

Waste Minimization in a Chlor-Alkali Plant

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Abstract

This paper presents an analysis of different techniques used for waste minimization in one of the units of a chlor-alkali plant. The main focus of this paper is the evaluation of source reduction alternatives. It uses a criterion in which the economic performance of the process that includes all the waste related costs within an environmental accounting framework is considered. This paper also finds the various other possibilities to reuse the sludge produced in the above-mentioned unit.

Introduction

The rapid industrialization of India in the recent past has been the striking feature of Indian economic development. The common indicators of economic welfare, such as national product and income have reflected the growth of the industry as a major indicator for the development of the nation. But the other angle of industrialization has been the serious damage to the surrounding environment due to the wastes and pollutants generated from the industries. The irreparable damage to the surface and ground water, air and soil; the growing emergence of hazardous and toxic wastes from the production processes; the uncontrolled dumping of highly contaminated hazardous wastes are some of the shocking landmarks of our progress.

Since waste disposal regulations currently in effect in India have become more stringent, chlor-alkali plants can no longer depend on end-of-pipe treatment as the sole method of pollution control of their wastewater and wastes, and must bear the burden of additional waste disposal costs. In-plant modification and development of more effective pollution control technology, directed toward decreasing waste output and increasing production and management efficiency, not only solve wastewater and waste treatment problems but also alleviate costs.

The term *waste minimization* means the reduction, to the extent feasible, of waste that is generated prior to treatment, storage, or disposal of the waste. Industrial waste minimization technologies include source reduction, pollution prevention, recovery, and reuse. Application of technologies that decreases pollutant concentrations per unit production, water use, and chemical dosage improve efficiency. Of the industrial waste minimization processes carried out in chlor-alkali plants, source reduction is usually the lowest cost alternative, particularly for improving management and production process.

Primary brine plant [operations performed]:

This is the 1st unit of the plant and is a center for various activities like saturation of the brine, purification etc. Following is a brief description of various sub units in the mentioned unit.

- **Brine saturation:** The return brine from cell plant [220-226 gpl] is re-saturated in the saturator by addition of NaCl / KCl salt to achieve brine concentration of 320 gpl.
- **Purification:** The salt contains unwanted impurities viz. Ca^{2+} , Mg^{2+} and SO_4^{2-} . These impurities are removed by adding Na_2CO_3 , NaOH and BaCO_3 . The mixture is agitated and allowed to flow into the settler magna flock addition is done for coagulating the precipitate.
- **Settling:** The precipitated impurities are dragged towards the settler bottom by the rotation of racker arm. The settled liquid is allowed to overflow through the launder into the surge tank. The settled precipitates are periodically removed.
- **Filtration:** The clarified brine from the settler is pumped to the filters from the surge tank. In case of De Nora plant, sand bed filters are used and for the membrane plants, anthracite filters are used. The suspended particles are filtered brine tanks. Filters are periodically backwashed to remove the arrested impurities.
- **Acidification:** The brine from the De Nora storage (NaCl/KCl) has to be acidified (pH 4-6), before sending to electrolytic cell plant. In membrane system, the stored brine is sent to secondary brine plant for further treatment (to convert the brine to ppb quality).
- **De chlorination:** The feed brine after electrolysis gets depleted to 60 gpl and also gets contaminated with free Cl_2 to the extent of 600-700 ppm. Hence de-chlorination system for removal of free Cl_2 . De chlorination is done by vacuum system. Return brine from cell plant is acidified to 2.0 pH and collected in lean brine tank which contains about 70 ppm of free Cl_2 is pumped into the saturator after neutralization. This cycle is continued.

The settler unit is the prime source of sludge generation. The sludge generated by this unit is around 1699 MT on a monthly basis. It is inorganic brine sludge containing mud, NaCl, KCl, water, CaSO_4 , BaSO_4 , $\text{Mg}(\text{OH})_2$, caustic soda/potash, Na_2CO_3 and traces of Hg to the extent of 32.49 ppm on dry basis.

