ICRS-11
11th International Conference on Radiation Shielding
&
RPSD-2008
15th Topical Meeting of the Radiation Protection & Shielding Division of ANS
FINDING YOUR WAY THROUGH THE SHIELDING MAZE!
• APRIL 13-18, 2008 • CALLAWAY GARDENS, PINE MOUNTAIN, GEORGIA, USA •

Decommissioning and safety issues of liquid-mercury waste generated from high power spallation sources with particle accelerators

S. Chiriki, J. Fachinger, H. K. Hinssen, R. Moormann, A. Bukaemskiy, R. Odoj

Forschungszentrum Juelich GmbH, IEF-6, D-52425 Juelich, Germany,

Email: s.chiriki@fz-juelich.de

Corresponding author:

Mr. Suresh Chiriki

Phone: 0049 2461 61 3215

Fax : 0049 2461 61 3133

	total number
pages	24
tables	2
figures	6

(Table caption on page 15, Table I on Page 16 and Table II on 17)

(Figure captions on 18, figure 1 to figure 6 (page 18, 19, 20, 21, 22, 23, and 24))

Abstract

Large spallation sources are intended to be constructed in Europe (EURISOL nuclear physics facility and ESS-European Spallation Source). These facilities accumulate more than 20 metric tons of irradiated mercury in the target, which has to be treated as highly radioactive and chemo-toxic waste. Because solids are the only appropriate (immobile) form for this radiotoxic and toxic type of waste solidification is required for irradiated mercury. Our irradiation experimental studies on mercury waste revealed that mercury sulfide is a reasonable solid for disposal and shows larger stability in assumed accidents with water ingress in a repository compared to amalgams. For preparation of mercury sulfide a wet process is more suitable than a dry one. It is easier to perform under hot cell conditions and allows complete Hg-conversion. Embedding HgS in a cementitious matrix increases its stability.

I. Introduction

Worldwide demand for neutron-based research is increasing. High power spallation targets (1 - 5 MW) are used in advanced research facilities and projects as SNS, EURISOL, ESS or JSNS, where a high energetic proton beam generates neutrons by spallation of mercury (2 m^3 or about 25 metric tons). About 2 10^6 GBq/MW (10 y after end of 40 y irradiation) of radionuclides ranging from atomic number Z = 1 to Z = 81 are present in the liquid mercury[1, 2]. Hg-194 ($t_{1/2}$ = 512 y) is an important nuclide because of is short lived daughter nuclide Au-194, emitting high energetic γ-radiation. Hg-194 cannot be separated from target mercury. For that the irradiated mercury has to be considered as high-level radioactive waste and must be treated and disposed in a safe way. Besides of the radiotoxic impact of mercury its pronounced conventional or bio-toxicity has to be taken into account. Disposal of irradiated mercury in liquid form is not permissible[3]. Different types of treatments are possible to transform the mercury to a solid form. The objective of the present study is to find suitable solid mercury compounds and mercury unit operations for solidification.

II. Selection of a solid mercury compound suitable for disposal

The biotoxicity of conventional mercury waste resulted in major effort to control its disposal. Solidification and stabilization technologies are used to immobilize mercury. On basis of that experience and on data of solubility, chemical thermodynamics, mercury reactions with nonmetals (e.g. sulfur, chlorine and selenium) and metals (Ag, Cu) a few solid compounds of mercury were selected here for more detailed examinations. Because of its noble character mercury does not form high temperature stable compounds[4]. Hg-sulfide, -selenide, -(I)-chloride, -sulfate and amalgams with noble metals show a small solubility in water and are stable in aqueous environments. The alloys of mercury (amalgams) are mostly solid or semi-solid at room temperature. Hg(I)chloride and $HgSO_4$ were however not considered in detail because their solubilities are larger compared to the other compounds. Stability in aqueous environments also in presence of γ -irradiation is another important selection criterion, having accidents with water ingress into the repository in mind. γ -irradiation may enhance dissolution by radiolytic reactions, forming high reactive species in the aqueous solution.

