

Formation of cinnabar—estimation of favourable conditions in a proposed Swedish repository

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Abstract

A deep repository for permanent storage of mercury will be designed and built in Sweden. The preferred chemical state for mercury in such a repository would be the sulphide HgS (cinnabar), which is a highly insoluble and the dominating natural mercury mineral. The possible formation of HgS from HgO or Hg(0) by reaction with a sulphur source (S, FeS or FeS₂) is discussed from thermodynamic considerations, and pe–pH-diagrams are constructed by using the computer code MEDUSA to illustrate under which conditions HgS would dominate. Calculations of the speciation (PHREEQE) under varying conditions (S/Hg-ratios, presence of chloride) are given.

Long-term laboratory experiments are performed, where the formation of HgS from the basic components is demonstrated (after mixing under various conditions and storage at room temperature for up to 3 years).

The feasibility of HgS-formation with time in a geologic repository under conditions representative of deep granitic bedrock (calcium-bicarbonate buffered to pH 7–8.5) is discussed, as well as effects of alkaline conditions (concrete environment, pH 10.5–12.5). Formation of soluble polysulphides is not expected as long as the S/Hg mole ratio is within 1–1.3 and pH is below 10.5–11. Concrete should be used with caution. Suitable ballast materials could be introduced that would reduce porewater-pH that otherwise would be above 12.

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1. Introduction

Essentially all use of mercury in the Swedish 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 reducing 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 several alternatives have been considered such as bentonite and concrete, as well as metallic containers. Eventually, the barriers will degrade and any soluble or volatile mercury compounds in the waste should therefore be converted to the sparingly soluble state (HgS), either prior to the storage or spontaneously due to reactions occurring within the repository with time. Thus, the stabilization of mercury by conversion to sulphide is crucial to ensure long-term immobilization in a permanent storage. Previous studies have demonstrated the formation of HgS in laboratory scale by stirring elemental mercury and sulphur in various proportions at 200 °C [4] and at 40 °C [5]. An immediate production of meta-cinnabar and cinnabar was observed. To minimize formation of mercury vapour, it is desirable to transform the various chemical mercury species in the waste into the sulphide at room temperature. An investigation of potential methods for stabilizing mercury reported by the Swedish Environmental Protection Agency suggests that pyrite (FeS₂), pyrrotite (FeS) and elemental sulphur would react with mercury oxide, as well as

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elemental sulphur would react with elemental mercury, to form cinnabar [6].

The objective of this study is to assess under which conditions (theoretically) it is feasible to generate cinnabar from a mixture of liquid elemental mercury or solid mercury(II)oxide and solid sulphur or solid iron sulphide at room temperature. Furthermore, the purpose of the study is to verify and demonstrate conditions that are favourable for the formation of cinnabar, as well as conditions where undesired side-products would be generated.

2. Thermodynamic considerations

The direction of a hypothetical reaction can be assessed from the over-all free-energy change of the reaction (representing a stability constant) calculated from standard free energy changes of formation for the proposed reactants and reaction products. A negative value would indicate a forward direction, however nothing about reaction kinetics or on energy barriers that would prevent the reaction from reaching equilibrium. However, such calculations could be used for screening purpose by sorting out reaction pathways that are thermodynamically impossible: Would a certain set of starting conditions (initial species, presence of water, pH, etc.) promote a proposed stoichiometric reaction or would this reaction not be possible? This is the approach that is used in the present study—predicting under which conditions various mercury species would react with a selected sulphur source to yield HgS, and verifying the indicated result experimentally.

The selected chemical states of mercury are Hg(0) (elemental) and Hg(II) (as HgO), and the selected sulphur sources are elemental S, solid FeS and FeS₂. Reactants/products that were used to balance the proposed reactions are water and its constituents. Thermodynamic data used in the calculations are given in Table 1. The pure phases at 1 bar and 25 °C was used as the reference state.

