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Characteristic Change of Effluent from a Chlor-alkali Industry of India due to Process Modification

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Abstract

This paper highlights different techniques used for waste minimization in one of the units of a chlor-alkali plant in Uttarpradesh, India. This paper points out various possibilities to reuse the waste produced in the above-mentioned unit. The main focus of this paper is on the evaluation of waste minimization at source due to process modification. The possible improvement of the treatment of effluent is also duly considered.

Key words: Brine solution, chlor-alkali plant, pH, process modification, waste minimization.

Introduction

In a chlor-alkali industry, Chlorine (Cl_2) and sodium hydroxide (NaOH) are manufactured by electrolysis of a salt solution. The chlor-alkali process is the most economically important electro-synthetic process. Chlorine is needed in the production of 85% of all pharmaceuticals, 98% for water disinfection[1]. Out of the 112 elements that make up the world we live in, 99% of earth's crust, atmosphere and oceans comprise just 12 elements and one of them is chlorine[2]. In chlor-alkali industry, power consumption accounts for approximately 60 to 70% of the total cost [3]. The chlor-alkali industry is an energy intensive process and it is the second largest consumer of electricity, 2400 billion kWh, among all the electrolyte industries[4]. Three processes viz. mercury, diaphragm and membrane cell electrolysis are generally adopted[5]. The membrane cell electrolytic process is most modern and has economic and environmental advantages. In the membrane cell process, the chlorine discharges at the anode and the hydrogen discharges at the cathode are kept apart by a selective polymer membrane that allows sodium ions to pass into cathode compartment and react with hydroxyl ions to form caustic soda[6, 7]. The main input of raw material is sodium chloride (NaCl). Caustic soda, chlorine gas and hydrogen gas are produced simultaneously by the electrolysis of purified brine solution in membrane cell electrolytic process. Sodium chloride contains chlorine which is removed at the anode, chloride (Cl^-) is oxidized to chlorine. The ion-selective membrane allows the counter ion Na^+ to freely flow across, but prevents anions, hydroxyl (OH^-) and chloride from diffusing across. At the cathode, water is reduced to hydroxide and hydrogen gas. At the cathode, positive hydrogen ions pulled from water molecules are reduced by the electrons provided by the electrolytic current, to hydrogen gas, releasing hydroxide ions into the solution.

The non-permeable ion exchange membrane at the centre of the cell allows the sodium ions (Na^+) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda (NaOH).

In primary brine plant, saturation of brine, purification of brine, settling, filtration, acidification, de-chlorination are performed. The return brine from cell plant (190-200 gpl) is re-saturated in the saturator by addition of NaCl / KCl salt to achieve brine concentration of 300gpl to 315gpl. The salt contains unwanted impurities Ca^{2+}, Mg^{2+} and SO_4^{2-}. These impurities are removed by adding Na_2CO_3, NaOH and $BaCO_3$. The mixture are agitated and allowed for coagulating the precipitate. The precipitated impurities are dragged towards the settler bottom by the rotation of the arm. The settled liquid is allowed to overflow through the launder into the surge tank. The settled precipitates are periodically removed.

The clarified brine from the settler is pumped to the filters from the surge tank. The suspended particles are filtered in brine tanks. Filters are periodically backwashed to remove the arrested impurities.

In membrane system, the stored brine is sent to secondary brine plant for further treatment (to convert the brine to ppb quality). The feed brine after electrolysis gets depleted to 50 gpl and also gets contaminated with free Cl_2 to the extent of 500-600 ppm. Hence de-chlorination system for removal of free Cl_2. Dechlorination is done by vacuum system. Return brine from cell plant is acidified to pH 2.0 and collected in lean brine tank where from it is pumped into the saturator after neutralization. This cycle is continued.

The settler unit is the prime source of sludge generation. The sludge generated is around 1500 MT on a monthly basis. It is inorganic brine sludge containing mud, NaCl, KCl, water, $CaSO_4$, $BaSO_4$, Mg $(OH)_2$, caustic soda/potash, Na_2CO_3. Present investigator suggests using this sludge as compost and as fertilizer.

