

Formation of dioxins from carbonaceous materials in production of anhydrous magnesium chloride

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1. Introduction

The main part of the magnesium production in the world is based on electrolysis of anhydrous magnesium chloride. Several processes for production of anhydrous magnesium chloride are based on reaction of chlorine, magnesium oxide and carbonaceous materials at 500-1200 °C. These processes form a variety of chlorinated hydrocarbons (CHC) as undesirable by-products, among which dioxins are considered the most toxic.

This is also the case in the classic IG Farben process, where the magnesium oxide is chlorinated in shaft furnaces. This process has been in operation in Norsk Hydro's magnesium plant in Porsgrunn, Norway since 1951. The production process is described by Oehme et.al /1/.

The formation of chlorinated hydrocarbons, and especially the toxicity of dioxin like components, was not fully recognized until the early seventies /2/. From 1970 tests with various reducing agents were conducted in Porsgrunn, and in 1976 the change from coal to coke as reducing agent was made. This reduced the formation of the various chlorinated hydrocarbons in the range of 65 to 90 % /3/. However, the mechanisms for CHC formation from the various carbon sources were not fully investigated, and when the emissions had to be reduced to very low levels to comply with the new environmental standards in the eighties, laboratory tests and full scale tests were again undertaken to study the formation of CHC. In parallel to these tests cleaning methods for the aqueous effluents generated by scrubbing the off gas, were under development. Equipment for cleaning the waste water was installed in 1989.

In the literature, very few references describing CHC formation and discharges connected to magnesium production are found, despite the fact that CHC formation in carbochlorination processes have been studied since the mid eighties /4, 5, 6/.

The emphasis in this paper is put on the laboratory tests and the subsequent full-scale tests performed in 1991 and 1992.

2. Materials and methods

2.1 Introduction, lab scale tests

As earlier mentioned, a substantial reduction in CHC formation was achieved by changing from coal to coke as reducing agent. For further reduction, search for other more suitable carbon sources was started. The hypothesis was that the content of volatile matter (VM) was correlated to the amount of CHC formed. In order to evaluate different carbon sources with respect to their ability to form CHC, a laboratory apparatus was built for high temperature chlorination tests. In this apparatus different carbon sources were chlorinated under varying conditions and the amount of CHC was measured. The results showed that all types of carbons give, more or less, formation of chlorinated compounds. Based on these lab tests, a petrol coke (petcoke) was chosen for the full scale tests.

2.2 Short term full scale tests

The petcoke itself has very low content of VM, but the coke is sprayed with dedusting oil. This must be regarded as VM and the amount is approximately 0.2 %. The furnaces are vertical shaft furnaces where the feed are charged at the top. Chlorinated hydrocarbons are formed inside the furnace and transported out by the off-gas. The off-gas consists of the gaseous components water vapour, CO₂, CO, HCl, Cl₂ and air in addition to dust. Experiences from earlier experiments have shown that CHC stick to dust particles. In order to get a representative sample of CHC the principles for isokinetic sampling had to be used. Samples of the off-gas were sucked through a probe and led through an apparatus for dust-collection, further absorption in a solution of Na₂SO₃ and adsorption on silica gel which is inert in this environment. The gas was finally filtered through a glass fibre filter. All parts of the equipment were extracted with toluene at Norsk Hydro Research Centre. The clean-up and analysis were performed at Alta Analytical Laboratories in California.

Earlier experiments had shown that, in addition to the influence of the carbon source, the formation of CHC varies with the operational conditions of the furnace. For the testing of raw material based on 100 % petcoke, 3 of 16 furnaces were picked out. These tests lasted for about 1.5 day. The sampling period typically varied between 6 and 8 hours, long enough to include the normal fluctuations in the operational conditions. Three reference measurements were conducted some days before and three measurements some days after the test with petcoke.

2.3 Long term full-scale tests

In order to follow-up the experiments performed on the 3 furnaces in 1991, long term full scale tests with the whole chlorination plant were executed in the spring of 1992. The furnaces were charged with raw material based on 100 % petcoke in 2 periods, altogether in 10 days. The sampling program consisted of 3 separate measurements with petcoke and 3 reference measurements with the normal coke.