3. Repository conditions

Location of a repository for mercury waste in crystalline bedrock (granite) at a considerable depth has been proposed. The conditions in deep granitic bedrock (depth from less than 100 m down to 1000 m) have been studied within the Swedish nuclear waste program [7]. Generally these waters are Na–Ca–HCO₃-dominated with total dissolved solids in the range of 100–500 mg/l and with pH of 7.2–8.5 (buffered by

the HCO₃-system). Concentrations of organics (low molecular weight fulvic acids) are well below 0.1 mg/l. The redox potential is often determined by the Fe²⁺–FeS₂-equilibrium (e.g. $p_e = 5.46 - 1.143 \text{ pH}$ [17]). These conditions would be expected after long time in a repository located in this bedrock. Concrete constructions would lead to a local pH of at least 10.5 (initially above 12).

A repository close to the Swedish coast could be intruded by saline waters, either from the ocean (west-coast) or the Baltic Sea (east-coast). Relict saline waters are frequently encountered in eastern Sweden (from the Litorina Sea some 7000 years ago, a precursor to the Baltic Sea), giving Na–Cl-dominated waters with salinities generally not above 5 g/l, i.e. chloride concentrations of some 100 mM at the most [8,9].

Thus, in calculations of mercury speciation at equilibrium in a deep repository the expected conditions after long time would be pH of 7–11 and p_e of 5.46–1.143 pH (or above, up to at least the level of 11.5 – pH, or theoretically to 20.8 – pH [17] if aerated water would intrude), low levels of organics, and low levels of chloride (1 mM-level), however with a remote possibility of local high salinities giving chloride levels up to 100-times higher.

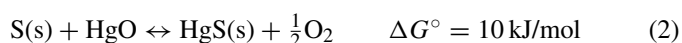
4. Thermodynamic calculations

4.1. Reactions with elemental sulphur

The fundamental reaction for generation of cinnabar (HgS) is:

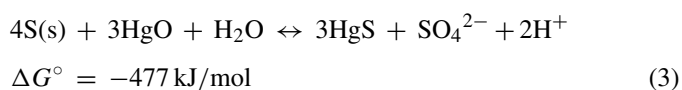


As shown by the negative ΔG° , formation of cinnabar is theoretically feasible by mixing elemental mercury and sulphur under anaerobic as well as aerobic conditions. It would be convenient if both the elemental and oxidized mercury form cinnabar under the same conditions.



The equilibrium oxygen fugacity is 10^{-3.50} bars according to reaction (2). Thus, formation of cinnabar is favoured as long as the oxygen fugacity is below this level, which is achievable in many subsurface environments.

An excess of sulphur leads to formation of cinnabar, as well as of SO₄²⁻ under anaerobic conditions (3).



Considering factors as pH and availability of oxygen, reaction (3) indicates that oxidation of sulphur leads to a lower pH, and an alkaline environment favours the formation of cinnabar since deficiency of hydrogen ions favours the reaction to go to the right. The disproportionation of S(0) into S(-II) and S(VI) leads to more sulphide formation under anaerobic conditions whereas aerobic conditions lead to increased oxidation and content of sulphate. Besides the promotion of cinnabar formation, an alkaline pH due to presence of for example Ca(OH)₂ might lead to precipitation of the sparingly soluble CaSO₄, which removes sulphate,

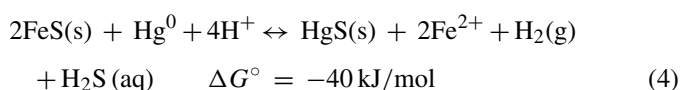
Table 1
Standard free energy changes of formation at 298 K

Species	ΔG_f° (kJ mol ⁻¹)	Reference
H ₂ O	-237	[16,17]
HgO(s)	-56	[16]
HgS(red)	-46	[18]
Fe ²⁺	-83	[17]
FeS(s)	-100	[16,17]
FeS ₂ (s)	-167	[16,17]
H ₂ S(aq)	-28	[16,19]
SO ₄ ²⁻	-744	[16,17]

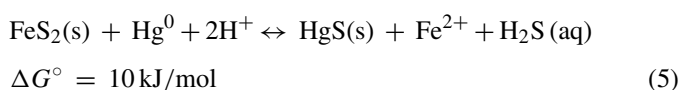
thus promoting the sulphur oxidation and the favourable anoxic conditions. Aerobic/alkaline systems would probably involve precipitation of CaCO_3 and a lower pH governed by equilibrium of the $\text{Ca-CO}_2\text{-H}^+$ system.