In the chlor-alkali process the wastewaters are generated from Aluminum Chloride plant, Stable bleaching plant, Membrane plant, CSF plant, Hypochlorite plant, Brine purification plant and from domestic uses. All these wastewaters are coming finally to the effluent treatment plant.

Chlor-alkali industry, being red category industry, generating huge wastewater and solid waste like brine mud. High TDS, TSS, Chloride, free chlorine are the main problem. Mercury is present in the waste generated from mercury and diaphragm process.

Extensive studies are conducted by many researchers to evaluate the characteristics of effluent from chlor-alkali process and the prospective waste minimization approaches are also identified. Attempts are also made to suitably use the waste products generated from this industry.

Out of all the industrial waste minimization processes carried out in Chlor-alkali plants, source reduction is usually the lowest cost alternate, particularly for improving production process[8].

A chlor-alkali plant of Chile recycles the brine sediment as mineral additive in compost and uses it as sorbent for removal of heavy metals from wastewater[9]. The major waste stream from the chlor-alkali process consisting of brine muds are filtered or settled, the supernatant is recycled and the mud is dried and landfilled[10]. The modern membrane electrolysis process uses large cells to produce chlor-alkali product without environmental repercussions. A single cell can be up to $5m^2$ in size and can produce 0.65 mg/day of chlorine[11]. Studies show that anode and cathode reactions in chlor-alkali process can be enhanced significantly by magnetic modification of electrode surfaces and it is observed that the flux (current density) by magnetic modified electrode is larger than the flux of non-magnetically modified electrodes[12] by a factor of 3.22 ± 0.08. The Olin Chlor-alkali Becancour Plant reduced waste by 80% by installing membrane electrolysis, a new hydrochloric acid burner and a new membrane evaporator (Olin Chlor-Alkali)[13].

The brine sludge generated in membrane cell plant is non-hazardous, but diaphragm and mercury cell plant is hazardous. Approximately one lakh metric ton of brine sludge is generated from all units in India. It is, therefore, essential to find alternate use of brine sludge instead of storing on land. Fly ash generated in captive power plants of Chlor-alkali industry is required to be used, not to be disposed on land. 8 units of 11 captive power plants generated around 8.18 lakh metric ton of fly ash per annum. All the fly ash had been utilized in cement manufacturing, brick manufacturing and road construction[14].

1886.37 MW energy saving per annum was achieved by design modification at chlorine compressor discharge in a chlor-alkali plant of Dahej of India[15].

By replacement of 2nd generation elements with latest 5th generation elements H electrolyser, savings of 28, 02,000 KWh/Annum were achieved in a chlor-alkali plant of Madhya Pradesh of India[16].

The objective of the present paper is to study on waste minimization in a basic drug plant producing sodium hydroxide and prospective measures to be undertaken to meet the need of proper environmental management. Corrective actions are taken to reduce wastage and to improve characteristics of wastewater by process modifications.