The off-gas from the shaft furnaces is washed in 3 scrubber stages, further cleaned in a wet electrostatic precipitator (ESP) /7/ and finally in an incinerator. The scrubbed off-gas from all furnaces is combined in the inlet of the ESP. Therefore it was decided to perform the sampling

before and also after the ESP. The sampling period was 24 hours. The isokinetic sampling was performed according to the method described in /7/. The soxhlet extraction of all sampling compartments was performed at Norsk Hydro Research Centre in a specially designed equipment. The clean-up and analysis were performed at Alta Analytical Laboratories in California. In order to verify the variance in the method, 2 parallel samples were taken in the outlet gas from the ESP in the last experiment.

3. Results and discussion

3.1 Short term full-scale tests

With respect to the formation of dioxins the results were quite satisfactory. Table 1 gives the dioxin concentrations in the off-gas calculated on the basis of furnace, ton product and day (24 hours). The results are given for the sum of dibenzofurans, the sum of dibenzodioxins and toxic equivalents according to the Nordic model, N-TEQ. The results from petcoke tests are given in bold characters.

Table 1. Results from off-gas analysis in tests with petcoke and normal coke
The figures are presented as $\mu\text{g pr furnace, day and ton product}$.

Type of measurements	Σ dibenzofurans	Σ dibenzodioxins	Toxic eqv. N-TEQ
Reference 1	75094	9377	956
Reference 2	113752	17473	2149
Reference 3	69362	8401	790
Petcoke 1	12429	623	141
Petcoke 2	27141	1780	261
Petcoke 3	8323	596	105
Reference 4	22518	5462	468
Reference 5	414775	58163	3860
Reference 6	109964	12526	1166

On average basis, the formation of Σ dibenzofuranes and Σ dibenzodioxins are reduced with respectively 88 % and 95 % with petcoke compared with the normal coke. The reduction in toxic equivalents, I-TEQ, is about 90 %. These results confirm the importance of the carbon source in the process.

3.2 Long term full-scale tests

The concentrations in inlet and outlet gas of the ESP given as toxic equivalents according to the Nordic model, N-TEQ ng/Nm^3 is shown in Figure 1. In these experiments the cleaning efficiency of the ESP varied between 94 % and 97 %. The measured concentrations in the samples taken in parallel in the outlet gas from the ESP in the last experiment were 7.91 and 7.96 ng N-TEQ/Nm^3 .

One interesting feature is that the petcoke produced relatively more dibenzofurans than dibenzodioxins, 20-40 times more, than the normal carbon source did (6-8). This indicates different precursors and/or different reaction mechanisms involved in the dioxin formation from these two carbon sources.

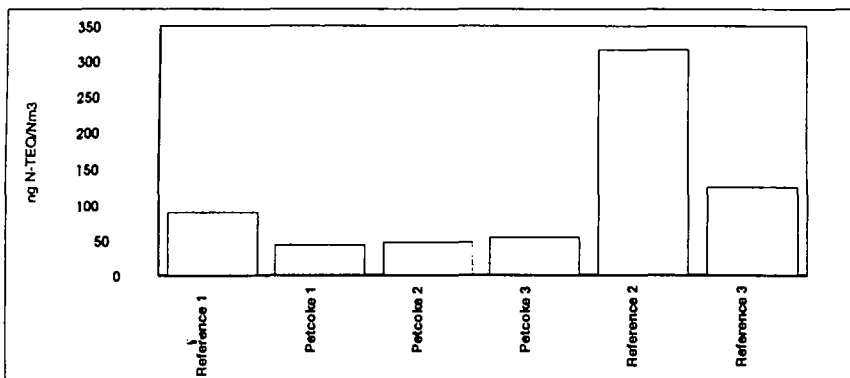


Figure 1. Concentrations of dioxins in inlet ESP with petcoke and normal coke

The concentration in inlet ESP is lower with petcoke than with the normal carbon source. The results are, however, not so clear as in the experiments in 1991, the reason may be the distance between the sampling points. On average basis, the reduction in toxic equivalents, N-TEQ, is about 70 %. But even with such a reduction in dioxin formation, cleaning equipment would still be needed.

Unfortunately, impurities in the anhydrous magnesium chloride increased with a factor of 4 after some days operation with petcoke. Therefore, for production of high quality anhydrous magnesium chloride it was necessary to continue with the same carbon source as earlier.

With the cleaning equipment installed at the Magnesium plant in Porsgrunn, the dioxin discharges are below 2 g N-TEQ to air and 1 g N-TEQ to water on a yearly basis.

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