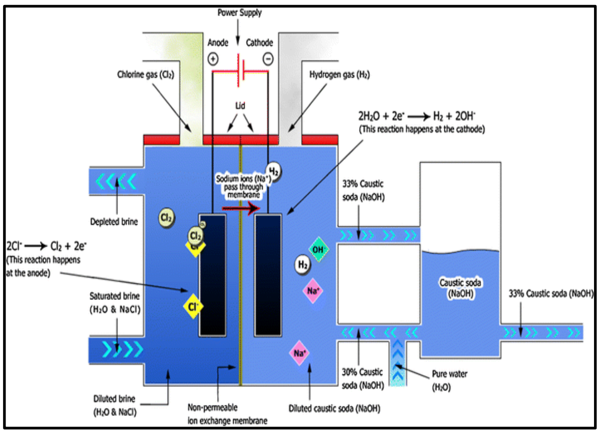
A Flow diagram showing brine sludge generation from all the stages in manufacturing process is shown in Figure 2.3

2.3 Quantity of brine sludge generation:

To work out the quantity of brine sludge generated from each units, data was collected during site visit from concerned responsible departments.

Comparative data of production and sludge generation is presented intable2.1 for interpretation.

Fig. 2.3 brine sludge generation from various stages of production



Unit	Production in TPD	Brine sludge generation in TPD	Specific sludge generation in (MT of sludge per MT Production)
Unit-A	1085	89	0.082
Unit-B	1120	112	0.1
Unit-C	1400	100	0.071
Unit-D	1250	80	0.064
Unit-E	800	86.11	0.107
Average specific sludge generation			0.084

Table 2.1 comparison of production and sludge generation from different units.

Characteristics of Brine sludge as given by various units is presented in table 2.2

Sr .no	Constituents, % by weight	Unit -A	Unit -B	Unit -C	Unit -D	Unit -E
1	$BaSO4$	6.2	5.1	7.4	4.5	5.2
2	CaCo3	8.8	7.3	7.5	6.9	7.5
3	$Mg(OH)_2$	5.2	7.3	5.4	8.3	3.8
4	NaCl	6.2	8.6	7.6	6.8	10.1

5	Insoluble	28.6	24.8	22	25.6	23.7
6	Moisture	45	47.1	49.5	48.1	50.7

Table 2.2 Characteristics of brine sludge from various units

2.4 Comparative overview of prevailing Brine sludge management practises:

Like Process, similar arrangements have been provided for sludge handling and disposal measures in above five units.

For dewatering of brine sludge, RVDF is most common unit operation adopted.

After dewatering, sludge cake is collected in tractor trolleys and transported to captive TSDF site for disposal.

All the units have constructed TSDF site for their captive disposal of brine sludge.

3. RESULT AND CONCLUSION

Interpretation of data of above industries, interaction with process experts and reference of standard literary sources of authorities it can be concluded that manufacturing process of caustic soda, generation of brine sludge, handling and disposal of brine sludge is similar, not only in the industries under the study but also throughout this industry segment.

Membrane cell electrolysis process is employed for electrolysis of the solution of salt and water. Electrolysis yields NaoH, Chlorine and Hydrogen gas. Purification of salt solution before electrolysis generates huge quantity of solid waste called as brine sludge.

From Table 2. it is clear that for production of 1 MT of caustic soda approximately 84 kg of brine sludge is produced. This means for production of approx.10,000 MT caustic soda which is average per day capacity of the country, 840 MT brine sludge is estimated to be produced per day in the entire country.

From table 2.2 average moisture content is found as 48% in sludge. Hence, it is clear thar high volume of sludge is due to high moisture content. Out of 84 kg,48% is moisture per ton of production. If dewatered with suitable method can reduce the sludge up to 43.6 MT.

Further, presence of chloride in sludge restricts its potential to be used in any construction application.

For dewatering the sludge, RVDF is used in all the units, reason might be the low operating cost. But it should be noted that, Rotary vacuum drum filter (RVDF), patented in 1872, is one of the oldest filters used in the industries. Its low cost is accompanied with disadvantage of low moistureremovalcapacity.Design capacity this technology is 50 to 55% removal which means 45% to 50 % water remains with the sludge. Due to high moisture, below are the key environmental issues;

1. Large volume of waste
2. Transportation cost is high
3. Disposal cost increases due to large volume.
4. More leachate generation.
5. More Chances of ground water contamination.
6. Chances of spillage during handling.
7. Large environmental foot print.

Although MoEFCC has declared the brine sludge as non-hazardous waste, no guidelines have been published so far for its disposal as a non-hazardous waste. As a consequence of this it is being dumped into captive or common hazardous landfill site and caustic soda unit operators are paying huge cost due to this since theconstruction and operation of hazardous waste landfill site ishighly costly. High cost is due to various layers of liner system at the base, at the sides as well as in covers. Various liners are;

1. Compacted clay liner/Compacted amended soil layer of 150 cm with permeability (k) < 10^{-7} cm/second.
2. HDPE/ Geomembrane layer > 1.5 mm
3. Geo textile layer
4. Leachate collection layer (sand and gravel) of 30 cm with (k) >10^{-2} cm/second.

Above is the specification of single composite liner system. For double composite liner system, cost almost doubles.

Although Chlor alkali forms around 74% of basic chemicals sector in India and fetched tremendous revenue, neither proper and specific waste management guidelines have been in existence nor much research has been done in the field of waste management of chlor alkali sector.

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