

## Diffusion tests of mercury through concrete, bentonite-enhanced sand and sand

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Received 11 January 2006; received in revised form 4 July 2006; accepted 19 August 2006

Available online 25 August 2006

### Abstract

The transport by diffusion of Hg(II) and Hg(0) through a barrier of concrete or bentonite-enhanced sand was examined under aerobic conditions. Sand was used as a reference system parallel to the two systems. Speciation of mercury was performed with a purge and trap method, where dissolved Hg(0) was purged with nitrogen gas from the sample, through a trap for volatile oxidized mercury species and finally trapped in an oxidative solution. The apparent diffusion coefficient (from Fick's second law of diffusion) for oxidized mercury was  $1 \times 10^{-14}$  m<sup>2</sup>/s in Standard Portland concrete and  $4 \times 10^{-13}$  m<sup>2</sup>/s in quartz sand. The diffusion of Hg(0) seemed to be faster than for Hg(II), Hg(0) was however oxidized to Hg(II) under aerobic conditions, and after 45 months only 1–10% of the total mercury concentration was Hg(0).

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**Keywords:** Mercury diffusion; Concrete; Bentonite-enhanced sand; Apparent diffusion coefficient of mercury

### 1. Introduction

Essentially all use of mercury in society shall be terminated, according to Swedish directives [1–3], and mercury in industry and private use shall be collected. Waste and other residues containing more than 1% of mercury shall be prepared for permanent storage in a repository. The preferred chemical state suitable for disposal would probably be the sparingly soluble sulphide HgS, which is the dominating naturally occurring mercury mineral (the common red cinnabar and the black meta-cinnabar). Cinnabar would be highly insoluble under the anoxic conditions expected in a groundwater saturated repository in deep crystalline (granitic) bedrock, which is the proposed disposal concept [1,2].

Barriers that would separate the waste from the groundwater have been suggested, and some alternatives have been considered such as bentonite and concrete, as well as metallic containers. Both bentonite-enhanced sand and concrete are com-

mon in barrier constructions to retard the leaching and transport of dissolved components from the waste in disposal facilities e.g. landfills and in the Swedish repository for intermediate-level nuclear waste. The major mineral component of bentonite is montmorillonite, which has an ability to swell (up to 15 times) and a high cation capacity. The main reason for using bentonite in constructions is the swelling capacity that reduces the porosity of the material under pressure. Concrete constructions are common for incorporation of hazardous waste due to the tortuosity, the low porosity, the fixation of metals that form sparingly soluble hydroxides at high pH and production of a solid monolith.

The groundwater flow through the barriers will be very low and diffusion will be the dominant mechanism for mercury migration through the barrier. The diffusion coefficient of mercury ions in water and aqueous-organic solvents [4] and vapours through porous substances under reduced pressure [5] has earlier been investigated. The self-diffusion coefficient of mercury was found to be independent of the diameter (0.6–1.0 cm) of the diffusion cell [6]. The results from these earlier investigations are not relevant in this study since the conditions are different.

The investigation of the diffusion of mercury is important for the performance assessment of the various proposed disposal concepts. In this study, the diffusional transport of Hg(II) and elemental Hg through barriers of concrete or bentonite-enhanced

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sand was examined under aerobic conditions. This would represent the conditions expected in a repository with concrete containers or barriers exposed to aerobic water (closing stage when air is present, or a future stage when the repository could be exposed to aerated waters). The objectives were to determine the apparent diffusion coefficient of mercury in concrete and bentonite-enhanced sand and to investigate the speciation of mercury under these conditions.

## 2. Experimental

### 2.1. Materials

Three different solid materials were investigated: quartz sand, concrete and bentonite-enhanced sand (BES). The bentonite used in this investigation (supplied by Carl Roth GmbH, Karlsruhe) contains montmorillonite (70%, w/w), quartz (9%, w/w), mica (2%, w/w), feldspar (5%, w/w) and calcite (1%, w/w). BES was prepared with a bentonite to sand ratio of 0.11. Concrete was made from Standard Portland cement (Optiroc Pour Fine), and water (10%, w/w). The quartz sand (Prolab) had a size range of 150–210  $\mu\text{m}$ . Elemental mercury (99.95%, Merck) or powdered yellow mercury(II) oxide (99%+, Aldrich) were used in the solutions. Prior to use, all cells, tubings and bottles were washed with 1 M  $\text{HNO}_3$  and rinsed with deionized water.