II.A. Experiments

Irradiation experiments are conducted on solid mercury compounds also embedded in a cement matrix form to find out their dissolution behavior. These experiments are conducted under argon atmosphere to simulate anaerobic conditions of a European final repository. The temperature is chosen to 50 - 60°C, representing the conservative case of large heat generation by waste in a mixed repository. The aqueous solutions selected for leaching experiments are deionised water (DI), opalinus clay water and two salt brines, typical for European repositories (see TABLE I). Red mercury sulfide, mercury selenide (Aldrich) and amalgams prepared in our laboratory were used in these irradiation experiments. Copper amalgam, prepared at room temperature by long term mixing of copper powder and mercury under acidic reaction conditions, were ignored in these examinations because mercury movement onto the amalgam surface was observed, which indicates an incomplete reaction.

Besides experiments on pure compounds some leaching experiments on mercury compounds embedded in cementitious and concrete matrices are performed. In order to quantify the retention behavior of a cement matrix, a soluble mercury compound ($Hg(I)NO_3$) was embedded in a cement specimen, too. The cement type used is an ordinary Portland cement (CEM I 52. 5 R) manufactured by a German Portland cement distributor. A water to cement ratio of 0.4 - 0.45 was employed in using freshly distilled water. The ingredients of each sample corresponded to cement /Hg weight ratio of 10. The experimental procedure was as follows: The specimens (in quantities of some grams) were transferred to 30 ml glass ampoules containing 10 ml of leaching solution, sealed and mixed thoroughly. The glass ampoules for anaerobic tests were filled with argon gas before they were sealed by melting, whereas the glass ampoules for aerobic tests contained air. The hydration products of these samples were characterized after curing of 28 days. After that the ampoules were irradiated for 3 months period in the storage tank of spent fuel elements in the FRJ-2 (DIDO) reactor under γ-irradiation. Fig. 1 compares the measured dose rate in these experiments and dose rates calculated for an activity of $1.4\ 10^5$ GBq of Hg-194, which is expected in a 5 MW target. Two different geometries for a Hg-194 waste package are assumed. It becomes obvious that experimental dose rates are sufficiently high. After irradiation the solutions are analyzed by cold vapor atomic absorption spectrometry for determination of the mercury concentrations in the aqueous phase.

II.B Results on specimen without cementitious matrix

The first results series on leaching of mercury sulfide and silver amalgam in argon atmosphere under γ-irradiation are shown in Fig. 2. The release of mercury from silver amalgam is more pronounced than for red mercury sulfide (cinnabar) by about one order of magnitude except for deionised water. This is in coincidence with literature data showing that amalgams are not stable in a chloride environment. For red mercury sulfide (cinnabar), a more complex behavior has to be assumed. It is known that mercury sulfide, which is almost insoluble in pure water, may undergo some dissolution under strongly oxidizing conditions, as is possible in water radiolysis by formation of oxygen species and in case of brines and clay water additionally of chlorine species. Fig. 2 indicates that the dissolution of mercury from HgS in opalinus clay water is only about 5 - 10 µg/l, but an order of magnitude larger in brine 2. For comparison we have to consider that the solubility of elemental mercury in water at room temperature is about 50 µg/l. The strong influence of γ-irradiation on dissolution rates of HgS becomes obvious by comparison of the blind (unirradiated) specimen in brine 2 with irradiated ones: HgS-specimen without irradiation reveal dissolution rates by more than an order of magnitude smaller than irradiated ones. For Ag-amalgam this difference is much smaller. The dissolution of HgS comes probably from oxidation reactions forming soluble mercury sulfate (Hg_2SO_4) or reduction reactions forming polysulfide compounds (HgS_2^{2-}), but chlorine may play some role too. The altogether small amount of mercury dissolved from HgS in salt brines and clay water shows the strong stability of HgS and its suitability as solid compound for disposal. Literature data[5,6] indicate that the mobility of mercury in aquatic environments without radiation varies with pH and redox conditions: Oxidizing environments result in medium Hg mobility, reducing environments however in very low mobility up to immobile. Acidic environments generate a high mobility, but in neutral to alkaline environments a very low mobility up to immobility was observed. We carried out therefore experiments under oxidizing (aerobic), anaerobic/neutral and anaerobic/acidic conditions for the most promising compounds HgS (Fig. 3a) and HgSe (Fig. 3b). Oxidizing conditions were examined by introducing an oxidizing agent (ferric chloride) in addition to air (aerobic conditions): These experiments revealed that the mercury mobility increased in oxidizing environments. Fe(III)chloride is reduced by Hg to Fe(II)chloride and an equivalent amount of HgCl is formed. Also, a low pH value increases the solubility. Comparing the dissolution behavior of HgS and of HgSe in these experiments, HgSe is found to be even slightly more stable than HgS, although altogether similar dissolution behavior was detected. Also results on HgSe underlined the increased dissolution rate in presence of Cl-.

