

CHAPTER 16

THE ALKALI INDUSTRY

CHARACTERISTICS OF THE WASTE WATER

The principal products of the alkali industry are soda and caustic soda. The manufacturing methods of these products are related since the sodium carbonate produced constitutes the raw material for the production of caustic soda (sodium hydroxide). Both products are usually produced by the same plant. Sodium carbonate is generally manufactured by the Solway ammonia-soda method:



The product, sodium hydrogen carbonate, is easily separated from ammonium chloride due to its lower solubility, and it is transformed into sodium carbonate by a calcination process in pans:



The carbon dioxide is recycled to the process.

The liquid containing ammonium chloride is treated with lime and the ammonia is stripped and recycled to the process.

Sodium carbonate is treated with calcium hydroxide to form sodium hydroxide (caustic soda) according to the following equation:



Sodium hydroxide can also be produced by the electrolysis (mercury electrodes) of molten sodium chloride, chlorine also being produced.

For the production of sodium carbonate and sodium hydroxide water is used at approximately 10 m³/ton.

The characteristics of the effluent are shown in Table 16.1. The effluent is mainly the result of using lime in the ammonia recovery process, see Table 16.2.

TABLE 16.1

Composition of waste water from the production of sodium hydroxide and sodium carbonate

	Waste water from manufacture of sodium carbonate	Waste water from manufacture of sodium hydroxide
CaO (mg/l)	185	116
MgO (mg/l)	42	20
CO ₃ ²⁻ (mg/l)	117	124
Cl ⁻ (mg/l)	113	160
pH	9.2	7.7
Permanganate value (mg/l)	16	23
Alkalinity (meq/l)	8.3	8.5
Total solid (mg/l)	1115	2100

TABLE 16.2

Approximate composition of effluent from ammonia recovery process

Components (g/l)	
CaCl ₂	110
Ca(OH) ₂	15
NaCl	60
CaSO ₄	4
CaCO ₃	6
Sand	5

The waste water from the chlor-alkali industry causes more problems than the waste water from the manufacture of sodium carbonate and sodium hydroxide since it contains mercury. Mercury is highly toxic and causes the so-called Minamata diseases.

Table 16.3 gives a characteristic analysis of waste water from the chlor-alkali industry.

As the quantity of waste water from the chlor-alkali industry is relatively high, the waste water problem is really serious.

The total loss of mercury is 50-200 g/ton of sodium hydroxide produced. It is possible to avoid mercury pollution completely by changing to the so-called diafragma process. However, the sodium hydroxide produced by this process is more contaminated.

TABLE 16.3

Typical analysis of the waste water from the chlor-alkali industry

Components (mg/l)

Metallic mercury	0.5-4
Hg ⁺ and Hg ²⁺	0.2-3
Na ⁺	300-2000
Cl ⁻	500-3500
pH	9-12
Suspended particles	5-100

The sources of mercury pollution in the chlor-alkali process are:

1. From cleaning of the electrolysis cells
2. From the condensor cooling the gases (hydrogen and chlorine)
3. Washing the amalgam for removal of sodium chloride
4. From the urine of workers. It often contains 40-50 µg mercury/l
5. From general cleaning processes

In this context it must be mentioned that sodium hydroxide produced in this way contains mercury as a contamination. The use of the sodium hydroxide can therefore increase the concentration in the water. Investigation by Helge Bergström (1969) has shown that sodium hydroxide contains between 0.4 and 3 µg mercury/g.

Treatment of waste water from alkali plants

Waste water from soda production is composed mainly of lime and can easily be purified by settling. Sulphate present in the waste water can be removed by the addition of barium chloride followed by settling since the barium sulphate formed has a very small solubility product. The heavy deposit of barium sulphate precipitated helps to speed up clarification.

As seen in Table 16.2, the waste water from the recovery processes has a high concentration of calcium chloride. Calcium chloride can be produced as a by-product by evaporation and crystallization of this waste water.

The above use of barium chloride is rather expensive and in some instances it has been substituted by cheaper materials. It is possible, for example, to remove suspended matter in the waste water by saturating it with carbon dioxide to precipitate calcium carbonate. The relatively high alkalinity of this effluent makes it possible to use iron or aluminium salts afterwards for clarification instead of the expensive barium chloride.

Accumulation of the waste water in a large settling lagoon with a capacity of 100000 m³ or more is widely used instead of using the separate precipitation and settling steps. The clear solution produced consists mainly of calcium and sodium chloride, and is discharged into special wells and drainage systems. In the course of this process the suspended solid and the residual caustic soda sludge, mainly consisting of calcium carbonate, will settle. The clarified waste water is usually discharged into the receivers at a time of high water.

Waste materials are used to a large extent for the construction of the banks around the lagoons.

Obviously the method described is very primitive. It requires large areas of land and if the banks break, causing flooding, serious damage to agricultural land in the neighbourhood and large losses in fish stocks will result. There has therefore been a tendency to limit the use of this method in recent years.

It is possible to utilize the sludge. The precipitated chalk can be dried and sold as agricultural lime. It is also possible to dry and burn the calcium carbonate and return the lime produced to the caustic soda production process. Despite many suggestions it is not easy to eliminate or reduce the waste water problem of this industry to any great extent.