### 2.2. Procedures

The intention was to simulate repository conditions representative of deep granitic bedrock. These conditions (depth from less than 100 m down to 1000 m) have been studied within the Swedish nuclear waste program [7–9]. Granitic groundwaters are generally Na–Ca– $\text{HCO}_3$ -dominated with total dissolved solids in the range 100–500 mg/l and a pH of 7.2–8.5 (buffered by the carbonate system). Concentrations of organics (low molecular weight fulvic acids) are well below 0.1 mg/l. The redox potential is generally determined by the redox pair Fe(II)/Fe(III) or the Fe–S-system, giving a  $p_e$  of about  $-3$ . Sand and BES were slightly compacted in cylindrical PTFE cells (gave solid samples with dimensions 30 mm in diameter and 27 mm length), to a dry density of 1.5 kg/dm<sup>3</sup>. Concrete was prepared according to the manufacturer's instruction, cast in the cells, and aged for 1 week in a sealed plastic box with high humidity. No other parameters (e.g. tortuosity, constructivity,

Table 1  
Initial components and conditions of the six experimental systems

Mercury	Barrier	Sample code	Wc <sup>a</sup>	Solution	pH	Cond. <sup>b</sup>
HgO	Concrete	CII <sup>c</sup>		Concrete leachate	12.5	480
HgO	BES <sup>d</sup>	BII <sup>c</sup>	23	BES leachate	8.5	45
HgO	Sand	SII	17	Deionized water	7.0	0.09
Hg(l)	Concrete	C0		Concrete leachate	12.5	480
Hg(l)	BES	B0 <sup>c</sup>	23	BES leachate	8.5	45
Hg(l)	Sand	S0 <sup>c</sup>	17	Deionized water	7.0	0.09

<sup>a</sup> Water content % (w/w) of wet material.

<sup>b</sup> Conductivity (mS/m).

<sup>c</sup> Duplicates.

<sup>d</sup> Bentonite-enhanced sand.

porosity) were measured since this was outside the scope of the study.

The cell ends were connected with PTFE-tubing to liquid-filled bottles (Fig. 1), one containing a mercury source (an excess of elemental mercury or yellow mercury(II)oxide) and one without mercury (the receiving chamber). The liquid levels were at the same height in both chambers, to minimize pressure gradients. The solid and liquid phases were separated by a 1- $\mu\text{m}$  cellulose filter (Munktell).

The liquid phases were prepared by leaching pieces of the corresponding solid material, in order to minimise the effects of dissolution reactions. BES was leached with a solution of  $\text{NaHCO}_3$  (1 mmol/L) and  $\text{NaCl}$  (1 mmol/L) (pH 8.5, conductivity 45 mS/m) in order to maintain relevant carbonate and salinity levels. For the concrete systems, crushed concrete was leached with deionized water (L/S 10). A reference system that contained sand and deionized water was also prepared.

Each solid phase (concrete, BES and sand) was combined with the two Hg sources for a total of six systems (Table 1) with duplicates of each system except for sand/Hg(II) and concrete/Hg(0). The mercury concentration was then measured as a function of time in both chambers for up to 45 months. The experiments were carried out at room temperature (19–21 °C). The solutions were stirred regularly and flushed into the tubings. After break-through, or after 45 months if no break-through was observed, the cells were opened and the solids were cut into 2–5 mm thick slices, digested in  $\text{HNO}_3$  in a microwave oven, and analysed for total mercury. In addition, the concentration of Hg(0) was measured in the source bottles that initially contained elemental mercury.

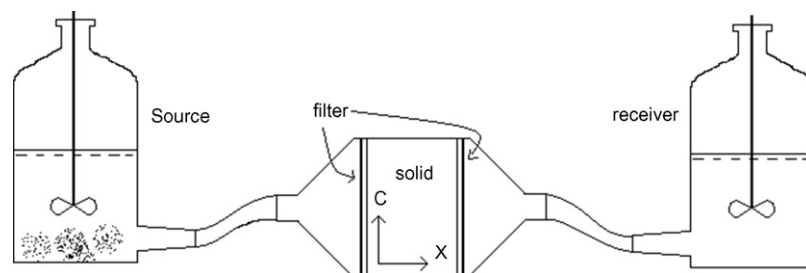


Fig. 1. Set-up of the diffusion experiments (source with solid HgO or Hg(l): solid samples with dimensions 30 mm in diameter and 27 mm length).  $C$  is the concentration of mercury in the solid sample at time  $t$  ( $\text{mol}/\text{m}^3$ ) and  $x$  is the distance into the sample at time  $t$  (mm).

