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Feasibility of compacted bentonite barriers in geological disposal of mercury-containing waste

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Abstract

The growing concern regarding the threat to human health posed by mercury in the environment has prompted the Swedish Government to plan for disposal of mercury-containing waste in deep geologic formations. The purpose of the present 3-year project is to determine the major prerequisites and evaluate the feasibility of utilising bentonite barriers for such a purpose. The scope of the present paper is to present the results from the work carried out during the first year.

The design concept should be such that the excellent materials properties of high-density bentonite can be utilised. Also, the chemistry should be adjusted in such a way that any deterioration of bentonite becomes tolerable, and such that the mercury species in solution either appear in low concentration, or in a form that has a low mobility.

It is concluded that safety analyses may be based on modelling of the speciation in combination with diffusion through bentonite in one dimension. The results of such modelling will be compared with actual migration data from actual waste forms comprising highly compacted mixtures of spent mercury-containing batteries and bentonite.

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1. Introduction

In many of its forms, mercury is detrimental to human health. It has become recognised to an increasing degree how mercury can transfer between different forms, move around in the environment and eventually affect human health. The main reason for this mobility is the ease with which mercury switches

between the oxidation numbers 0, 1 and 2 in combination with the high vapour pressure of elemental mercury as well as methyl mercury, which is readily formed through biological metabolism. Mercury also has the potential to move around in the form of ionic species, preferably as organic complexes, e.g. bonded to organic sulphur.

In concordance, international restrictions on mercury have been tightened, and in Sweden, the use of mercury is intended to be terminated altogether. The residual mercury is to be treated and deposited in a geological repository with a clay barrier between the waste and the rock ([Safe disposal of mercury, 2001](#)). The alternatives considered for

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treatment are solidification, sulphidation and amalgamation.

2. Purpose and scope

As will be explained below, the proper utilisation of clay is of paramount significance for the adequate functioning of such a repository. In concordance, a 3-year project has been initiated with the purpose of investigating the following aspects:

- (A) conceptual design;
- (B) the source term, i.e. the composition of leakage from the enclosed waste;
- (C) the potential for the formation of mobile mercury containing species;
- (D) manufacturing of the buffer in the form of pellets and/or blocks;
- (E) dimensioning of the bentonite barrier and the assessment of likely materials properties;
- (F) theoretical calculations on the formation of different species containing mercury together with their migration;
- (G) experimental investigations of the behaviour of mercury-containing waste enclosed in bentonite;
- (H) technical and economical optimisation.

The purpose and scope of the present paper is to describe the results from the first year's work.

3. Design concept

For many years, research and development activities on nuclear waste have been carried out in parallel to that of hazardous chemical waste. It has also been pointed out (Proceedings, 1991) that a high potential exists for substantial synergistic benefits through cross-breeding of these two areas, particularly in view of the solutions developed for the most long-lived nuclear waste.

In reality, hazardous chemical waste is for the most part deposited at the surface under drained conditions while long-lived and high-level nuclear waste in most programmes is intended to be deposited in geologic formations well below the ground water level. It might therefore be tempting to assume that the major difference relates to the low permeability of the surrounding rock in the latter case. However, in a number of the nuclear programmes, the most important property of the natural barrier is to provide a stable chemical and mechanical environment to the technical barriers.

Actually, it is the bentonite barrier—in combination with a corrosion-resistant canister—which gives rise to the extremely long containment times arrived at in various safety analyses (SR 97-Post-closure safety, 1999). In these cases, the bentonite provides an extremely high resistance to flow of water such that the dominating mechanism for transport is diffusion. Moreover, in the case of the copper canister, the rate