The main conclusion drawn from these results is that the stability of amalgams during accidents in a repository is less than that of chalcogenides. Further, formation of amalgams from elements without un-reacted mercury creates chemical engineering problems under hot cell conditions. Ag-amalgam as most easy to produce amalgam creates major costs because of the high Ag content. Despite of its still better dissolution behavior mercury selenide (HgSe) was not considered for detailed studies: High costs and biotoxicity of selenium (Se) are major disadvantages and HgS was chosen as solid compound for final disposal. For that we concentrate our further studies on HgS.

II.C Results on specimen embedded in a cement matrix

In Fig. 4 the dissolution behavior of mercury compounds (HgS, Hg(I)nitrate) from cement matrices is shown. As additional parameter the influence of the Hg/cement ratio on dissolution behaviour is studied for HgS. A photo of diverse Hg/cement matrix specimens is presented in Fig. 5. Due to large density differences of mercury compounds and of cement a homogeneous Hg distribution in cement was difficult to achieve: Here further improvements are required. As expected the retention of soluble $HgNO_3$ is relatively small compared to HgS. As in alkaline environments and chloride environments, HgS is sufficiently stable. Perhaps, pore size distribution and cement degradation have some influence on mercury dissolution from cement [7].

III. Chemical engineering studies on mercury solidification

There are two ways of HgS formation from Hg: The dry process from elements and wet processes via dissolution of Hg in oxidizing acids and subsequent precipitation of HgS. The dry process[8,9] was examined in several laboratory studies by stirring sulfur and mercury in various portions e.g. at 200°C and at 40°C. The formation mechanism is not fully understood, but empirical results indicate that mercury sulfide under alkaline conditions has a maximum formation yield. Presence of HgO in addition to elemental mercury also increases the formation yield. Sulfur may disproportionate into S (-II) and S (+VI) under anaerobic conditions[10], which leads to more efficient sulfide penetration whereas aerobic conditions lead to increased oxidation and content of sulfate. A problem of the dry process is an incomplete Hg-conversion.

The wet process precipitates meta-cinnabar from solutions of Hg^+ and Hg^{2+} ($HgNO_3$ or $HgCl_2$) by treatment with gaseous H_2S or with sulfide solutions at low temperatures followed by a filtration step. A reaction scheme is given in fig. 6. The wet process precipitates meta-cinnabar from solutions of Hg^+ and Hg^{2+} ($HgNO_3$ or $HgCl_2$) by treatment with gaseous H_2S or with sulfide solutions at low temperatures followed by a filtration step. A reaction scheme is given in fig. 6. A few experiments were already done on the wet process dissolving Hg by HNO_3 and precipitating HgS by $(NH_4)_2S$, indicating an almost complete Hg conversion. The analyses of HgS formed are presented in TABLE II for different Sulfide/Hg ratios. Whereas for a mole ratio S/Hg of 2 in the solution the product is almost stoichometric HgS with a slight Sulfur excess, a ratio of 4 leads to a more pronounced excess of sulfur in the precipitate. The concentration of Hg in the filtrate was negligible. Both processes are under investigation particularly concerning the question whether they can be easily handled in hot cells. The wet process seems to be more suitable for solidification of irradiated mercury, also because a complete mercury conversion to a solid phase is easier to achieve, because reaction times are far smaller and because required chemical engineering unit operations are more adequate to hot cell conditions.