### 2.3. Analysis

Measurements of pH and conductivity were made regularly during the experiment. The pH was measured with a glass electrode calibrated in the range pH 7–10 or 10–12. The electrical conductivity was measured with a platinum conductivity cell at 25 °C according to the European standard [10]. Samples were taken from the two chambers every third month and were centrifuged (3000 rpm for 4 min) to eliminate suspended matter. The supernatants were preserved with nitric acid. Total mercury in the supernatant was analyzed by flow-injection cold-vapour atomic absorption spectrophotometry with stannous chloride as reduction agent. Speciation of mercury was performed with a purge-and-trap method, where Hg(0) was removed from the sample solution by nitrogen gas, led through a trap (10 mmol/L KCl and 0.6 mmol/L HCl) for volatile oxidized mercury species and finally trapped in a solution of KMnO<sub>4</sub> (17 mmol/L) and H<sub>2</sub>SO<sub>4</sub> (500 mmol/L) [11].

### 2.4. Apparent diffusion coefficient

Diffusion is the net transfer of matter from a region of high concentration to one of low concentration. A part of the total amount will be bound to the solid material, and the driving potential is not the total concentration, but the concentration of dissolved matter. In a through-diffusion experiment a tracer is allowed to diffuse from one solution through the sample to another solution. The apparent diffusion coefficient of mercury was determined from the concentration profile of Hg in the cells. Fick's second law of diffusion can be expressed as

$$\frac{\partial C}{\partial t} = D_a \left( \frac{\partial^2 C}{\partial x^2} \right) \quad (1)$$

where  $D_a$  is the apparent diffusion coefficient (m<sup>2</sup>/s) of mercury in the solid material,  $C$  the concentration of the diffusing mercury (mol m<sup>-3</sup>),  $t$  the diffusion time (s), and  $x$  is the distance  $x$  (m) from the mercury source. Assuming an infinitely plane source, from which mercury diffuses into a cylinder of infinite length and a concentration independent of diffusion, the concentration profile can be expressed by [12–15]:

$$C(x, t) = \frac{M e^{[-x^2/4D_a t]}}{2(\pi D_a t)^{1/2}} \quad (2)$$

where  $M$  is the amount of mercury per unit area (mol m<sup>-2</sup>). The apparent diffusion coefficients were determined from a plot of  $\ln C(x)$  versus  $x^2$  at time  $t$ .

### 3. Results and discussion

The water composition in the receiver bottles at the end of the experiment are shown in Table 2. Break-through was observed only in the sand and BES system in contact with Hg(II), both within 15 months. The concentration profiles of mercury as a function of the squared distance in the solids after 15 months (break-through) or 45 months (no break-through) are shown in Fig. 2. Apparent diffusion coefficients were determined from the average value of two possible gradients of each replicate.

The apparent diffusion coefficient for Hg ranged from  $0.3 \times 10^{-14}$  to  $1.7 \times 10^{-14}$  m<sup>2</sup>/s in Standard Portland concrete, from  $1.5 \times 10^{-13}$  to  $6.5 \times 10^{-13}$  m<sup>2</sup>/s in BES and from  $3.0 \times 10^{-13}$  to  $3.0 \times 10^{-12}$  m<sup>2</sup>/s in quartz sand (see Table 3). The similar values for the apparent diffusion coefficient for BES and sand is probably a consequence of the water content (BES 23%, sand 17%) and the similar porosity between the two barrier materials in this investigation. Bentonite is more fine-grained than sand, and normally the porosity of e.g. bentonite-enhanced

Table 2  
Conditions in the chambers at the end of the experiment

	HgO <sup>a</sup>				Hg(I) <sup>a</sup>					
	CI <sup>b,c</sup>		BII <sup>b,c</sup>		SI <sup>b</sup>	C0 <sup>b</sup>		B0 <sup>b,c</sup>		S0 <sup>b,c</sup>
C <sub>source</sub> (μmol/dm <sup>3</sup> )	59	59	73	73	242	5.5	0.155	0.155	0.050	0.125
Hg(0)/C <sub>source</sub> (%)	–	–	–	–	–	1	10	10	n.a. <sup>d</sup>	4
C <sub>receiver</sub> (μmol/dm <sup>3</sup> )	0	0	0.26	0.26	4.5	0	0	0	0	0
Experimental time (day)	1355	1355	1332	1332	568	1383	1367	1367	445	886
pH	9.1	11.1	8.8	8.7	6.9	9.2	8.8	8.6	5.8	5.4
Cond. (mS/m) <sup>e</sup>	130	150	82	81	n.a. <sup>d</sup>	116	89	87	n.a. <sup>d</sup>	14

<sup>a</sup> Hg source.