Material and Methods

The present study was conducted in a bulk drug industry (Chlor-alkali plant) producing chlorine (Cl_2) and sodium hydroxide (NaOH). The selected Chlor-alkali plant was visited in two subsequent years (2011 and 2012). In the first visit, extensive studies of the in-plant processes were made. Samples were collected from the final effluent stream and analyzed for the parameters pH, TSS, TDS, COD, BOD, Mercury, and Free Chlorine. Thorough study of the in-plant processes revealed that there was enough scope of process changes to minimize waste generation and accordingly some suggestions were put forward to the management of the industry by the present investigator. The suggestions were followed in toto. After one year, similar observations were made regarding the quantity and quality of the effluent generated from the same industry. Some of the important recommendations were the following. i. Most of the equipments in the primary brine like settler, purifier are kept open. A fraction of solution is evaporated and dropping out causing process losses and increase wastewater load. Suggestion was to cover the equipment to prevent losses. ii. Highly concentrated Sulphuric acid (92-98%) is used to dry chlorine. 20 kg Sulphuric acid is consumed per metric ton of chlorine produced. Spent acids were wasted in wastewater. Suggestion was made either to sell the spent acids to another industry which will use it or to re-concentrate the acid and use it again in the plant process itself by the same industry. iii. The waste gas containing chlorine used to emanate during normal operation and large amount of chlorine gas was emitted to the environment during irregular plant operation and in emergencies. Suggestion was made to use weak caustic soda solution to absorb the same to produce sodium hypochlorite. iv. Present investigator suggested providing suitable dosing of hydrogen peroxide and sodium bisulphate to neutralize and reduce chlorine content in wastewater. v. The then practice was to bring together wastewater streams from stable bleaching powder and from aluminum chloride and the pH of mixed wastewater would stand at 11-12. This was further neutralized with 26 liter of commercial hydrochloric acid daily. Similarly, wastewater stream from membrane plant and brine purification plant having low pH of 3-4 was neutralized with 32 kg soda ash daily. Present investigator altogether stopped acid/alkali consumption, instead all wastewater streams are suggested to mix in primary ETP for intermixing and automatic neutralization. vi. Present investigator suggests using the sludge generated in the treatment plant as compost, as fertilizer and also using it as a feed material in cement manufacturing, brick manufacturing and road construction. vii. Aim should be for zero emission of hydrogen as using hydrogen to generate DC power within cell house should be explored in hydrogen based fuel cell [17].

Results and Discussion

Results of implementation of suggestions provided by the present researcher were observed after one year. It was seen that both the quantity and the quality of the effluent generated from the industry showed remarkably improved condition.

The equipments are covered now to retain process fluid and to save process loss thereby reducing wastewater quantity also. This spent acid is now being sold to an agent who has accepted this quality. Simultaneously, industry is also attempting to re-concentration the used and diluted acid in closed loop system and thereafter consumption has reduced to 0.1 kg of Sulphuric acid per metric ton of chlorine produced. Emission of chlorine gas is stopped by absorbing chlorine in weak caustic soda. Intermixing of waste streams automatically neutralizes each other and the pH stands at 7 to 9.

Table 1 reflects changes in characteristics of wastewater observed before and after implementation of modifications. Quantity of effluent is reduced substantially. pH has changed from highly alkaline condition to almost neutral to slightly alkaline. TSS, TDS, COD, BOD, Chloride and residual chlorine values are reduced to a great extent.

Table-1
Characteristic Change in Effluent Generated from Chlor-alkali Industry due to Process Modifications

Parameters	**Effluent Characteristics**	
	Before Modification	**After Modification**
Volume (m^3/h)	30 – 50	20 - 40
pH	8 – 12	7 – 9
TSS (mg/l)	2500	< 1200
TDS (mg/l)	7400	< 2000
COD (mg/l)	250 – 300	< 200
BOD (mg/l)	35 – 55	< 35
Mercury (mg/l)	0.001	0.001
Chlorides (mg/l)	4800	< 1000
Free Chlorine (mg/l)	1000	< 400

Table 2 shows the saving of materials due to modification. Consumption of hydrochloric acid and soda ash are reduced to a remarkable extent.

Table-2
Saving of Materials due to Modifications

Materials	**Quantity consumed per annum before modification**	**Quantity consumed per annum after modification**
Soda ash	11,000 kg	Nil
Hydrochloric acid	9000 liter	Nil

Conclusion

It is revealed that minimization of waste is amply achieved by adopting certain measures. The following conclusions can be drawn from the above investigative research. Preference has to be given to membrane process. Re-concentration of brine has to be done in closed vessels. Recycle of brine wastes are to be done. Chlorine has to be scrubbed from tail gases to produce hypochlorite. Brine mud settling ponds must be lined to prevent ground water pollution. Alternate use and recycle of brine mud should be searched to make wealth from waste. It is seen that it can be suitably used in cement plant. There is more scope of research to evolve alternative use of the same as huge quantity of solid waste generate in chlor-alkali plants as brine mud.

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