

Mercury is among the most toxic elements in general. Detailed studies of mercury speciation in natural aquatic environments are complicated by the fact that mercury - with its three redox states - forms a rather wide variety of species, both organic and inorganic. The situation is rendered even more complex by the reality that the various ionic and molecular species of mercury have different physico-chemical and toxic properties. Most mercury compounds have low solubilities in natural waters and organic forms accumulate in aquatic organisms (BERNHARD, 1988). The predominant species of dissolved mercury in an oxygenated natural water depend primarily on the pH and chloride concentration of the aquatic environment. This is due to the very stable chloride complexes of divalent mercury, and the stable form of mercury in seawater is the  $HgCl_4^{2-}$  anionic complex (BENES and HAVLIK, 1979; STUMM and MORGAN, 1989).

Mercury also shows a pronounced tendency to become adsorbed on solid particles such as suspended material and various sediment matrices. Clay minerals have for a long time been recognized as suitable agents for the removal of toxic elements and other pollutants from aqueous solutions. They show a particular propensity to adsorption of metal ions, and have thus found frequent use as scavengers for heavy metals (including Hg) over a wide range of concentrations. Bentonites, both synthetic and natural, have particularly strong sorption properties with regard to metal ions. This is mainly a consequence of their structure where sheets of  $SiO_2$  tetrahedra are partly substituted with octahedrally coordinated aluminium. In addition, various ionic (both cationic and anionic) substitutions are possible and occur frequently in natural bentonites. There are usually differences in the coordination on the surfaces of sheets and on the edges. This leads to the formation of different reaction sites and, consequently, differing surface potentials (/charge) on the bentonite. A possible effect of this is the interaction of adjacent charge sites and the electrostatic neutralization of surface charge by substituting elements/ions. Characteristic for bentonite are therefore multiple heterogenous sites and multiple functional groups.

In this work, investigations of Hg adsorption and desorption on natural Na- and Ca bentonite in various buffer systems were carried out. The released ions from bentonite in deionized water, the loss of dissolved  $Hg(II)$ , and the influence of the pH and chloride concentration on the formation of mercury complexes was studied. The Hg contents in solution were determined by cold vapour atomic absorption spectrometry (MAY and STOEPLER, 1984) using  $SnCl_2$  and  $H_2SO_4$  as reducing agent and amalgamation on gold wire. The released ions from bentonite into solution were determined by the use of a modified ion chromatography Dionex system 12 (NGUYEN, 1989). In deionized water, high amounts of cations and anions is released from Na bentonite. High loss of Hg was found from the buffer solution at pH 6 by volatilization into the atmosphere. In the pH range from 3 to 13, dissolved  $Hg(II)$  adsorbed well on bentonite as correlated with  $Hg(OH)_2$  which are the predominant species in the solution. With the addition of increasing concentration of chloride ions, the uptake of Hg is reduced because of the occurrence of chloro-complexes.

Bentonite adsorbed mercury(II) species from the solution at pH 5,00-5,50 with a capacity of 0.32 mol/kg and follows the Langmuir model. Adsorption kinetics of Hg on bentonite depends on the components in solution and on the form of bentonite as well. The results obtained show a low adsorption rate of dissolved  $Hg(II)$  on Ca bentonite in buffer pH 8 solution.

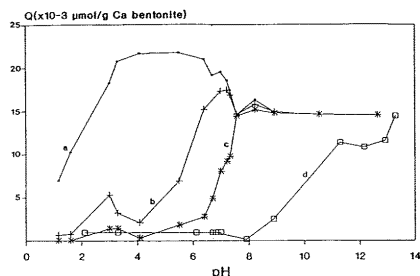


Fig. 1. Effect of pH and chloride concentration on the adsorption of  $Hg(II)$  on Ca-bentonite (Niederbayern, Germany: a) deionized water; b)  $10^{-3}$  mol/L NaCl; c)  $10^{-2}$  mol/L NaCl; d) 0.5 mol/L NaCl ( $0.045 \times 10^{-6}$  moles  $Hg(II)$  and 2 g bentonite equilibrated in 40 ml deionized water for 24 h at 294 K)

Natural calcium bentonite can be used for the elimination of dissolved inorganic mercury from natural waters. In deionized water (pH 5.50), an amount of 60 g  $Hg(II)$  can be adsorbed on 1 kg bentonite after 24 hours. The pH value and chloride ions influence the Hg uptake on bentonite. In the pH range from 3 to 13 and a chloride concentration below  $10^{-3}$  mol/L, a high uptake may be observed. With increasing chloride concentration from  $10^{-3}$  to 0.5 mol/L, the amount adsorbed is reduced because of the occurrence of chloro-complexes. In addition, chloride salts or hydrochloric acid can be used for extraction of the adsorbed Hg from the bentonite. Hydrochloric acid of 0.1 mol/L extracts about 80% of adsorbed Hg from bentonite.

#### REFERENCES

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Afin de bien élucider la participation de précurseurs d'origine terrestre et/ou marine lors de la formation des substances humiques sédimentaires (SHS) dans les estuaires, nous avons fait appel à la technique de Pyrolyse - Chromatographie en Phase Liquide - Chromatographie en Phase Gazeuse (Pyrolyse - CPL - CPG); d'autres méthodes analytiques plus classiques (analyse élémentaire, spectroscopie d'absorption en infrarouge et spectroscopie de résonance magnétique nucléaire du  $^{13}C$ ) ont été également utilisées pour acquérir certaines informations complémentaires et indispensables sur la matière humique en question.

L'analyse des substances humiques extraites de sédiments récents de l'estuaire de l'Elorn (France) indique que ces composés, et plus particulièrement les acides humiques, possèdent de nombreuses propriétés communes à leurs homologues lacustres : teneurs relativement élevées en azote et en soufre et faible taux d'aromaticité. Lors de la pyrolyse, des bilans pondéraux des différentes fractions produites, et de celles constituant le pyrolysats sont établis; la distribution des hydrocarbures saturés et insaturés, des iso-cyclo alcanes et des alcènes dans le pyrolysats des acides humiques sédimentaires (AHS) est étudiée et comparée avec celle des AHS de différentes origines. L'étude des hydrocarbures biomarqueurs (distribution et rapports stéranes / hopanes) issus de la pyrolyse des AHS confirme la participation de précurseurs d'origine algale dans les processus conduisant à la formation des substances étudiées. Ces résultats se confirment pour l'ensemble de la zone estuarienne, quel que soit l'emplacement du site étudié (partie amont, médiane ou aval de l'estuaire).