Chloroorganic compound balance with particular reference to water pollution by pulp mill effluents

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Introduction

Chloroorganic compounds are known to be the most toxic pollutants of bleached kraft pulp mill effluents. These compounds are formed in the course of delignification of wood, by chlorination of low and high molecular weight organic compounds. Many chloroorganic compounds are known to be bioavailable, to accumulate in fish, and to cause mutagenic effects. When studying pulp mill effluent impact on receiving waterbody ecosystem it is important to know the most relevant stages of pulp production in respect to formation of chloriorganic compounds, in order to improve technology and to reduce pollutant discharge.

Such a study was carried out at Baikalsk Pulp and Paper Mill (BPPM). The BPPM has a multi-stage treatment system, in the course of which effluents go through biological and physico-chemical stages and a storage basin before discharge into lake Baikal. The high purity of Baikal waters and the sensitivity of its water ecosystem made this study important. The physico-chemical stage of bleached pulp effluent treatment is used only at this enterprise in the USSR which made dealing with the problem of chloroorganic balance in BPPM effluents very important.

Pulp bleaching at BPPM is carried out in three stages:

- ***Stage 1***
  Chlorination with molecular chlorine. Chlorine when interacting with lignins and extractive substances forms many chloroorganic compounds of various molecular masses, with good solubility in water and alkali.

  Pulp after having been chlorinated is deluted with water and condensated from evaporation, and then filtered. Chlorination products and reagent residues (hydrochloric acid and some other acids) are removed with the filtrate.

- ***Stage 2***
  An alkaline extraction of residual lignins and chloroorganics (mainly coloured).

- ***Stage 3***
  Treatment with hypochlorite and chlorine dioxide for further delignification. Not only lignins, but also hemicelluloses as well as cellulose are oxidised at this stage.

Measuring the concentrations of individual chlororganic compounds in such complex mixtures as kraft bleaching effluents is a laborious task.

The most general rapid and simple indicator to characterise chloroorganic content is "Total Organic Chlorine" (TOCl). This value indicates the amount of chlorine included bound to organic compounds and is accepted in the world practice when regulating pulp mill effluent quality.

Analytical Methods

To separate chloroorganic compounds from effluent two methods were used initially: repeated diethyl ether extraction, and adsorption on active coal.

During extraction, mainly low molecular-weight compounds are isolated. It is important that in course of this process chlorinated phenols, guaiacols, anisols are formed. These compounds are very toxic to fish and are thoroughly regulated everywhere. Then, using known methods, extracts were separated into: phenols, acids and neutral compounds. Separating and measuring resin compounds were carried out in several cases, because they are included neutral, acidic and phenolic compounds. TOC measuring (EOCl) was carried out after extraction has been done, using two methods:

1. Extracts combustion followed by argentometric titration (Schöniger Method), and
2. Direct neutron activation analysis of chlorine contents in carefully dried extracts.

It was initially found that not all chloroorganic compounds are isolated from effluents by extraction. High molecular chlorinated lignin substances remain in effluents.

The chloroorganic compounds present in bleached pulp effluents are separated most completely by adsorption on active coal (AOCl). We have tested two adsorption methods described in AOX measuring instructions. According to the first method, powdered active coal is added to effluents, the mixture is agitated and coal is filtered out. The more complete isolation is obtained by the second method: coal is put in a glass tube with a diameter of about 5 mm, and effluents are sucked through it by means of a vacuum pump. Similar methods are accepted as standard in the USA, Canada, Germany and Scandinavian countries.

Besides the effective separation this method is advantageous, because the coal and chloroorganics obtained are easily mineralized, thus AOCl content can be measured with traditional methods. One of those is the Schöniger method: coal adsorbate is burned on platinum wire, the mineralized residue is dissolved, and the chlorine content is measured by mercurymetric titration in solution. The Schöniger method is rather simple, but only used for analysis of polluted effluents. TOCl concentrations higher than 5 mg/l can be determined. Total chloroorganic contents are seldom more than 3 mg/l at BPPM.

Neutron activation method was also used to analyse BPPM effluents and biological objects for TOCl contents. Detection limits of this method are 1000 times lower compared to Schöniger's method. Neutron activation method is realizable unfortunately, only at research nuclear reactors or by using radioisotope sources. We mainly used it for validation of other analytical methods.

To overcome the shortcomings of the two previous methods, a complex device was developed for measureing adsorbable organic halogen (AOX). This device has been engineered by W. Merz, employed by BASF (Germany), in cooperation with members of the Martin Luther University (Halle) and the Technology Laboratory (Ilmenau).

The device called AOX-analyzer combines fully automated combustion of coal adsorbate in a vertical tube according to Merz, modified coulometric titration and computer data treatment. Operation of the whole device is controlled by a special program: after adsorption of halogenorganic (in particular, chloroorganic) compounds on active coal, a sample is burned in a quarz tube located in the furnace, which is operated by a computer. Coulometric detection makes it possible to deal with a great range of concentrations of organically bound halogen 0.001 to 1 mg/l water. Analysis of strongly polluted effluents require proper dilution of samples. As for TOCl measurements, the standard error is 3 % with a concentration of 0.01 mg/l. The analysis time for one sample is 10 min.

With a special top on the device one can measure volatile organic halogen in effluents. It is important for pulp mill effluent analyses, because one of the chlorlignins degradation products is chloroform, predominant in bleach effluents.