Following reactions take place in the purifier:

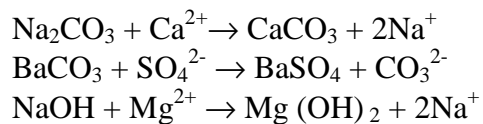


Table 1.1 Raw material consumption:

S.No.	Name of raw material required	Name of product	Consumption of raw material per unit of output [per MT of production]
1	NaCl	Caustic soda lye	1.63 MT
2	Na ₂ CO ₃	-do-	5 Kg
3	NaOH lye	-do-	19000 Kg
4	BaCO ₃	-do-	20000 Kg
5	Na ₂ HSO ₃	-do-	0.691 Kg

Table 1.2 Pollutant data

S.No.	Pollutants	Quantity of pollutants discharged (mass/day), in kg	Concentration of pollutants in discharger (mass/volume)
1	Mercury	0.0018	0.0066 ppm
2	S.S	5.8065	21.6 mg/l
3	B.O.D.	5.4839	20.39 mg/l
4	C.O.D.	17.042	63.38 mg/l

The methods of disposal practices adopted for both the categories of hazardous as well as solid wastes (in terms of composition and quantum) are as follows:

Table 1.3 Percentage distributions in sludge.

Component	Percentage (%)	Component	Percentage (%)
Moisture	37.57	CaSO ₄	5.80
NaCl	12.73	CaSO ₃	15.70
Acid insoluble	19.70	Mg (OH) ₂	6.40
BaSO ₄	2.10	Hg	24 ppm

The brine slurry from mercury cell process is passed through the rotary drum filters, the filtrate is recycled back (brine solution) to the process and the residual is collected and transferred as cake to the NaCl sludge pit specially designed for the purpose at the backside of the company premises. From the data, it can be concluded that nearly 638 MT of water is wasted in the form of moisture in sludge. Among the other important chemical species, which are wasted per month, include 216 MT of NaCl and 24 ppm of mercury. This shows that a large amount of valuable materials like water, NaCl etc are wasted. The enormous quantity of waste

generated by this unit is prime concern of the chlor-alkali companies. So, instead of treating wastes, the aim should be to minimize the wastes.

Some basic strategies to minimize wastes are as follows:

- Inventory management
 - Inventory control
 - Material control
- Production process modification
 - Operation and maintenance procedures
 - Material change
 - Process equipment modification
- Volume reduction
 - Source segregation
 - Concentration
- Recovery
 - On-Site recovery
 - Off-Site recovery

Proper control over raw materials, intermediate products, final products and the associated waste streams are now being recognized by industry as an important waste reduction technique. In many cases waste is just out-of-date, off-specification, contaminated, or unnecessary raw materials. The cost of disposing of these materials not only includes the actual disposal costs but also the cost of the low cost raw materials or product. There are two basic aspects to inventory management: controlling the types and quantities of materials in the plant inventory; and controlling the handling of raw materials, along with the finished products and waste streams in the production facility.

The former aspect, referred to as inventory control, includes techniques to reduce inventory size and hazardous chemical use while increasing inventory turnover. The latter aspect, referred to as material controls, includes methods to reduce raw material and finished product loss and damage during handling, production, and storage. Handling waste as if it were a product helps reducing waste and increasing the potential for recovery. Many of the techniques discussed in this paper can be applied to waste material as well as to raw material and finished products. Purchasing only the amount of raw materials needed for the production run or a set period of time is one of the keys to proper inventory control. Excessive inventory often results from a purchasing department getting a “good deal” on a chemical and buying a tank-car load when only a drum is needed. The excess must be disposed off because it goes out of date before it can be used.

Better application of existing inventory management procedures should be coupled with education programs for purchasing personnel on the problems and costs of disposing of excess materials. Additionally, the set expiration dates on materials should be evaluated, especially for stable compounds, to see if they are too shot. Another approach to inventory control is to purchase the material in the proper amount and the proper size container. If large quantities of a material are used, then purchasing it in bulk will produce less waste, both I product loss and empty packaging, than if it were purchased in drums or bags. On the other hand, small containers

may be better than bulk purchases if the material has a short shelf life or is not used in large amounts. If surplus inventories do accumulate, steps should first be taken to use the excess material within the plant.

