Universal Journal of Environmental Research and Technology
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Available Online at: **www.environmentaljournal.org**
Volume 3, Issue 1: 50-54

Open Access **Research Article**

Assessment of Hazardous and Non-Hazardous Status of Solid Waste Generated at ETP of Bromine Plant for Its Potential Use

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Abstract:
Recently, environmental problems related to brominated flame retardants have become a matter of great concern. Bromine has been extracted from sea brine. The main problem related to bromine production was disposal of the sludge. The sludge generated in the process was analyzed for its constituents and it was found to contain Calcium sulfate which was nothing but crude gypsum. Gypsum is one of the non-hazardous compounds which can be used as a source of sulfate and as a source of silica. It can easily be use for construction and increasing height of bunds of evaporation of ponds. Because of easy availability of gypsum i.e. sludge which was generated from bromine plant, can be use as amendments for reclamation.

Keywords: Bromine, Gypsum, Non-hazardous, Sea brine, Sludge

1. Introduction:
India's annual consumption of bromine and its derivative is about 1% of global consumption of 4, 68,000MT (Million Tonnes). There are nine manufacturing units in the country having a capacity to produce 7245 TPA (Tonnes Per Annum) of bromine from sea brine. Bromine is used in flame retardants, drilling fluids, gasoline additives, pesticides etc. The most important group of flame retardants is brominated flame retardants (BFRs), which contain a diversity of chemicals. Some BFRs polybrominatedbiphenyls (PBBs), tertabromobisphenolA (TBBA), hexabromocyclododecane (HBCD) (Wit, 2002). In India, nearly 290 million tonnes of industrial wastes are generated annually of which, around 7.2 million tonnes is hazardous and requires careful disposal (Pappu*et al.*, 2007; Saxena*et al*., 2002). Due to inherent hazard in transporting bromine over long distance, bromine manufactures have diversified into production of bromine derivatives. Solaris Chemtech Limited (SCL) Gujarat (India) has a production capacity of 3,500 TPA and 10,000 TPA of liquid bromine from its two units respectively. The industry is facing problems for the disposal of sludge which is found to contain crude gypsum formed due to reaction of sulfuric acid and lime. The main sources of the gypsum are the manufactures of mineral acids. The approximate generation of sludge was 250 MT/ month from the Stored Origin and 750 MT from the recent Origin. Gypsum can also be used in agriculture for the treatment of alkaline soils (Miller*et al.,* 1986;Pawan*et al.,* 1986). The present paper deals with evaluation of the hazardous categoryof solid waste generated at ETP of Bromine plant as per schedule II (1972) of MoEF guidelines for handling and management of hazardous waste. By analyzing the quality of sludge generated in the plant different alternatives will be suggested to utilize this solid waste (MoEF vol-1, vol-2; Hazardous Waste Management Series 2005).

2. Materials and Methods:
2.1. Study area
Samples were collected from the Sol3aris Chemtech Limited Gujrat (India). The average annual rainfall of the region was around 280-300 mm. The mean maximum temperature during summer and mean minimum temperature during winter was recorded to be 46^0 C and 5^0 C respectively with relative humidity of 65 to 70%.

2.2. Process details and description
The above mentioned industry has been producing Bromine from sea bittern. Bittern was acidified with sulfuric acid and heated to 80^0 to 90^0C in the heat exchanger. The preheated bittern is fed to stripping column, where chlorine gas is injected at the bottom. The reaction mass is heated up to 110^0C at atmospheric pressure by direct injection of steam to stripping column the chlorination of bittern results in release of bromine vapor as chlorine replaces bromine in magnesium bromide.

Bromine vapor is sent to a series of condenser for condensation of bromine. The water vapor and un-reacted chlorine vapors are scrubbed in to the bittern circulation scrubber. The bottom of the condenser goes to the separator where water and bromine are separated. The process flow diagram was depicted in Fig a.