4.2. Reactions with iron sulphides

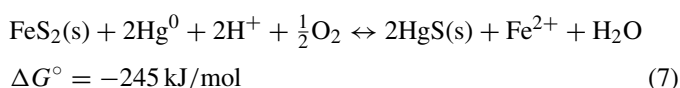
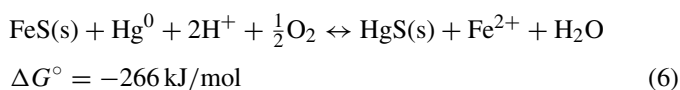
Iron sulphides were investigated in this study, as the Swedish EPA reports that pyrite and pyrrhotite would react with mercury oxide to form cinnabar. Pyrite is a potential sulphur source and electron acceptor, which is interesting to compare with the iron sulphide troilite, which has the same sulphide electron state as cinnabar. The thermodynamic calculations of the behaviour of elemental Hg mixed with solid troilite (FeS) show spontaneous formation of cinnabar, hydrogen sulphide and hydrogen gas under acidic anaerobic conditions (see reaction (4)).



Pyrite (FeS_2) appears to be a less suitable sulphur source for formation of cinnabar unless pH is far below the expected pH-range of 7–10.5 (or higher in the presence of concrete), considering the ΔG° value corresponding to $\log K = -1.76$ (5).

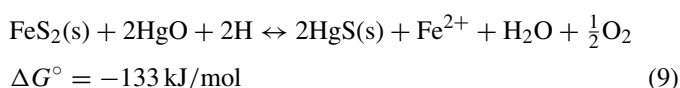
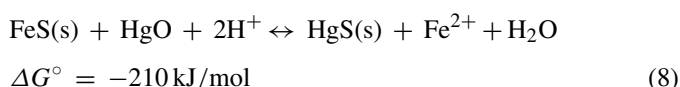


Instead, allowing initially limited aerobic conditions give spontaneous reactions that yield cinnabar from both troilite and pyrite, see reactions (6) and (7).



As shown (reactions (6) and (7)) an oxidizing agent is needed for elemental mercury to oxidize. Thermodynamic calculations on reactions with Fe(III) as oxidizing agent do not show spontaneous formation of cinnabar.

Cinnabar can also be formed from mercury oxide and either of the iron sulphides under acidic anaerobic conditions (8) and (9):



The interpretations of the calculations indicate that there is no easy and general choice of conditions for both elemental and oxidized mercury. Formation of cinnabar from mer-

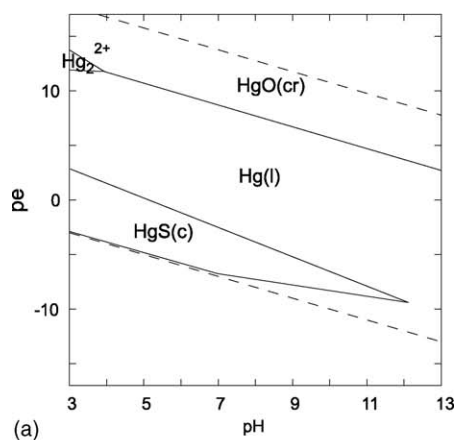
cury oxide using the iron sulphides is best carried out under acidic, anaerobic conditions and from elemental mercury under acidic, initially limited aerobic conditions. At alkaline, anaerobic conditions ($\text{pH} > 7$) H_2S (see reactions (4) and (5)) dissociates to HS^- including a higher chemical free energy change ($G^\circ = 40 \text{ kJ/mol}$). This leads to non-spontaneous reactions between elemental mercury and the iron sulphides and the reactions are impossible. Formation of cinnabar from iron sulphide consumes hydrogen ions (reactions (6)–(9)), and an alkaline environment prevents the formation of HgS since deficiency of hydrogen ions forces the reactions towards the left.

