

Chlorine production with highly reduced mercury emission

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When designing and building new mercury-based chlorine plants special attention must be given to features which will help reduce mercury pollution of the environment. The article describes a new Swedish chlorine plant including mercury emission limits set by the authorities, general principles and some specific details in the plant design to minimize mercury losses and practical experience after nearly one year of operations.

Introduction

KemaNord's new electrolytic chlorine plant in Stenungsund is the first plant of its kind in Sweden, and maybe in the world, to be designed and constructed with the express purpose of reducing as far as possible mercury pollution of water and air. The special mercury emission reducing features were built into the plant in order to conform with new strict Swedish antipollution laws. Considering the increasing concern in many countries today about mounting mercury contamination of the environment it is believed that other chlorine producers would be interested in learning about the background and principles of this plant and the results which have been achieved after nearly two years of operation.

Mercury emission levels

When KemaNord decided to take up chlorine production in 1967, mercury pollution of water and air had been vigorously debated in Sweden for a considerable time. Zoologists had observed serious damage to certain bird species apparently caused by mercury poisoning and fishes caught at certain industrialized locations had been shown to contain too much mercury to be fit for human consumption, i.e. the mercury content exceeded 1 ppm which the Swedish

National Health Service had set as an upper limit [1, 2, 3, 4]. The Swedish chlorine industry was blamed for some of this mercury pollution.

Obviously there was a strong incentive to base a future chlorine production on a mercury-free method.

A study concerning the relative merits of the diaphragm and the mercury cathode processes showed that the absence of mercury emission and the low electric power consumption, which are the main advantages of the diaphragm method, should be balanced against high purity caustic soda, high cell productivity and low steam consumption and operating costs characteristic of the latter method.

Under conditions with high wages, relatively high priced steam and low priced electric power as well as absence of brines and salt deposits, the amalgam process showed considerable economic advantages. The difference in caustic soda quality was an important point as only very pure caustic is marketable in Sweden.

The next step was a very careful study of the mercury levels which could be expected in a mercury cathode plant specifically designed to reduce mercury losses.

Mercury discharges from conventional Swedish chlorine plants have been investigated by H. Bouveng, Swedish Water and Air Research Laboratory [5] and his findings are summarized in Table 1.

Table 1. Average mercury emission from Swedish chlorine plants in 1967

Discharge to waste streams	30-40	} g of Hg/ton* of chlorine
Discharge with the hydrogen	5-10	
Discharge with the ventilation air	15-25	
Discharge with the caustic soda	c. 5	

* metric ton

According to Bouveng the mercury emission in 1967 to air and water amounted to 55-80 g of mercury per ton of chlorine, approximately half of which ended up in the waste streams. Assuming a chlorine production of 250,000 tons, the total mercury discharge in Swedish waters should thus be 7-10 tons during that year.

A thorough analysis of the various process streams within a plant and their implications for the mercury emission indicated that it should be technically possible to drastically reduce the above mentioned losses and keep the emission within acceptable limits. This would naturally mean a plant with many features different from those of a conventional chlorine unit.

In 1968 KemaNord made an application to the Swedish Water Court for a permit to build a new chlorine plant. During the Court's deliberations biologists and hydrologists were consulted as to the anticipated effects of the effluents on the receiving waters. Based on their reports, the Court allowed construction and operation of a plant producing 90,000 tons of chlorine per year under the condition that the yearly mercury discharge to the waste streams should not exceed 50 kg, that is about 0.5 g of mercury/ton of chlorine. This should be compared to Bouveng's estimated figure of 30-40 g/ton of chlorine previously considered normal for plants of this type.

The local board of health stipulated that the emission of mercury with the hydrogen should not exceed 0.5 g/ton of chlorine and the amount of mercury discharged with the ventilation air should be limited to 1 g/ton of chlorine.

Special design details

The plant was designed and built by Friedrich

Uhde GmbH in close cooperation with KemaNord. To meet the above mentioned emission levels many new details were included in the design, the most important of which were the following.

- (i) Special design of various pieces of equipment, particularly the electrolytic cells.
- (ii) Strict segregation and extensive re-use or recirculation of mercury contaminated water, thereby reducing the amount of discharged waste water.
- (iii) Special treatment of floors, central drainage of the floors to waste water-collecting facilities.
- (iv) Special treatment of brine sludge.
- (v) Special purification procedures for hydrogen and caustic soda.
- (vi) Final purification treatment for mercury contaminated waste water.

For the hydrogen purification a method was selected which comprised of cooling to 25°C, compression to 3.5 atmospheres (51 psig) followed by a second cooling step to 5°C. This should theoretically reduce the mercury content to about 1 mg/Nm³H₂.

To purify the caustic soda, filtration in a pre-coat filter containing activated carbon was chosen.

For the water treatment there was a choice between several alternative methods which had to be tested and evaluated. All the procedures listed below were effective with regard to mercury removal, but all except one were dropped in the final analysis for reasons apparent from the following discussion.

1. Precipitation of mercury as sulphide

Mercury is precipitated with sodium sulphide at pH 10 using iron (III) chloride as co-precipitant. The process appears to demand close supervision and is fairly labour-consuming and expensive. The sludge disposal may cause problems.

2. Fixation of mercury on ground granite

As proposed by Professor P. G. Kihlstedt, Royal Institute of Technology, Stockholm, this method involves adsorption of the mercury on freshly-ground granite. The adsorption appears

to be due to a combination of ruptured crystal lattices and local supersaturation of silicic acid in the water. The mercury is fixed as a silicate.