IV. Outlook

Planned future work deals with other matrix materials to be used for Hg disposal. Only matrix materials hardening at low temperatures are suitable for Hg compounds. Polysiloxane based matrices will be studied in order to achieve an additional improvement of Hg retention in repositories. Further, the chemical engineering studies on formation of HgS by the wet process will be continued. Additional laboratory scale experiments will be performance studies.

Acknowledgements:

This work is supported by the European Community under the FP6 “Research Infrastructure Action-Structuring the European Research Area” Project EURISOL DS under Contract No. 515768 RIDS.

REFERENCES

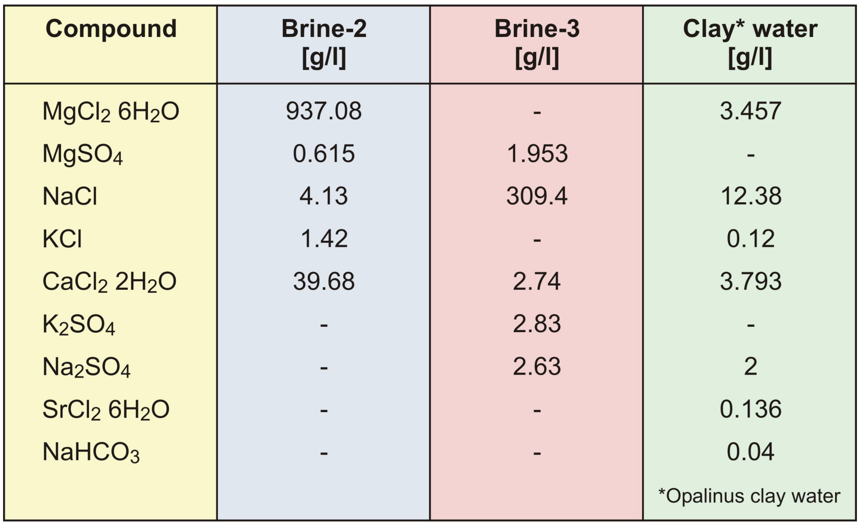
1. RAPP. B, DAVID. J. C, BLIDEANU. V, DORE. D, RADIKAS. D and TIOLLIER. N, “Activation calculation of the EURISOL mercury target,’’ EURISOL DS-Task5-TN-06-09 (2006).
2. BONGARDT. K, LENSING. B, MOORMANN. R and SCHAAL. H, “Nuclide inventories in Hg-targets,’’. EURISOL DS-Task5-TN-06-03 (2006).

3. R. MOORMANN, “Safety and Licensing of the European spallation Sources (ESS),” Jül-Report No. 4136, Forschungszentrum Juelich, Juelich, Germany (2004).
4. B. EICHLER and R. DRESSLER, “Löslichkeit von Kernreaktionsprodukten im Quecksilber-Spallations-target – Bedeutung für das Betriebsverhalten und Möglichkeiten der Kalkulation”, PSI-Report No. 99-02, Paul Scherrer Institut, Villigen , Switzerland (1999).
5. J. A. TOSSELL, “Theoretical studies on the formation of mercury complexes in solution and the dissolution and reactions of cinnabar,’’ *American Mineralogist*, **84**, 877 (1999).
6. K. PAQUETTE and G HEIZ, “Solubility of cinnabar (red HgS) and implications for mercury speciation in sulfidic waters,’’ *Water, Air, and Soil Pollution*, **80**, 1053 (1995).
7. C. PERLOT, J. VERDIER and M. CARCASSES, “Influence of cement type on transport properties and chemical degradation: Application to nuclear waste storage,” *Materials and Structures*, **39**, 511 (2006).
8. L. N. OJI, “Mercury disposal via sulfur reactions,’’ *J. Environ Engg*, **124**, 945 (1998).
9. M. FUHRMANN, D. MELAMED, P. D. KALB, J. W. ADAMS, L: W. MILIAN, “Sulfur Polymer Solidification/Stabilization of elemental mercury waste,’’ *Waste Management (Oxford, United Kingdom)*, **22**, 327 (2002).
10. M. SVENSSON, A. DUEKER, and B. ALLARD, “Formation of cinnabar - estimation of favorable conditions in a proposed Swedish repository,” *Journal of Hazardous Materials,* 136, 830, (2006).