4.3. Effects of redox conditions and pH

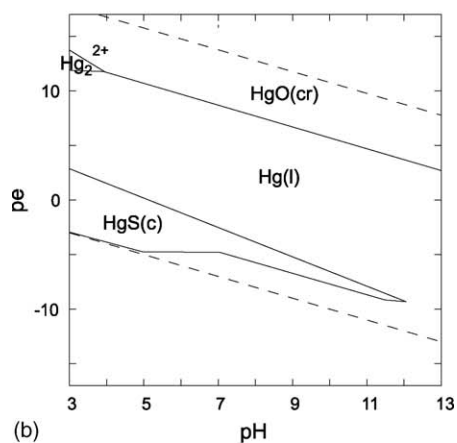
Predictions of the redox and pH dependent behaviour of mercury in water were made with the MEDUSA software, using its original database. MEDUSA [10], is a graphical interface to the chemical speciation codes PREDOM and PREDOM2. The latter (which was used here) is based on the SOLGASWATER algorithm [11]. The pe–pH diagrams in Fig. 1 represent equilibria of cinnabar, starting with mercury and sulphur, troilite or pyrite at a mole ratio $\text{S/Hg} = 1$. As visualized, an aqueous system containing mercury and sulphur develops a larger stability region of cinnabar over a wider pH scale (Fig. 1a) compared with aqueous system containing mercury and troilite (Fig. 1b) or mercury and pyrite (Fig. 1c). The cinnabar stability region of the pyrite-system has a limited extent but the region broadens along the redox axis at pH below 6.5. A similar broadening is also found in the troilite-system, and the two iron sulphides would be feasible for generation of cinnabar under acidic conditions and low redox potential. Increasing the amount of sulphur 10-times results only in a limited increase on the cinnabar stability region at high pH. As a consequence the stability region of ionic mercury is replaced by mercury sulphate and the region is slightly increased. Adding chloride ($\text{Hg:Cl} = 1:100$) to the systems leads to formation of mercury chloride complexes (HgCl_2 , Hg_2Cl_2) in the aerobic region of the diagrams but have no major impact on the stability regions of cinnabar (Fig. 2).

4.4. Excess of sulphur

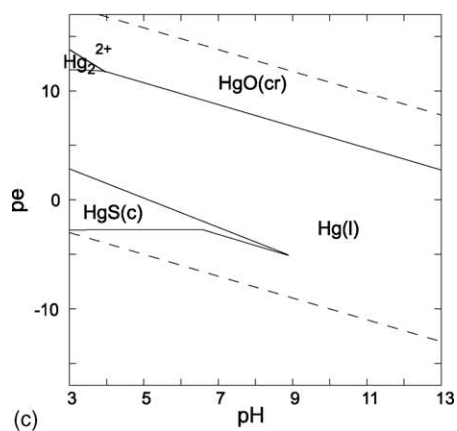
An excess of sulphur in alkaline systems could lead to a formation of the soluble mercury polysulphides, especially the disulphide (HgS_2^{2-}) [6,12]. The impact of this species under different solution compositions was investigated by modelling of the systems with the PHREEQC software [13], using the MINTeq database. Other mercury polysulphides than the disulphide are negligible. The dominant equilibrium compositions of the mercury and sulphur species in solution under anaerobic conditions as a function of the ratio S/Hg are given in Fig. 3 (please note the logarithmic scale). Initial species are elemental sulphur and mercury and chloride is omitted as mercury chloride complexes are formed under aerobic conditions (Fig. 2). A five-time excess of sulphur does not affect the precipitation of cinnabar (Fig. 3), and all elemental mercury is oxidized already at 1:1 ratio. A consequence is that the pH decreases from 7.0 to 3.6 at ratio $\text{S/Hg} = 1.5$. To achieve alkaline conditions the



(a)



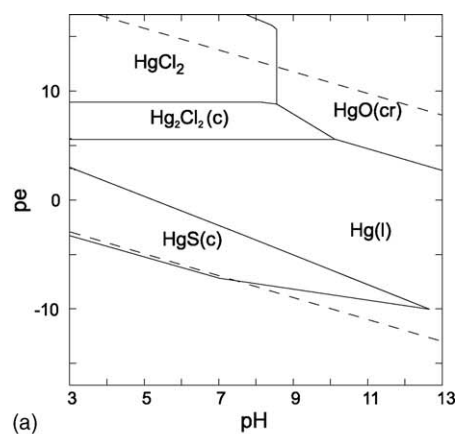
(b)