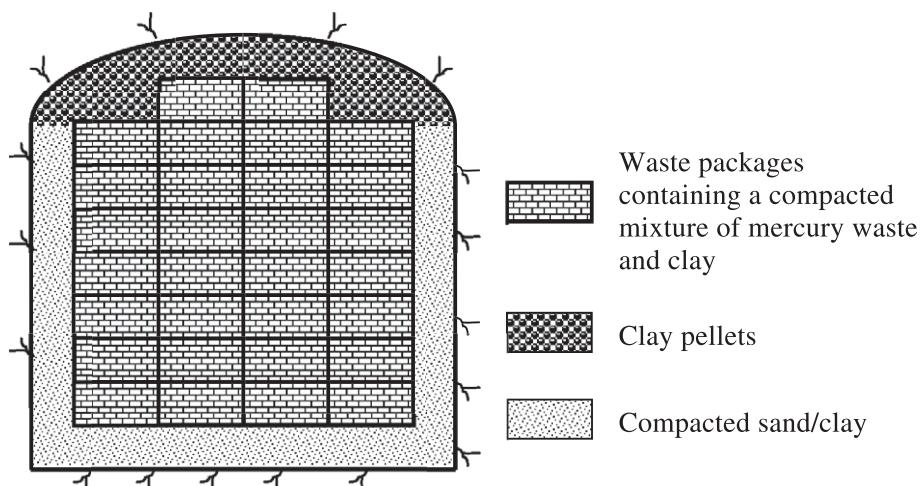


Fig. 1. The design concept used in the present study.

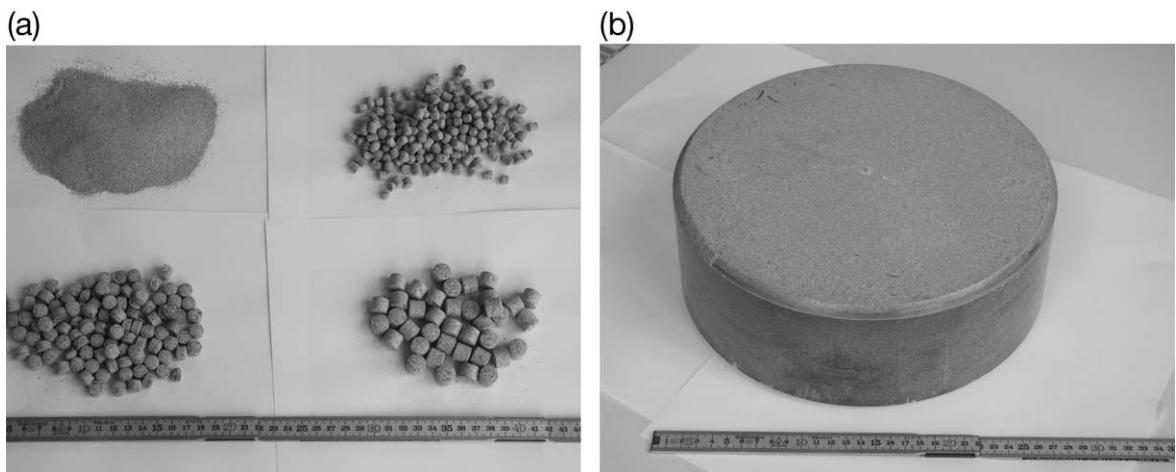


Fig. 2. Pellets and blocks for the design concept in Fig. 1. (a) Examples of pellets prepared by die compaction. Uncompacted powder is also shown for comparison. (b) A high-density block of bentonite prepared by uniaxial compaction at about 100 MPa. The diameter of the block is about 280 mm.

of transfer of reduced sulphur species is substantially hampered further by low solubilities in combination with anionic exclusion. Such species will eventually corrode the copper canister.

In surficial repositories for hazardous waste, it is usually assumed (European Community, 1999) that water percolates through the repository to a limited extent and that a fraction of the hazardous substances dissolve in that water.

There is more to this than solely differences in approaches on safety analyses. In order for bentonite to show its best materials properties, the swelling pressure should be on the order of several MPa, which corresponds to a drained soil cover on the order of at least 200 m! Conversely, in a rock excavation at a depth of a few hundred meters, such a swelling pressure might actually have a beneficial effect on the rock in terms of improved stability.

The approach taken in the present work is that the transport resistance of a properly swollen and pressurised¹ bentonite in combination with pertinently tailored pre-treatment should provide the protection required without the need for a high-cost, high-performance containment container. The tailoring should

be such that the concentration of mobile species in the pore fluid should be low.

The reference design concept used in the present study is shown in Fig. 1.

4. Manufacturing of blocks and pellets

The above-mentioned requirement of a suitable swelling pressure implies that the bentonite must be introduced with a pertinent density (with regard to the smectite content, etc.).

For sodium-based bentonites, two modes of swelling exist: crystalline and osmotic. Crystalline swelling takes place only during addition of low fractions of water (about two layers of water molecules between the silicate layers) while osmotic swelling can take place for much larger additions. However, the presence of electrolyte inhibits osmotic swelling. Such electrolyte may be present both in the mercury waste and in the ground water. Therefore, the dimensioning should be such that the swollen bentonite in the repository will be in the crystalline state of swelling.