Table captions

TABLE I. Composition of brines used for leaching experiments (* Opalinus clay water)

TABLE II. Results of experiments on formation of HgS by the wet process



Compound	Brine-2 [g/l]	Brine-3 [g/l]	Clay* water [g/l]
$MgCl_2$ $6H_2O$	937.08	-	3.457
$MgSO_4$	0.615	1.953	-
NaCl	4.13	309.4	12.38
KCl	1.42	-	0.12
$CaCl_2$ $2H_2O$	39.68	2.74	3.793
K_2SO_4	-	2.83	-
Na_2SO_4	-	2.63	2
$SrCl_2$ $6H_2O$	-	-	0.136
$NaHCO_3$	-	-	0.04
			*Opalinus clay water

S.Chiriki et. al., Table I

	mole ratio Hg:$(NH_4)_2S$ 1:2	1:4
Hg (mol %) in precipitate	49.1	37.1
S (mol %) in precipitate	50.9	62.9
Amount of Hg in filtrate (μg/l)	0.068	0.092

S. Chiriki et. al., Table II

Figure captions

Figure 1. Comparison of dose rates measured during irradiation experiments and those calculated for a representative source of Hg-194.

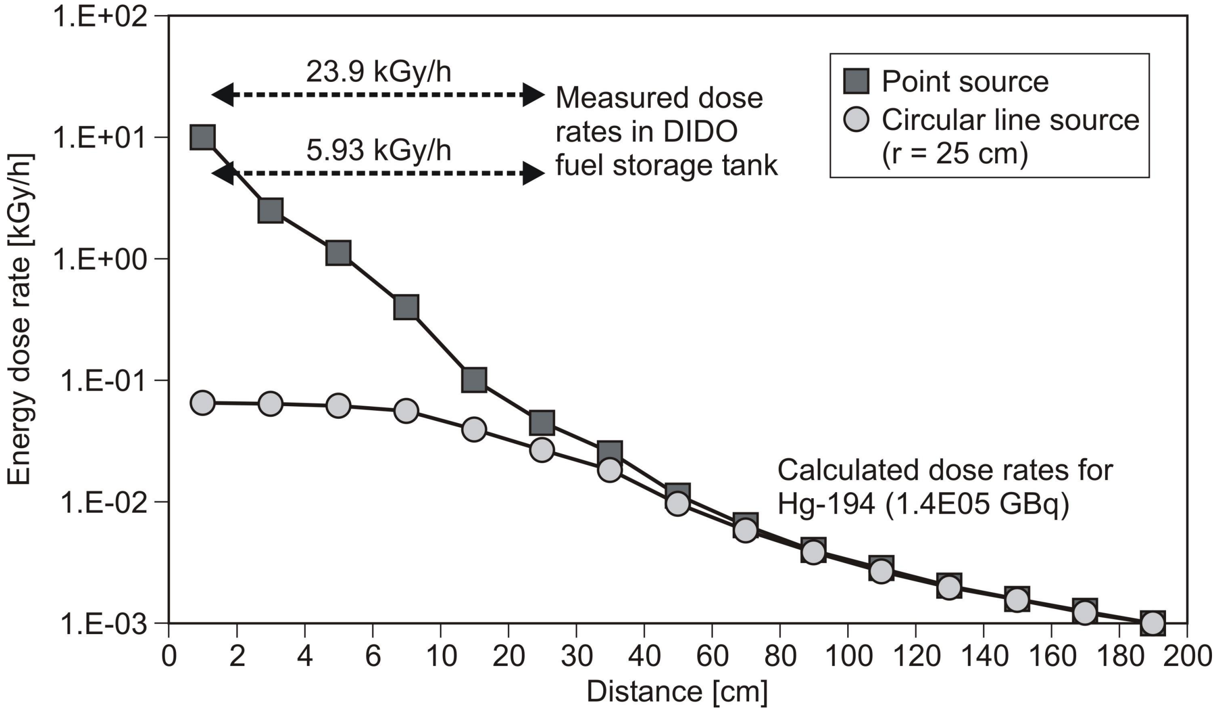
Figure 2. Mercury concentration in solution after 2 months treatment of HgS and Ag-amalgam under irradiation in diverse aqueous environments.