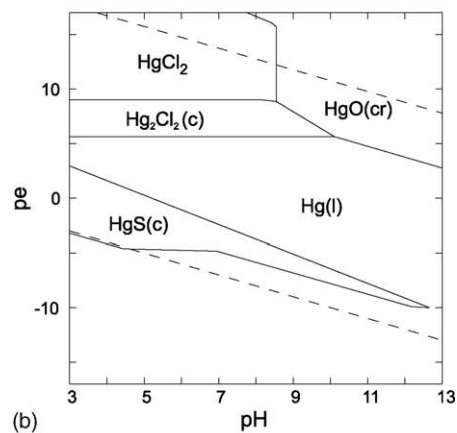
(c)

Fig. 1. *pe*-pH diagrams at 25 °C, Hg:S=1:1: (a) Hg+S; (b) Hg+FeS; (c) Hg+FeS₂.

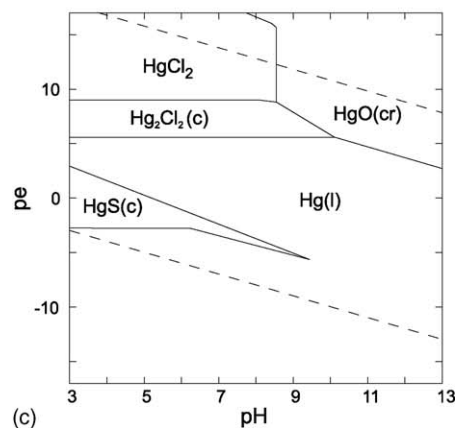
concentration was re-calculated with an addition of 3 mol of calcite (Fig. 3b). Comparing Fig. 3a and b, the addition of calcite increased pH from 3.6 to 6.4 while HgS₂²⁻ increased from 10⁻¹⁷ M to 10⁻¹⁰ M at a ratio S/Hg above 1.5. Apparently the pH of the solution influences the concentration of HgS₂²⁻ more than the sulphur excess. The dominant equilibrium compositions of two alkaline solutions with fixed pH (9.0 and 10.9, within the stability region of cinnabar) were calculated and are illustrated in Fig. 3c and d. The result shows that the concentration of HgS₂²⁻ increases drastically at the ratio S/Hg > 1 and reaches



(a)



(b)



(c)

Fig. 2. *pe*-pH diagrams at 25 °C, Hg:S:Cl=1:3:100: (a) Hg+S+Cl; (b) Hg+FeS+Cl; (c) Hg+FeS₂+Cl.

levels between 10⁻⁶ M and 10⁻⁵ M. Sulphur disproportionates into S(-II) and S(VI), which precipitates as gypsum Ca(SO₄). All oxidized mercury exists as disulphides and not as hydroxides. The results also show that the concentration of aqueous Hg(0) at ratio S/Hg > 1.5 is increased at higher pH (compare Hg(aq) in Fig. 3c and d) and reaches levels around 10⁻⁹ M at pH 10.9.

5. Experimental results

Thermodynamic calculations do not consider kinetics. Furthermore the lack of homogeneity is not considered. Hence,