<sup>b</sup> Sample code.

<sup>c</sup> Duplicates.

<sup>d</sup> Not analyzed.

<sup>e</sup> Conductivity.

Table 3  
Apparent diffusion coefficients (m<sup>2</sup>/s) with duplicates of each system except for sand/Hg(II) and concrete/Hg(0)

Barrier	Hg(II)		Hg(0)	
Concrete	$1 (\pm 0.7) \times 10^{-14}$	$0.6 (\pm 0.2) \times 10^{-14}$	$1 (\pm 0.5) \times 10^{-14}$	
BES	$3 (\pm 1) \times 10^{-13}$	$5 (\pm 0) \times 10^{-13}$	$4 (\pm 2.5) \times 10^{-13}$	
Sand	$4 (\pm 0.5) \times 10^{-13}$		$3 (\pm 0) \times 10^{-12}$	$5 (\pm 2) \times 10^{-13}$

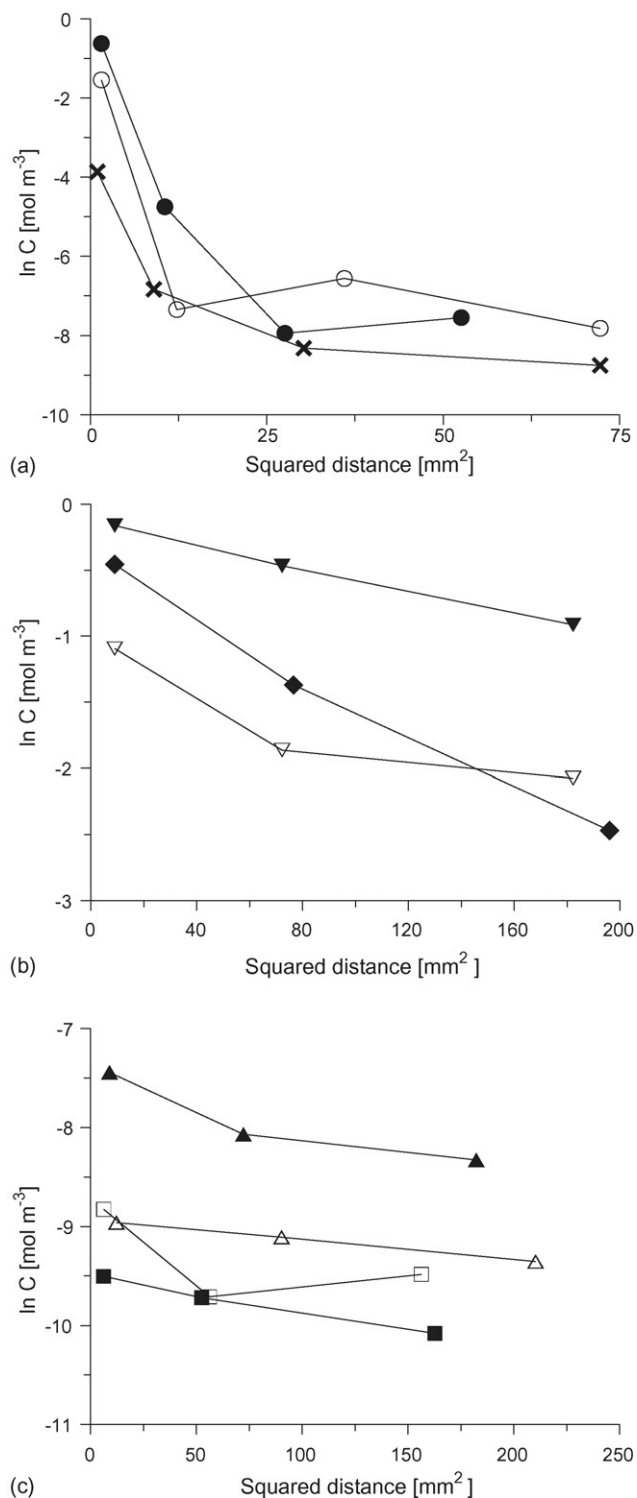


Fig. 2. Mercury concentration profiles at the end of the experiment (see experimental time in Table 2) in solids of: (a) concrete; (b) BES and sand with initially Hg(II); (c) BES and sand with initially Hg(0). (○) CII:1; (●) CII:2; (×) C0; (◆) SII; (△) S0:1; (▲) S0:2; (▽) BII:1; (▼) BII:2; (□) B0:1; (■) B0:2.

sand is considerably lower than for pure sand. Bentonite thus seems to be a rather inefficient sorbent for mercury.