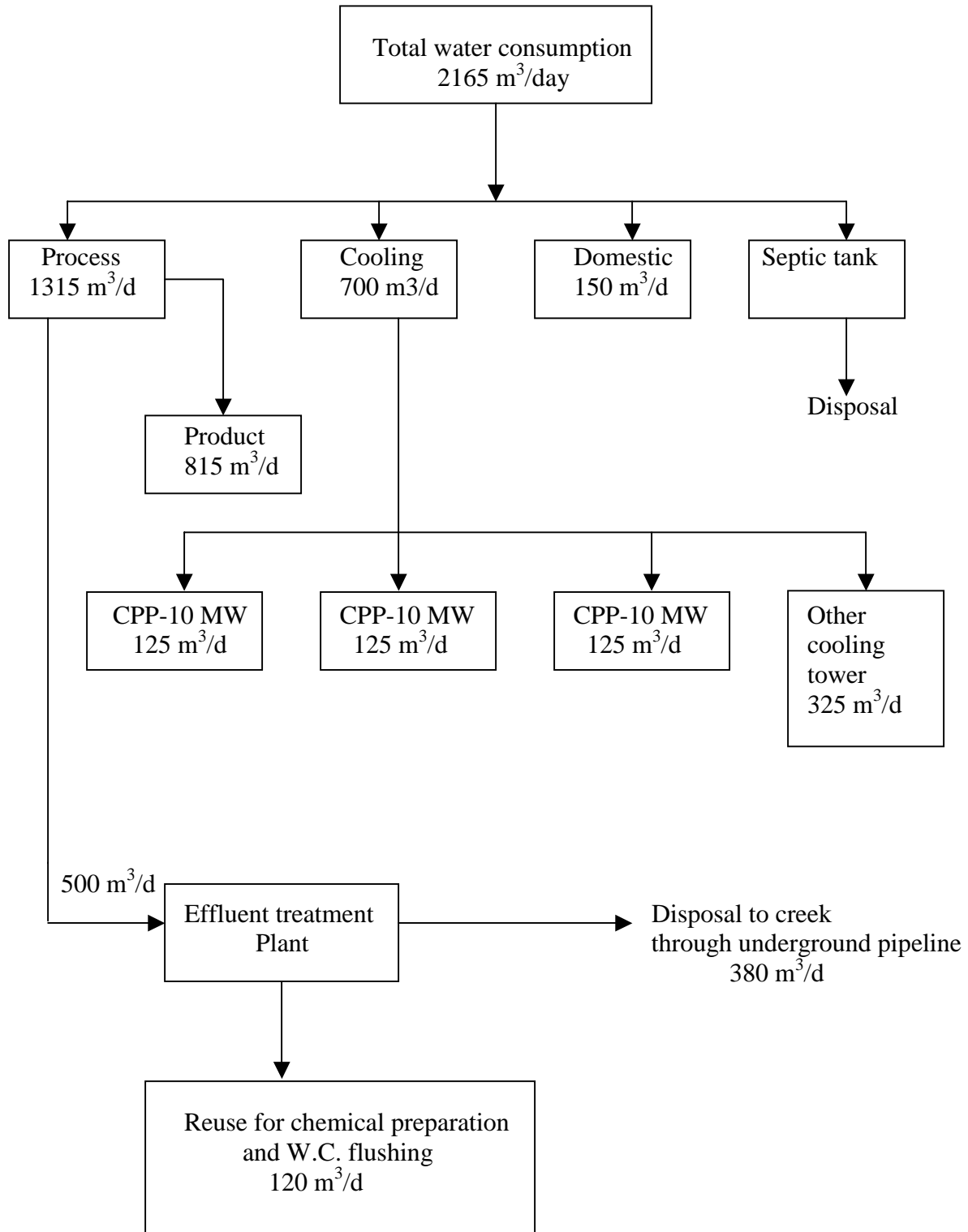
The ultimate in inventory control procedures is just-in-time (JIT) manufacturing, since this system eliminates the existence of any inventory by directly moving raw materials from the receiving dock to the manufacturing area for immediate use.

The raw material (salt) for the present plant is transported all the way from Gujarat, since the company has its own undertaking there. It is transported in trucks in gunny bags, and in the crushed form. The salt is poor in quality, which as per waste management strategies adds to waste generated. The following steps can lead to minimal waste generation:

- Instead of transporting raw material from Gujarat, the company can sell off the material there and buy a better quality raw material from the locality of the plant in Mumbai. This will not only save the transportation costs but also will minimize the waste generated.
- Since the raw material, i.e., salt is hygroscopic in nature, so it would be beneficial it is covered while kept in storage. If left open, the salt is vulnerable to dust and other impurities suspended in air that could affect the quality of the salt.
- The raw material should be washed and crushed before feeding into the saturator. Washing will deprive salt from impurities and crushing will increase the surface area, which again will result in more yields.
- If the material still could not be replaced, then an additional unit must be installed in order to enrich the quality of the salt. The cost will be recovered within the estimated time frame since enriching the raw material will improve the yield.
- Most of the equipments in the primary brine like settler, purifier etc are open. As a result a fraction of solution is evaporated. Covering the equipments will not only ensure the retention of process fluid but also save them from being degraded away due to rains.