Large amounts of mercury-contaminated granite resulting from the treatment must be deposited in a safe manner. The method is also fairly labour consuming. It should be mentioned however, that the mercury is tightly bound to the granite, and the method has been proposed as a means to restore or decontaminate mercury-polluted lakes [6].

3. Distillation

By distillation is meant the evaporation of mercury-contaminated waste water in a multi-stage evaporator.

Test runs have shown that no detectable mercury distils off. However, hypochlorite which is usually present decomposes at the distillation temperature and gives a chlorine-containing distillate, which cannot be used as make-up water for caustic soda or for cell cleaning. There might also be problems with the disposal of the distillation residue.

4. Ion-exchange/cation resins

An ion-exchange resin will extract the complexes HgCl_3^- and HgCl_4^{--} from the water phase, and is quite effective provided the water contains a certain amount of salt [7, 8].

The resin is rapidly destroyed by hypochlorite. If the hypochlorite is reduced with, for example, bisulphite, the active groups in the resin will be blocked by sulphite or sulphate ions.

5. Ion-exchange/chelate resins

On these resins, the mercury ions will be fixed as chelates to, for example, aminoacetic acid groups in the resin [9]. Addition of sodium sulphite to reduce the hypochlorite does not appear to cause any appreciable difficulties.

Disadvantages with this method are high resin price and risk of unwanted elution of the resin caused by occasional high salt concentrations.

6. Cementation

In cementation mercury ions are reduced to the metallic stage on non-noble metal surfaces such as iron, zinc or aluminium [10]. Pilot plant trials have shown good results at pH 3-4. At higher pH values iron hydroxide is precipitated, at lower values hydrogen is evolved. The iron is sensitive to hypochlorite which must be removed prior to the cementation. Furthermore, some iron hydroxide forms even at pH 3-4 and the iron surface must be periodically regenerated.

7. Chemical reduction

This method, which has been selected for the Stenungsund plant, involves chemical reduction of any ionic mercury to the metallic form and removal of the metal from the water phase by means of a pre-coat filter and activated carbon of a special type. The method gives mercury in an easily recoverable form as the metal can be distilled directly from the carbon, and is considered less labour consuming than the other procedures.

Operating experience

The chlorine plant in Stenungsund went on stream in April 1969 with a first stage yearly capacity of 45,000 tons. The current operating time of about 20 months should be sufficient to judge whether the original expectations have been justified.

In Fig. 1 the actual mercury discharge to the water during four week periods during these twenty months is shown. The mercury values are based on plant laboratory analyses as well as those of independent institutions such as the Swedish Water and Air Research Laboratory. Although it appears that in 1969 and the beginning of 1970 there has been varying mercury emission, it is still within the limits set by the authorities.

The irregular discharge is probably due to start-up and trimming troubles which might be expected in a new plant. From February 1970 the situation has stabilized and the mercury discharge during a four week period now amounts to 0.5-1 kg.

Practical cost figures for purifying mercury

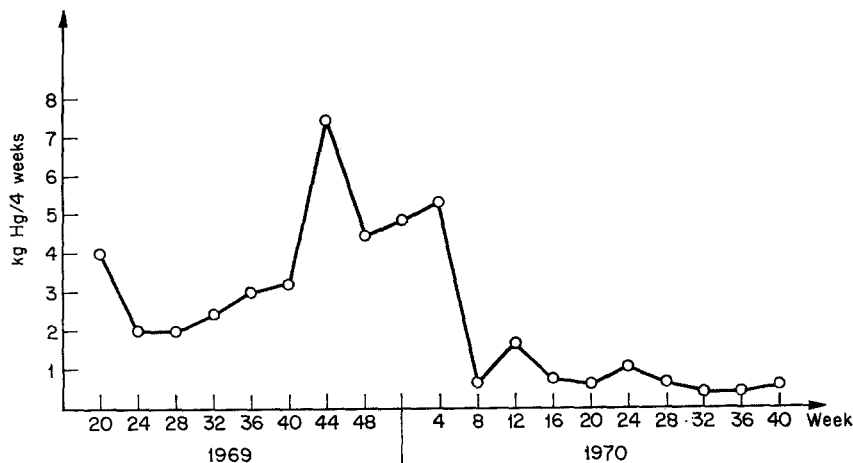


Fig. 1. Mercury discharges with the waste water

contaminated waste water are now also available. The system has been designed for 50,000 m³ of waste water per year. Total investment has been 500,000 Swedish crowns and operating costs, including maintenance, has been 35,000 Swedish crowns/year. After some trimming of the process the mercury content of the treated water has been reduced to an average of 0.3 ppm as compared to 12–30 ppm of metallic and ionic mercury in the untreated water.

The problems of purifying the caustic soda have been relatively small and the mercury content has in most cases been appreciably lower than 0.5 g/m³, being mostly about 0.2 g/m³. This should be compared to mercury levels in commercial caustic which only occasionally are below 0.5 g/m³ and are usually much higher.

The mercury discharge with the hydrogen has been somewhat lower than 0.5 g Hg/ton of chlorine. Concerning mercury in the ventilation air; keeping within stipulated values has caused problems and experiments are currently being carried out to improve the situation.

Special efforts are being directed towards stopping leakages of hydrogen.

Experience with the Stenungsund plant has shown that the mercury discharges from a new chlorine plant can be kept down to an acceptable level if careful and intelligent design is applied and daily operations are closely supervised.

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