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Leaching of mercury-containing cement monoliths aged for one year

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Abstract

A directive from the Swedish Government states that waste containing more than 1% of mercury shall be permanently deposited. The stabilization of mercury by conversion to a sparingly soluble compound like the sulphide is crucial to ensure long-term immobilization in a permanent storage. Immobilization by the solidification/stabilization (S/S) method and possible formation of HgS from mercury oxide or elemental mercury by reaction with a sulphur source (S or FeS) is investigated by a modified version of the NEN 7345 Dutch tank-leaching test. The diffusion of mercury during 11 months from 1-year-old mercury containing monoliths of Portland and slag cement is demonstrated. In a geologic repository under conditions representative of deep granitic bedrock (bicarbonate buffered to pH 8.6), a favourable monolith combination is slag cement with addition of the iron sulphide troilite. The apparent diffusion coefficient of mercury is estimated.

1. Introduction

A directive from the Swedish Government states that essentially all use of mercury in society shall be terminated (SOU, 2001; Swedish EPA, 1997; Sveriges Riksdag, 2001), and mercury in industry and private use shall be collected. Waste containing more than 1% of mercury shall be conditioned for permanent storage in a repository. Soluble mercury compounds should be converted to an insoluble form. 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 reducing conditions expected in a groundwater saturated repository in deep crystalline (granitic) bedrock, which is the proposed disposal concept (SOU, 2001; Swedish EPA, 1997). Thus, the stabilization of mercury by conversion to sulphide is crucial to ensure long-term immobilization in a permanent storage.

Some mercury waste may be suitable for immobilization by the solidification/stabilization (S/S) method. S/S with binders is a common encapsulation technology used for immobilizing contaminants of hazardous waste in two ways: (1) by chemically binding them in an insoluble form, and (2) by physically trapping them in a rigid and durable matrix. Conventional S/S methods include the fixation of metals that form sparingly soluble hydroxides at high pH and production of a solid monolith using Portland cement and fly ash. Mercury does not form sufficiently insoluble (hydr)oxides, and a sulphur source should be added to the mercury waste to generate mercury sulphide. In a mercury S/S process, the contaminated solid waste is mechanically mixed with a stabilizing agent, such as sulphur, sodium sulphate (Roy et al., 1992), reactivated carbon (Zhang and Bishop, 2002), or ferric-lignin derivatives (Zhuang et al., 2004) prior to solidification with a binder such as fly ash, lime and/or Portland cement (Chang et al., 1999; Conner, 1990; Razzell, 1990; Reid and Brooks, 1997; Roy et al., 1991). Leaching has been performed after 1 month of ageing in most of these

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studies, but recent studies on the formation of HgS from mercury oxide and elemental sulphur under alkaline conditions at room temperature showed a longer reaction time (Svensson et al., 2006). After 1 year the HgS yield was close to 100% under anaerobic conditions and 25–60%w/w under aerobic conditions. Troilite (FeS) as a sulphur source gave a HgS yield of 10% under anaerobic conditions and 50%w/w under aerobic conditions. Thus, the redox condition in a waste monolith would be a crucial parameter for the formation of HgS.

Leaching rates in monoliths are controlled by the rate of diffusion in the waste matrix (Côté and Bridle, 1987), which would depend on the solubility of the mercury compound. The rate of diffusion for different mercury compounds in a monolith is therefore an important process to investigate. Efforts should be directed towards minimizing the total porosity of the waste matrix, since it appears that solidified waste surrounded by water rapidly becomes saturated, also in the absence of a hydraulic gradient (Côté and Bridle, 1987). Previous investigations of diffusion in ordinary concrete and concrete containing blast furnace slag show that differences in diffusivities for a given metal reflect the different properties of the cement matrix. Slag cement has a higher proportion of small pores, lower total porosity than ordinary cement and a different foil-like morphology (Togerö, 2004).