The observed apparent diffusion coefficients appeared to be similar regardless of the starting conditions (Hg(0) or Hg(II)), at least for the concrete and BES-systems (see the observed

slopes of  $\ln C$  versus squared distance, Fig. 2). This is probably an indication of the oxidation of Hg(0) to Hg(II) under aerobic conditions. The physical solubility of Hg(0) is  $0.28 \mu\text{mol/l}$  at  $25^\circ\text{C}$  in anoxic water and  $264 \mu\text{mol/l}$  for mercury oxide at neutral or higher pH [16–18]. Elemental mercury oxidizes easily and the dissolved concentration increases with time, approaching equilibrium with HgO. The process is affected by the solution composition [11,19–21] as well as by the mercury/solution ratio. The presence of a highly mobile species, which would be Hg(0), is only observed in one of the sand systems (see Table 3), indicated by an apparent diffusion coefficient one order of magnitude higher than for Hg(II) in the same matrix.

For the systems initially containing elemental mercury, the distribution of mercury species was modelled with the geochemical software PHREEQC under respective barrier conditions (solution composition, pH, Hg concentration). The dominant species was Hg(OH)<sub>2</sub> (90–99%) and the second species was Hg(0) when modelling with the Hg(0) and Hg<sub>tot</sub> concentrations that were measured in the source chambers after 45 months (1% Hg(0) of Hg<sub>tot</sub> in the concrete solution, 10% in the BES solution and 4% in the sand/deionized water solution, see Table 2). As a consequence, the fraction of dissolved elemental mercury was higher during the early stages of the experiments. An indication of this can be seen in the apparent diffusion coefficients of sample S0:1 (sand/deionized water) and its replicate S0:2, which was an order of magnitude lower. The only parameter that differs between the samples was the experimental time, which was 20 months shorter for sample S0:1. Thus, all the apparent diffusion coefficients in Table 3 are probably for oxidized mercury (90–99%), except from sample S0:1 that probably contain a higher fraction of Hg(0). Investigations of the apparent diffusion coefficient for dissolved elemental mercury are recommended to be performed under anoxic conditions or during shorter experimental time and under continuous measurement of the Hg(0) concentration, since it is unstable under aerobic conditions.

Assuming  $D_a = 10^{-14} \text{ m}^2 \text{ s}^{-1}$  (standard Portland concrete), it would take some 2000 years to release 1% of the initial Hg(II)-concentration and 35,000 years for 50% through a 0.1 m barrier [22,23]. Thus, concrete is an efficient barrier for Hg(II), while sand or sand/bentonite are less efficient, as indicated by diffusion coefficients that are one to two orders of magnitude higher. Hg(0) would be expected to have significantly higher apparent diffusion coefficients but would be oxidized to Hg(II) in aerobic waters.

#### 4. Conclusions

The apparent diffusion coefficient for Hg(II) was  $1 \times 10^{-14} \text{ m}^2/\text{s}$  in standard Portland concrete and  $4 \times 10^{-13} \text{ m}^2/\text{s}$  in quartz sand under the present conditions. The apparent diffusion coefficient for Hg(0) could not be measured, but would (in quartz sand) be between the observed maximum value  $10^{-12} \text{ m}^2/\text{s}$  and  $10^{-9} \text{ m}^2/\text{s}$ , which is expected for diffusion of ions in solutions [23]. Dissolved Hg(0) would, however, be oxidized to Hg(II) under aerobic conditions, and after 45 months only 1–10% of the total dissolved mercury concentration in the solution was actually Hg(0). Thus, concrete can be considered as an efficient

barrier for Hg(II)(aq). The presence of aerated water would oxidize dissolved Hg(0) to Hg(II) and render it less mobile.

### Acknowledgements

SAKAB AB, the Knowledge Foundation and the SAKAB Kumla Environmental Foundation supported this work, which is gratefully acknowledged. We thank Dr. A. Düker for critical comments and advice.

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