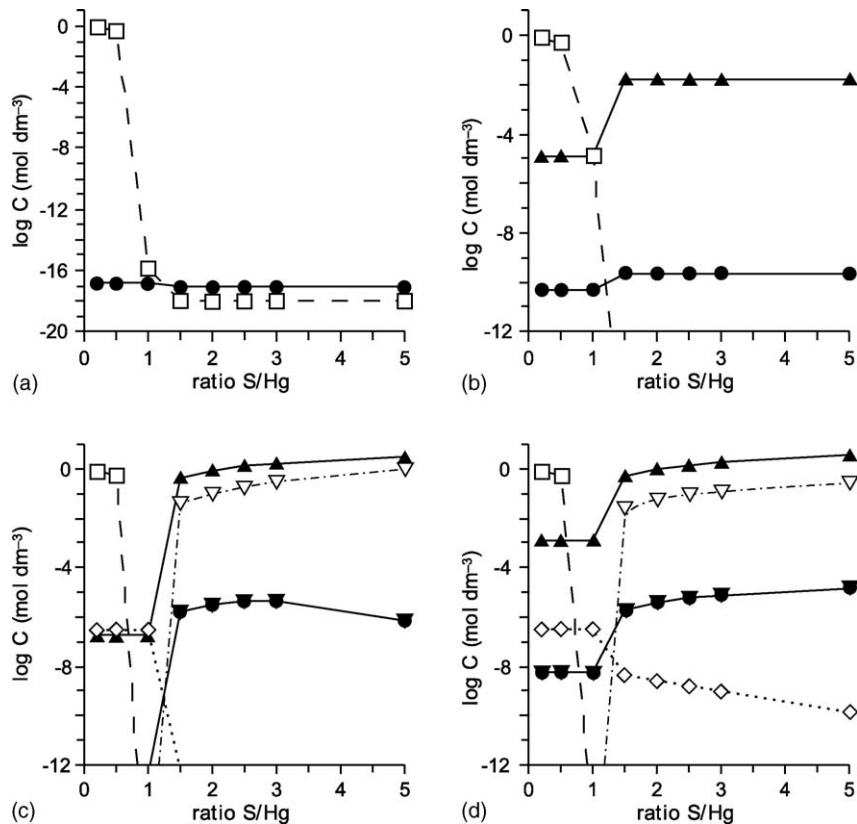


Fig. 3. Reaction products of Hg + S at equilibrium vs. the S:Hg ratio under anaerobic conditions at 25 °C: (a) Hg + S, decrease of pH from 7.0 to 3.6 when S:Hg is 1.5 or above; (b) Hg + S + CaCO₃, Hg:Ca = 1:3, decrease of pH from 9.9 to 6.4 when S:Hg is 1.5 or above; (c) Hg + S + Ca(OH)₂, pH kept constant at pH 9.0; (d) Hg + S + Ca(OH)₂, pH kept constant at pH 10.9. Symbols: (□) Hg(metal); (●) HgS₂²⁻; (▲) S(-II); (▽) CaSO₄; (▼) Hg(+II); (◇) Hg(aq).

long-term experiments on concentrated solid samples have been conducted in the laboratory for up to 3 years. Elemental mercury and yellow mercury(II) oxide were mixed with elemental sulphur or iron sulphide (natural pyrite crystals, FeS₂ and troilite, FeS) under various conditions (dry and wet; neutral/acidic and alkaline pH; aerobic and anaerobic), see Table 2. The parameters in Table 2 gave 36 combinations. The ingredients of each sample corresponded to a S/Hg mole ratio of 1.5.

Deionized water was used to wetting the samples, and Ca(OH)₂ was added to generate the high pH-conditions and to simulate the pH-buffering effect of concrete. A small amount of water was added to saturate the solid material. With time the pore water was equilibrated with the solid material. Measurement of pH was made after 37 months (on the pore water of the wet samples) by a flat membrane combined pH glass

electrode [14]. The anaerobic vials were cautiously filled with nitrogen gas before they were sealed by melting, whereas the vials for the aerobic tests were only loosely sealed with a screw cap.

The reaction rate was slow at room temperature. Minor amounts of HgS were formed in the dry sulphur—elemental mercury samples, but not indicated in the other dry samples. After 1 year (mercury oxide and sulphur) and 2 years (elemental mercury and sulphur), the result yielded close to 100% cinnabar under alkaline conditions.

Analyses with X-ray powder diffractometry after one (two for elemental mercury and sulphur) and 3 years gave similar results for the sum of red cinnabar and black meta-cinnabar. Possibly there was a slight difference in the distribution between the two forms, with a higher fraction of red cinnabar after 3 years. The SEM-picture in Fig. 4a, combined with EDAX and XRD, shows generated cinnabar from elemental mercury and sulphur.