2.3. Waste Water Generation

The quantity of de-brominated effluent generated from the stored region of SCL is 120 to 130m^3/d and was having pH 2.0 to 2.5. 2976m^3/d of waste water was generated from the process unit and acidified bittern and it was stored in to the wastewater treatment system. Wastewater from the other drains including acidified bittern is treated in ETP and sanitary waste in to soak pits.

2.4. ETP Description

2.4.1. Units of ETP

The existing ETP consists of preliminary and primary treatment of effluent the ETP has following units.

1) Equalization cum neutralization tank:
2) Sludge drying beds

The schematics of the existing treatment plant are shown in Fig b. The hot acidified debrominated bittern coming out of extraction tower and heat recovery unit is sent to ETP. The present production capacity of the old unit is 3500 TPA of bromine and quantity of gypsum degenerated at this site is 250 TPM, whereas the production capacity of new unit is 10,000 TPA of bromine and the quality of gypsum is 750 TPM (Total Productive maintenance). In the ETP, the acidity of bittern is neutralized by adding hydrated lime slurry. In this process of neutralization of bittern, calcium sulfate is produced by-product (solid waste).

2.4.2. Equalization cum Neutralization Tank

The neutralization unit consists of two compartment, one mixing tank, and two reaction tanks. Neutralization tank is provided with baffle for this compartmentalization. Neutralization is carried out by alkali (lime slurry 8% w/w $Ca(OH)_2$ and pH is adjusted within 6 to 8). This is achieved by providing mixing facility in the tank. The pH of sea bittern is 6 to 6.5 in the manufacturing process i.e. in the stripping column, the pH is maintained at 2.4 to 3.2 with the help of addition of H_2SO_4. The pH was brought back to neutral by addition of hydrated lime, $Ca(OH)_2$ 90%w/w.

The reaction scheme is described in the equations given below

$$Mg(Br)_2 + Cl_2 \longrightarrow MgCl_2 + Br_2 \uparrow$$

$$H_2SfO_4 + Ca(OH)_2 \longrightarrow CaSO_4 \downarrow + 2H_2O$$

2.5 Methods of analysis

2.5.1 Method of analysis for water

The pH of the samples is determined using the pH meter, by calibrating the pH meter using the buffer solutions of known pH values. EC (electrical conductivity) is determined by using the conductivity meter calibrated with conductivity standard (0.01m KCl with conductivity 1413 µ Scm^{-1}).Total suspended solids (TSS) and Total Dissolved Solids (TDS) is determined by gravimetric method. Nitrate, Sulfate and Phosphate is analyzed by spectrophotometeric method. A chloride of the samples is determined by using argentmetric method of precipitation. Oil and grease is determined by using the partition gravimetric method. Calcium and magnesium is analyzed by complexomertic titration with EDTA. Sodium potassium is analyzed on flame photometer. Alkalinity is determined with acid titrations (APHA, 2005).

2.5.2. Method of analysis for sludge samples

Sludge samples are dried and sieved through 2mm mesh prior to characterization. Chemical analysis of the ions is carried out to find out the total content of the components. Soluble cations present in the sludge samples are analyzed from saturation extract of sludge sample (Tan, 2000; USEPA, 1986). Sulfate content is analyzed by following turibidometric method (Singh et al., 1988). Gypsum content in the samples is analyzed by as content of Ca by complexometric method (Loveday, 1974;Dewiset al., 1970). The other microelements are analyzed by atomic absorption spectroscopy (Jackson1960).

3. Results and Discussion:

3.1. Physico-chemical characteristics of wastewater generated bromine plant:

Table1. depicts the Physico-chemical characteristics of waste water generated from liquid bromine plant and the treated effluent.The debrominated bittern is highly acidic in nature having pH 1.0± 0.4. It is neutralized in ETP and the pH is bought back to pH 7.52± 0.5. Total Dissolved Solids (TDS) are reduced to 256 ± 4.1g/l from 306 ± 3.06 g/l after treatment. Calcium content before treatment is 30.24 ± 1.5g/l and after treatment is 14.40 ± 2.5g/l. Magnesium content increases from 29.47 ± 2.6 g/l to 31.87 ± 1 g/l after treatment. Oil

and grease content after treatment is reduced to 1.8 ± 0.2 g/l from 2.8 ± 0.14 g/l.