In the present study a modified version of the Dutch tank-leaching test (NEN, 1995) was used to investigate the diffusion of mercury during 11 month from 1-year-old mercury containing concrete monoliths. Leaching of concrete monoliths by the Dutch tank-leaching test have been done earlier (Andac and Glasser, 1998, 1999; van der Sloot, 2000). Data on the apparent diffusion coefficient of mercury in cement systems have not been found. The main objectives of the study were: (1) to characterise the leaching behaviour of mercury from a well-defined cement matrix and estimate the apparent diffusion coefficient of mercury, (2) to compare the leaching properties of monoliths composed of Portland cement and a Portland-blast furnace slag cement, (3) to compare the extent of HgS formation using different sulphur sources (elemental sulphur and the iron sulphide troilite), and (4) to compare mercury leaching from monoliths initially containing elemental mercury or mercury oxide with monoliths where mercury was added as the sulphide.

2. Experimental

2.1. Materials

The concrete monoliths were composed of either Portland cement (CEM II, Cementa) or slag cement (SC, 50%w/w of Portland cement and 50%w/w of ground granulated blast furnace slag, Merit 5000, from Swedish Merox), quartz sand, and Milli-Q (Millipore) water. Elemental mercury (Hg(l), 99.95%, Merck) or yellow mercury(II) oxide (HgO, +99%, Aldrich) mixed with elemental sulphur (S, +99%, sublimated, Merck) or troilite (FeS, Merck) were added, see Table 1. The troilite was ground in a mill. The composition of the monolith was 25%w/w cement, 12.5%w/w water, 56 or 62%w/w sand, mercury either 1 or 5%w/w and a sulphur source giving an S/Hg mole ratio of 1.5 (0.24 or 1.2%w/w S). Reference systems were prepared containing black meta-cinnabar, HgS (Aldrich) at levels of 1 and 5%w/w.

Table 1
Composition of the samples

Sample	Mercury	Sulphur source	Binder
HgS1/CEM II	1% HgS		Portland
HgS1/CEM II SC	1% HgS		Portland/Slag cement
HgS5/CEM II	5% HgS		Portland
HgS5/CEM II SC	5% HgS		Portland/Slag cement
Hg1/S/CEM II	1% Hg(l)	S	Portland
Hg1/S/CEM II SC	1% Hg(l)	S	Portland/Slag cement
Hg1/FeS/CEM II	1% Hg(l)	FeS	Portland
Hg1/FeS/CEM II SC	1% Hg(l)	FeS	Portland/Slag cement
Hg5/S/CEM II	5% Hg(l)	S	Portland
Hg5/S/CEM II SC	5% Hg(l)	S	Portland/Slag cement
Hg5/FeS/CEM II	5% Hg(l)	FeS	Portland
Hg5/FeS/CEM II SC	5% Hg(l)	FeS	Portland/Slag cement
HgO1/S/CEM II	1% HgO	S	Portland
HgO1/S/CEM II SC	1% HgO	S	Portland/Slag cement
HgO1/FeS/CEM II	1% HgO	FeS	Portland
HgO1/FeS/CEM II SC	1% HgO	FeS	Portland/Slag cement
HgO5/S/CEM II	5% HgO	S	Portland
HgO5/S/CEM II SC	5% HgO	S	Portland/Slag cement
HgO5/FeS/CEM II	5% HgO	FeS	Portland
HgO5/FeS/CEM II SC	5% HgO	FeS	Portland/Slag cement

2.2. Procedures

2.2.1. Monoliths

The cement pastes, prepared by mixing sand, cement, blast furnace slag (in 50% of the samples), Milli-Q water, the sulphur source and mercury were cast into cylinder moulds (diameter 41 mm, height 42 mm). They were aged for 1 month in the dark at room temperature (19–21 °C) and 100% humidity. Thereafter the monoliths were aged for another 13 months under dry conditions. The long curing period allowed pozzolanic reactions between cement and the blast furnace slag to develop and mercury sulphide to form.