In systems with troilite and mercury oxide some 50%_{w/w} of the mercury was transformed into cinnabar after 1 year under acidic aerobic conditions. Under acidic anaerobic conditions the yield was 10%_{w/w}. Analyses performed after one and 3 years gave the same results. Under acidic, anaerobic conditions pyrite grains mixed with mercury oxide or elemental mercury remain intact without detectable reaction after 3 years. Samples with the same content but under acidic aerobic conditions show reduction of mercury oxide to the elemental form. Experimental results

Table 2
Components and conditions of the samples in the laboratory experiment [14]

Components/conditions	Alternatives
Sulphur source	(1) Sulphur, S; (2) synthetic troilite, FeS; (3) natural pyrite crystals, FeS ₂
Mercury source	(1) Powdered yellow HgO; (2) elemental mercury
Condition	(1) Dry; (2) wet and neutral/acidic; (3) wet and alkaline, Ca(OH) ₂
Atmosphere	(1) Aerobic; (2) anaerobic

Combinations: 3 sulphur sources × 2 mercury sources × 3 conditions × 2 atmospheres gave 36 different samples; exposure times: up to 37 months.

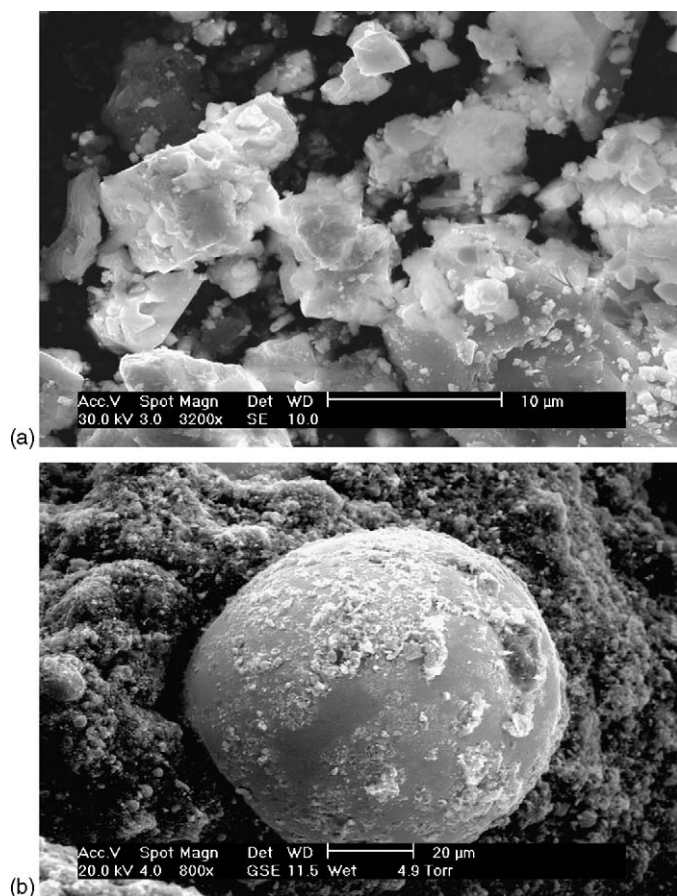


Fig. 4. SEM-pictures: (a) $\text{Hg}^0 + \text{S}$, anaerobic and alkaline conditions; generation of red HgS . (b) $\text{HgO} + \text{FeS}_2$, anaerobic and alkaline conditions; generation of elemental Hg .

indicate that both iron phases act as reducing agents for mercury oxide, in aerobic as well as anaerobic systems. From the SEM-picture in Fig. 4b it is obvious that mercury had partially been reduced to its elemental state in some samples initially containing HgO . Results from the experimental studies are discussed in detail elsewhere [14].

6. Discussion and conclusions

6.1. Thermodynamic calculations

Considering the conditions of the proposed concept of a future mercury repository, dry and aerobic at an initial stage and eventually water-saturated and anaerobic, both sulphur and iron-sulphide seem to be suitable for the formation of cinnabar from Hg(II) as well as Hg(0) . The thermodynamic considerations indicate that elemental sulphur is feasible to use as a sulphur source under alkaline, anaerobic conditions while the iron sulphides work well under acidic, anaerobic conditions for mercury oxide. Elemental mercury needs an initial oxidation stage, which is given under acidic, initially limited aerobic conditions. Considering the different oxidation states of sulphur in the iron sulphides, a comparison between the outcomes of the calculations indicate that troilite is more favourable, since the