This implies that it is necessary that the waste packages as well as the buffer/backfill material are relatively compact.

Roll pressing and die pressing can be used for manufacturing of pellets having a high density.

¹ Pressurised in this case refers to the effective pressure (= the swelling pressure), i.e. the difference between the total pressure and the hydrostatic pressure.

Examples of die compacted agglomerates are shown in Fig. 2. Bentonite mixed with ballast material can be compacted in situ provided that the distance to the roof is not too small.

Preparation of buffer and backfill have been studied in nuclear waste repository development programmes for many years (FUD-Program, 2001) and the resulting techniques are readily available. It has thus been demonstrated that large, as well as small, blocks of high-density bentonite can be prepared by isostatic as well as uniaxial compaction techniques. An example of such a block is also shown in Fig. 2.

It is the assessment of the present authors that manageable blocks of high density can be prepared also from a mixture of mercury waste and bentonite, and experiments to demonstrate this are presently underway.

It is conceivable that additions be made to the bentonite in order to improve the retention properties of mercury. This can be achieved by adding pyrite or sulphur, for example, to the bentonite. No particular difficulties are foreseen in this regard. The issue may, however, warrant some tests in the continued work in the present project. This will depend on the results obtained from some of the activities described below.

5. Source term

In Sweden, it has been proposed (Safe disposal of mercury, 2001) that all waste containing more than 1% of mercury by weight should be deposited in final storage situated in a geological formation. The approximate composition of this waste (Safe

Table 1
The approximate composition of the mercury-containing waste in Sweden in 2001

Responsible organisation	Origin	Volume (metric tons)
Boliden Mineral	Mining residues	5000
Eka Chemicals and Hydro Polymers	Chlorine-alkali process	400
SAKAB together with Swedish Environmental Protection Agency	Miscellaneous Batteries	2700
		1800

Only wastes that can be assumed to contain more than 1% of mercury is included.

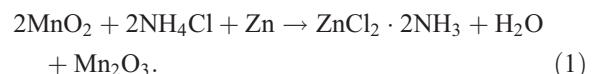
Table 2
The composition of the battery waste at SAKAB in 1995

Category	Amount (metric tons)	Mercury content (wt.%)
Unsorted	647	<2 ?
Alkaline	878	0.5–1.0
Mercury oxide	50	35–38

disposal of mercury, 2001; Forsgren, 1995) is given in Table 1.

Out of the generally occurring waste types, it was assessed that those comprising batteries might be possible to deposit without any special pre-treatment other than mixing with (possibly modified) bentonite and compaction. In 1995, the composition of the battery waste (Forsgren, 1995) was as shown in Table 2.

Much of the material in the “unsorted” category in Table 2 comprises *Lelanché* type of cells. The sum reaction is as follows:



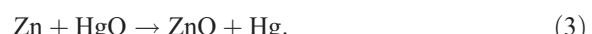
The electrolyte consists of ammonium and/or zinc chloride solution in water. Leakage may occur after heavy discharges, in which case acid is formed (Vincent et al., 1986). In old batteries, mercury chloride was added to the electrolyte to levels up to about 1.0% (Linden, 1995).

In alkaline manganese cells, the sum reaction is as follows:



The electrolyte consists of 40% by weight of potassium chloride in water. In old batteries, elementary mercury was added to the zinc as a corrosion inhibitor to a level of about 1% by weight of the entire battery.

In zinc–mercury oxide batteries, the sum reaction is as follows:



The electrolyte is usually an approximately 40% solution of potassium hydroxide. The mercury content is around 35% by weight.



Fig. 3. Sample material for the present project. (a) Unsorted batteries. (b) Zinc–mercury oxide batteries.

SAKAB has provided test material for the present project as shown in Fig. 3.

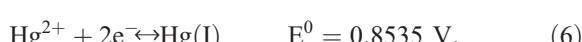
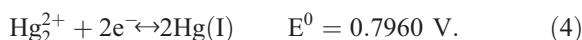
6. Speciation and transport

It is intended in the present project that transport calculations be performed and the results be compared with those of experiments. It is imperative, however, that reasonably correct conceptual models be set up before calculations are attempted. In the following, the conceptual model to be used is derived and described.