Wastewater analysis: In the chlor alkali plant water is used in large amounts as a raw material. This section looks at the wastewater reuse in the chlor alkali plant. In compliance with “The water (prevention and control) Act, 1974”, wastewater must be treated before discharge (i.e., end-of-pipe treatment). The most common process of treatment is to merge several waste streams and use appropriate technologies in series to clean this stream before disposal. This is called end-of-pipe non-distributed wastewater treatment. Starting in the 80s, and increasingly in the 90s, water reuse started to become popular as a means of reducing the total amount of water intake. This, in turn, not only saves upstream treatment of raw water but also reduces wastewater treatment costs. In addition, the concept of distributing the treatment among the various polluted streams and even decentralizing it gaining exceptions.

Water Balance of the chlor alkali plant



Until a few years ago, the problem of water treatment was considered as a set of sequential treatment operations of a single wastewater stream consisting of the wastewater from all unit operations. At the same time, without the concept of wastewater reuse, these processes were fed by fresh water only. Such a system is depicted for three water user processes (P_i) and three treatment units (T_i) in Fig. 1.2. One way of obtaining improved designs is the reuse of wastewater from one process to feed another without sending it to treatment first. This reduces the cost because the overall water intake is smaller (Fig 1.3). The next step is to introduce series parallel designs of the wastewater treatment unit without merging all the wastewater streams (Fig 1.4). Finally, treatment can be decentralize in such a way that some pollutants are removed from wastewater or selected process allowing the reuse of these waters (Fig 1.5).