stability region is larger. The surrounding pH and considering the formation of undesired side-products, such as elemental Hg and mercury complexes (i.e. HgS_2^{2-} , HgCl_2), govern the choice of sulphur source. Low pH is not recommended in the storage, since there is a risk for production of hydrogen gas in reaction with many metals under acidic, anaerobic conditions. Production of toxic hydrogen sulphide gas is also possible under acidic, anaerobic conditions. The hydrogen sulphide gas is however not decisive for choice of system conditions since it is soluble and converted to the non-volatile HS^- under alkaline conditions. Thus, neutral to alkaline anaerobic conditions are favourable for the permanent storage of cinnabar, which is in accordance with the expected conditions in a deep repository after long time (pH of 7.2–8.5 in deep granitic bedrock, buffered by the Ca-HCO_3 -system). Consequently, elemental sulphur is recommended as the most favourable sulphur source for generation of cinnabar.

Presence of chloride in an aquatic anaerobic environment does not seem to influence the formation of cinnabar (Fig. 2). It may, however, be difficult to reach the right pH interval for precipitation of cinnabar, and a buffer medium such as calcite or concrete would be helpful. A system in equilibrium with calcite has a pH of 8–10, depending on the hydrogen carbonate concentration. Concrete with ordinary Portland cement has an initial pH around 13. It is feasible to decrease the pH in concrete by mixing Portland cement and for example blast furnace slag. A mixture of 1:1 (Portland cement:blast furnace slag) would yield a pH of 12.

The modelling in Fig. 3 indicates that formation of cinnabar is feasible when raising the pH with calcite or portlandite. The concentration of the soluble mercury disulphide (HgS_2^{2-}) is low under acid to neutral conditions and at an excess of sulphur but increases drastically under alkaline conditions. The concentration of HgS_2^{2-} are below the Swedish criterion for drinkingwater (5 nmol/dm^3 [15]) as long as the S/Hg mole ratio is within 1–1.3 and pH below 10.5–11 under anaerobic conditions. At pH 11 the concentration of aqueous Hg(0) is higher than 5 nmol/dm^3 , and the concentration of total Hg seems to be reasonably low when buffering with calcite to pH 8–10 but too high when raising the pH to 11 with portlandite. Thus, calcite as buffering medium would be more suitable than ordinary concrete.

6.2. Experimental

Laboratory experiments gave successful results with almost quantitatively (100%) formation of cinnabar with portlandite in solid samples initially containing mercury and elemental sulphur. To be within the stability region of cinnabar it is important to prepare the optimal amount of portlandite (which control pH) to the mixture. Under acidic, anaerobic conditions pyrite grains mixed with mercury oxide or elemental mercury remain intact without detectable reaction after 3 years, though the reactions are thermodynamically favourable. An explanation could be that the grains were not small enough which might have prolonged the time of reaction. Samples with the same content but under aerobic conditions show reaction with reduction of mercury oxide to the elemental form. Experimental results indicate that the two

selected iron sulphides act as reducing agents for mercury oxide under many conditions leading to a minor formation of cinnabar. Iron(II) is easily oxidized, and the risk for reduction of divalent mercury to the elemental form is obvious. This may however be a temporary stage and further reaction may lead to formation of cinnabar from the elemental mercury.

6.3. Effects of other conditions

The waste in the repository will contain a minimum of 0.1% mercury, and the bulk has presumably effects on the chemical conditions. Influences from the bulk, for example Mn(II), organic substances, sulphate, etc. have not been considered in this study. Organic substances and sulphate are omitted in the modelling, since the expected levels are low in a deep repository. The influence from aqueous Fe(II) on the stability of cinnabar has not been investigated.

6.4. Choice of repository conditions

Most favourable conditions for a mercury waste repository with respect to the formation of HgS, would be:

- Anaerobic: like the expected conditions at equilibrium in a deep repository after long time, $p_e = 5 - \text{pH}$.
- Alkaline: pH of 7.5–10.5.
- Chloride in an aquatic anaerobic environment does not seem to influence the formation of cinnabar.
- Elemental sulphur is recommended as the most favourable sulphur source.

Acknowledgements

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