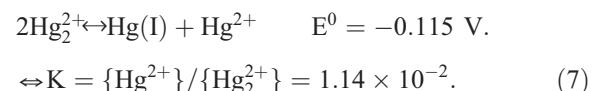
A relatively large number of papers (see, e.g. Svensson, 2001) describe the speciation of mercury in oxidising and reducing soils, fresh waters and sea waters, and in air. In summary, the conclusions are as follows.

Mercury has a high affinity to sulphur and to chlorine and, in comparison, a low affinity to oxygen.

Important thermodynamic potentials are as follows (Cotton et al., 1999).



The disproportion reaction is rapid and reversible



The implication of the above is that in the absence of complexation, mercury oxidises to Hg(I) only by oxidation agents having potentials in the range -0.79 to -0.85 V or when the availability of oxidising agents is limited. However, Hg(II) is a much stronger complexing agent than Hg(I), and therefore little or no Hg(I) may be formed even in cases of limited availability of oxidants.

Mercury readily forms elemental mercury under mildly reducing conditions. In this form, it readily forms amalgams with, e.g. zinc. The solubility of elemental mercury in water is 6×10^{-5} g/kg. (Cotton et al., 1999).

Under oxidising conditions and in the absence of chloride, the predominant species in water is Hg(OH)_2^0 (i.e. electrically neutral complexes in solution) at high pH values, and Hg^{2+} at low pH values.

In the presence of chloride, chloride complexes are formed, especially at low pH values: HgCl_2^0 at low chloride concentrations, and negatively charged complexes at high chloride concentrations.

In the presence of reduced sulphur—e.g. in the form of elemental sulphur or pyrite (FeS_2), HgS is formed. Under high pH conditions, species comprising HgS_2^{2-} may appear in solution.

Little has been found in the international literature on interactions between deteriorated battery material and bentonite. It is well known, however, that bentonite—or rather the active mineral montmorillonite—is not stable in the long term in a strongly acidic or alkaline environment. Therefore, a repository must be designed in such a way that either acceptable amounts of bentonite are consumed or some additive with a suitable pH buffering capacity is used.

In many cases, the transport of matter through soil is substantially reduced due to absorption onto the soil particles. In the case of relevant mercury species and bentonite, experiments show that such retention is probably of minor significance (Arnfalk et al., 1996). Any such effects are therefore neglected in the following.

Essential parameters and data for the speciation modelling are thus as follows.

- pH values around neutral or slightly alkaline (due to addition of pH-buffering material).
- Chloride levels as given by the content of soluble chlorides in the bentonite and the chloride content in the ground water at repository depth.
- Redox potentials initially oxidative but reducing in the long term.
- Reduced sulphur may be added to the bentonite, in which case migrating elemental mercury will form sulphide with a low solubility and a low concentration of anionic sulphide species.

The migration through the bentonite will largely be dictated by the mobility of the dissolved species (diffusion constants). It is possible that appropriate constants may not be found in the literature. In such a case, model substances may be identified whose diffusion constants resemble those of the actual ones within a factor of 2 or so. In this context, it is important to realise that the rate of migration of anionic species can be expected to be considerably lower than that of the other ones due to anionic exclusion.

7. Discussion and conclusions

In the present work, the feasibility of applying nuclear long-lived waste disposal concepts to chemical

hazardous substances is being tested. The elements needed for at least a simple safety analysis are identified and described in the present paper and will be tested experimentally and theoretically. In addition to mobility tests, the experiments include demonstration of a technique for compacting a mixture of spent batteries and bentonite clay.

If deemed feasible, the concept has a potential to provide a high-performance solution at moderate cost. The moderate cost may arise since only natural soil materials are used and since the processing involves only relatively simple and inexpensive steps like mixing, compacting and handling activities. The cost for the excavation is highly dependent on whether a new excavation is to be carried out or if some redundant but suitable rock cavity is available.

Important prerequisites for the efficient and validated utilisation of bentonite barriers in geological disposal of mercury waste include the following:

- A good basic knowledge of the microstructural and materials aspects of the bentonite to be used.
- A good basic knowledge on the interaction between
 - bentonite and the chemical substances present in the waste, as well as
 - bentonite and any better material added.
- A good understanding of conceivable mechanisms for loss of essential properties of the bentonite.

The knowledge bases should be adequate both for the purpose of design and for performance assessment.

It is not unusual that basic research receives inadequate funding because it has not been possible to describe or understand the relation to real technical needs sufficiently clearly. It is the hope of the present authors that this paper—albeit rather general and technical in nature—will highlight some important aspects in this regard.

Acknowledgements

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