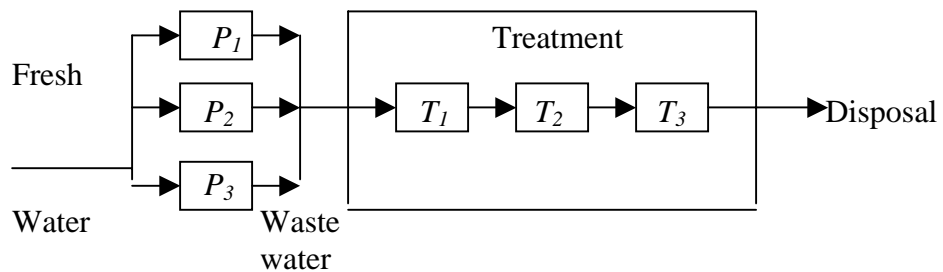


Fig 1.2

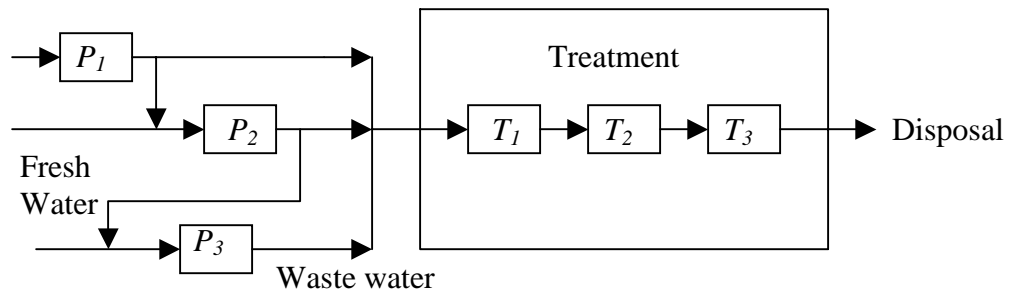


Fig 1.3

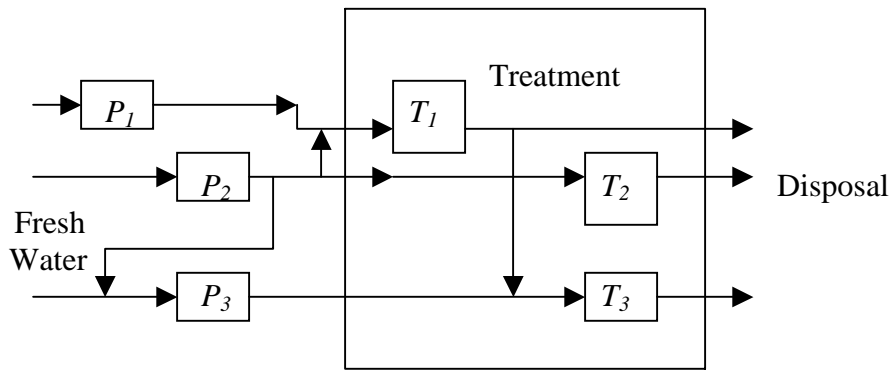


Fig 1.4

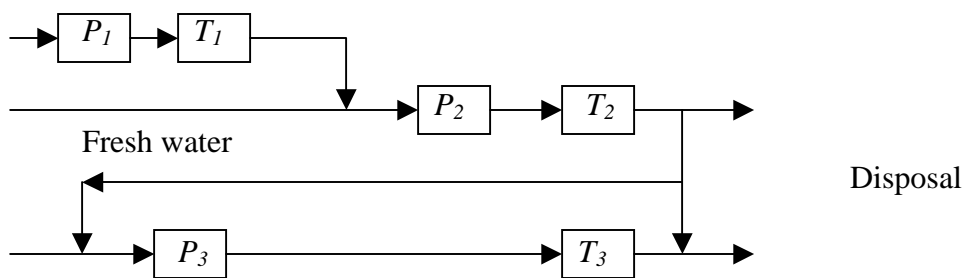
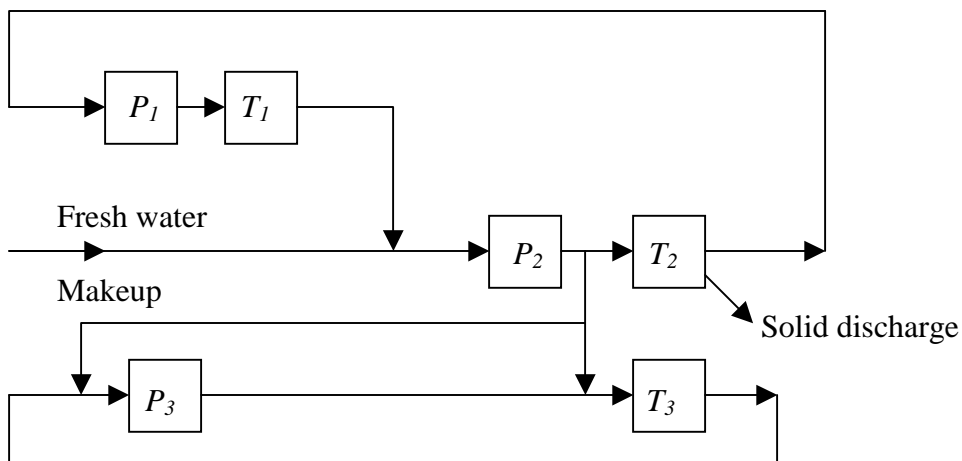


Fig 1.5

The concept of zero discharge applies alternatively to the total elimination of the disposal of environmentally hazardous substances or to the concept of a closed circuit of water, such that water disposal is eliminated all together, that is, 'liquid' discharge. Closed circuits are appealing because end of pipe regeneration does not have to be conducted to the full extent required for disposal as water can be reused with higher level of contaminants (Fig 1.6). Additionally, the absence of a discharge eliminates internal administrative costs associated with the enforcement of environmental protection agencies and local limits as well as the interface with other government agencies

Fig 1.6 A zero liquid discharge scheme.



Some issues which can be readily pointed out here are: -

- 1) In order for these zero discharge cycles to exist, waste water clean up should be thorough, something that could be too expensive to be realistic.
- 2) Unless an expensive total evaporation step is included, some water make up and disposal should take place to avoid the accumulation of certain species not being removed.

Conclusion: Waste minimization and water management in process plant has grown from a humble start in the early nineties to a mature field, where complex situation are analyzed and solved. This paper has reviewed several of these advances. Practical numerical challenges are still apparent. Some conceptual challenges remain defiant.

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