3.2. Physicochemical characteristics of sludge generated from bromine plant:

The sludge generated during the process of neutralization at ETP is collected. Two samples one stored origin and another recent origin are taken for finding out detailed chemical composition and percentage purity. From both of these analysis reports, the maximum percentage of calcium sulfate (Gypsum) 44.22 ± 0.15 to 47.60 ± 0.2% is observed in the sludge followed by magnesium sulfate 10.30±0.2 to 18± 0.32%, sodium chloride 7.44 ± 0.3% to 7.55± 0.35, potassium chloride 2-9% and silica 15.82 ± 0.4 to 16.1 ±0.4%. The composition of these sludge samples are given in Table 2.

Table 1. Physicochemical characteristics of Spent Bittern (Before treatment) and Neutralised Bitterns (After treatment)

Sr. no	Parameter	Before treatment	After treatment
1	pH	1.0 ± 0.4	7.52 ± 0.5
2	Turbidity (NTU)	15 ± 1.52	12 ± 0.5
3	Total dissolved solids(g/l)	306 ± 3.06	256 ± 4.1
4	Total suspended solids(g/l)	70 ± 3.6	62 ± 2
5	Alkalinity(mg/l)	-	462 ± 4.7
6	Chlorides(g/l)	158 ± 2.5	104 ± 2.6
7	Calcium(g/l)	30.24 ± 1.5	14.40 ± 2.5
8	Magnesium(g/l)	29.47 ± 2.6	31.87 ± 1
9	Sodium(g/l)	34 ± 2.0	28 ± 1.5
10	Potassium(g/l)	4.40 ± 0.2	8.80 ± 0.5
11	Sulfate(g/l)	37.00 ± 2	37.00 ± 2.5
12	Nitrate(mg/l)	6.50 ± 0.2	6.00 ± 0.7
13	Phosphate(mg/l)	BDL	BDL
14	Bromine(g/l)	0.13 ± 0.1	0.16 ± 0.1
15	Oil and grease(mg/l)	2.8 ± 0.14	1.8 ± 0.2

BDL: Below Detectable Limit

Table 2. Chemical composition of Sludge from Stored origin and Recent origin

Sr. no	Chemical composition	Percentage % (Stored origin)	Percentage% (Recent Origin)
1	Calcium sulphate ($CaSO_4$)	44.200 ± 0.15	47.600 ± 0.2
2	Magnesium sulphate ($MgSO_4$)	18.500 ± 0.32	10.300 ± 0.2
3	Magnesium Chloride ($MgCl_2$)	1.190 ± 0.1	11.000 ± 0.1
4	Sodium carbonate (Na_2CO_3)	0.070 ± 0.13	0.054 ± 0.2
5	Sodium chloride (NaCl)	7.550 ± 0.35	7.440 ± 0.3
6	Potassium chloride (KCl)	9.550 ± 0.28	2.570 ± 0.2
7	Ferrioc chloride ($FeCl_3$)	3.020 ± 0.11	4.800 ± 0.4
8	Zinc chloride ($ZnCl_2$)	0.003 ± 0.2	0.010 ± 0.1
9	Manganese chloride ($MnCl_2$)	0.070 ± 0.3	0.090 ± 0.2
10	Lead chloride ($PbCl_2$)	BDL	BDL
11	Cadmium chloride ($CdCl_2$)	BDL	BDL
12	Copper chloride ($CuCl_2$)	BDL	BDL
13	Chromium chloride ($CrCl_2$)	BDL	BDL
14	Nickel chloride ($NiCl_2$)	BDL	BDL
15	Cobalt chloride ($CoCl_2$)	BDL	BDL
16	Silica (SiO_2)	15.820 ± 0.4	16.100 ± 0.4