A modification of the producing process has been introduced by the Japanese. The so-called "Dual" method combines the production of soda and agricultural ammonium chloride, eliminating the process of ammonia stripping and hence the difficulties connected with waste water containing calcium chloride.

It has been shown that ammonium chloride is a useful nitrogenous fertilizer. However, if the soil is acidic, problems may arise because of the unfavourable effect of the ammonium chloride on the pH balance of the soil.

Treatment methods of the chlor-alkali industry

Mercury can be removed from waste water by several methods:

1. It can be precipitated as mercury(II)sulphide. This process will cause a sludge problem, as it is not possible to recover the mercury from the precipitated mercuric sulphide.
2. Direct distillation of the waste water can be carried out. The volatile compounds in the water will be removed and an enriched mercury residue will be produced. Since the mercury in this residue is contaminated, it is not possible to recover mercury from the sludge. This method has a high energy consumption and the running costs are high.
3. By means of organic reducing agents, Hg^+ and Hg^{2+} can be reduced to metallic mercury, which can be removed by sedimentation from the waste water. This method also has a relatively high running cost and it is only used for small quantities of waste water.
4. Activated carbon can take up approximately 15 kg of mercury/m³ activated carbon (Thiem et al., 1976). This method has been used in combination with a precoated filter to remove mercury. When the activated carbon is saturated it is possible to regenerate it by drying it and distilling off the mercury.
5. Ion exchange can be used to remove mercury from waste water (Fuxelius, 1970) and (Oehme, 1971). By formation of complexes mercury can be removed on an anion exchanger. Cation exchangers selective to mercury have also been developed (Högfeltdt, 1970). Oxidation of the metallic mercury present to the ionic form must be carried out before the ion exchange. As oxidizer such as chlorine can be used. The use of anion and cation exchangers is in many respects a good solution to the waste water problem in comparison with the other treatment processes available, but it causes some problems (Gardiner et al., 1971):
 - a) Mercury forms complexes, which makes it difficult to obtain a pure ion exchange process since the various complexes will have different equilibrium constants for the exchange process.
 - b) The ion exchangers are generally not very selective to mercury although new chelated ion exchangers with xanthate groups have improved the selectivity considerably (Swanson et al., 1973).
 - c) The presence of oxidizing or reducing compounds can harm the ion exchange materials.

From these considerations it is seen that xanthate ion exchangers would be preferred. The ion exchange capacity is approximately 1 meq/g for the xanthate ion exchangers on the market, which is slightly less than that of the general types of cation exchangers.

Fig. 16.1 is a flow-sheet of an ion exchange process for treating waste water from the chlor-alkali industry by means of a selective ion exchanger.

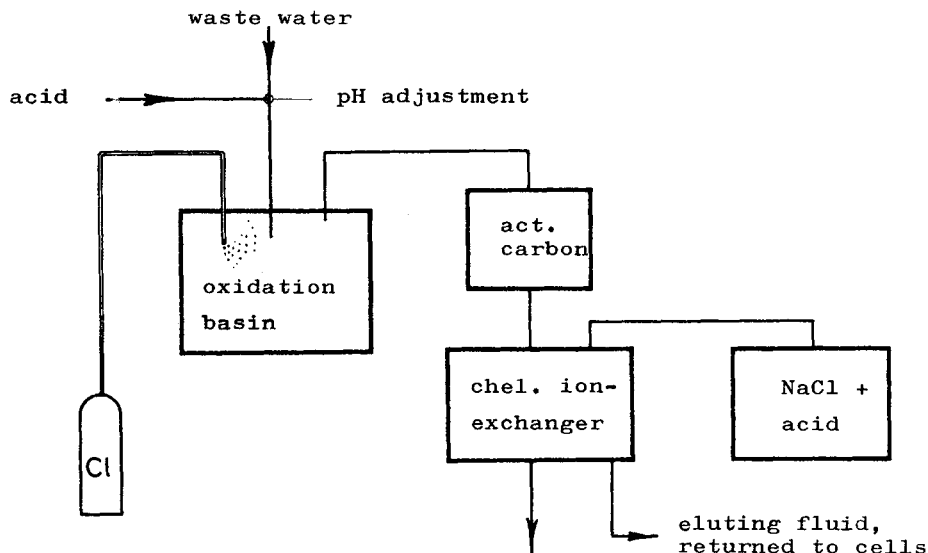


Fig. 16.1. Flow-sheet of an ion exchange process for treating waste water from the chlor-alkali industry by a selective ion exchanger.

The first step is oxidation at pH 6-7 using chlorine. The reaction time is 30 minutes. Before oxidation the pH must be adjusted since the waste water usually has a pH of 9-12. The pH is adjusted with sulphuric acid. After the oxidation process follows treatment on activated carbon, which removes the chlorine. The elution is carried out by acidified sodium chloride. The eluting fluid can be re-used in the electrolysis cell. Mercury(II)-ions, which are present in the eluant, will be reduced electrolytically to metallic mercury and the sodium chloride is used in the electrolysis processes.

Usually a two-step ion exchange is used as the efficiency of one step is 90% and a higher purification is normally required.

Using the two-step process it should be possible to reduce the concentration of mercury in the effluent to 0.5 mg/l or less.

Kanczor (1975) describes how it is possible to reach 5 $\mu\text{g Hg/l}$ in the effluent by use of a two-step ion exchange process. The second step is a highly selective ion exchange with the pH at 2.3.

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