BDL: Below Detectable Limit

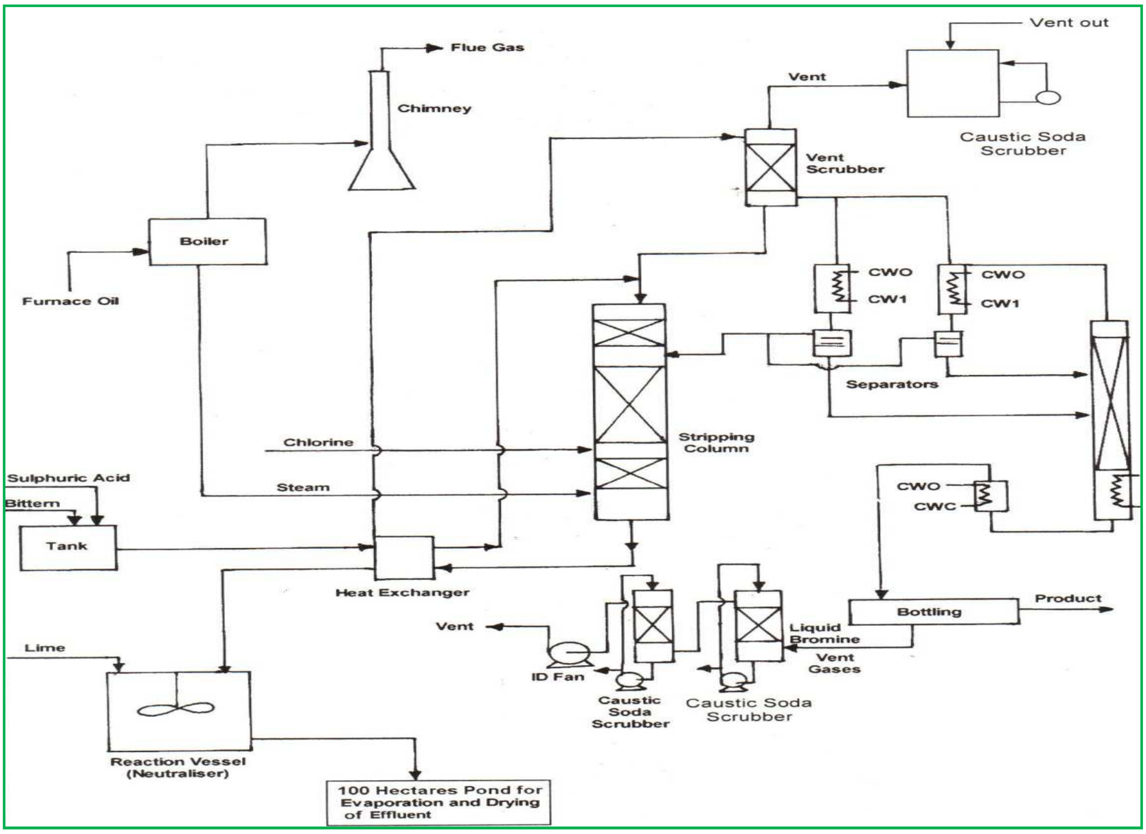

Figure a. Process details

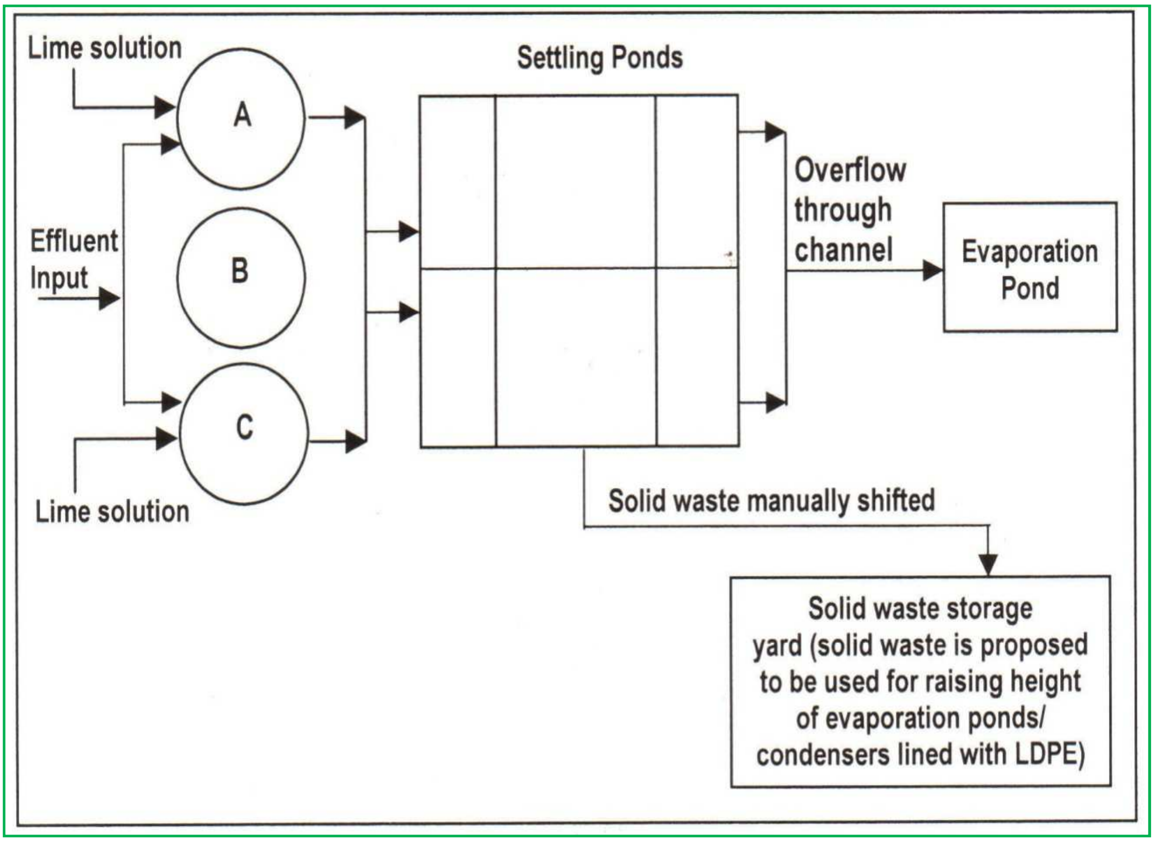

Figure b. Effluent treatment plan

4. Conclusions:

Following conclusions can be drown from the above study

1. The characteristics of treated effluent are very similar to the sea bittern.
2. Moreover, throughout the bromine extraction process, it is observed that after extraction of bromine the sulfate present in the debrominated bittern is neutralized with milk of lime in effluent treatment plant.
3. The sulfate is precipitated out in the form of calcium sulfate ($CaSO_4$) in the settling pond. So the solids (Solid waste) that are precipitated out in the ETP are nothing but calcium sulfate.
4. It is found that percentage purity-wise the sludge contains nearly 50% purity as Gypsum and it can seen from the detailed chemical composition of the sludge that it is absolutely non hazardous as it does not contain any harmful material as per the hazardous waste regulations.
5. Sludge which is generated from the bromine plant ($CaSO_4$) can be widely used for the reclamation, construction of bunds and increasing the height of bunds of evaporation ponds and condensers. It can also be used in agriculture for the treatment of alkaline soils (Higson, 1951; Hull, 1957).
6. It improves water penetration and workability of an impermeable sodicsoil (alkaline) and also increases aeration of many soils (improves sour soils) (Wallace, 1995; Wallace, 1997).
7. Industries can also utilize the gypsum sludge generated at ETP for the construction of bunds of condensers as sludge is absolutely non hazardous this would not only save the soil but also will be a long term solution as far as the disposal of gypsum sludge is concerned.

5. Acknowledgement:

The authors are thankful to Director, National Environmental Engineering Research Institute, Nagpur, India to provide the facilities required for our research paper work and for their kind co-operation.

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