Figure 3. Dissolution behavior of HgS (a) and HgSe (b) under irradiation in different aqueous solutions and different redox conditions.

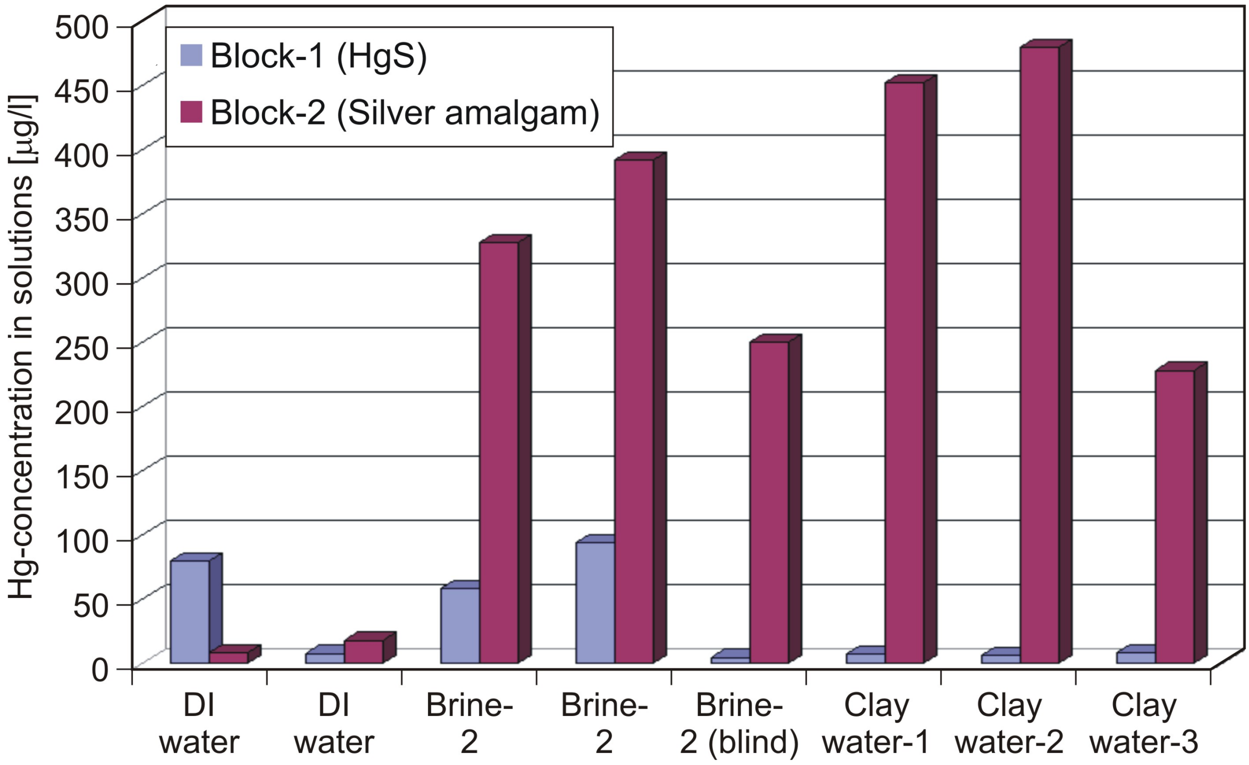
Figure 4. Dissolution behaviour of mercury compounds embedded in a concrete matrix under γ-irradiation.

Figure 5. Concrete specimen containing mercury compounds

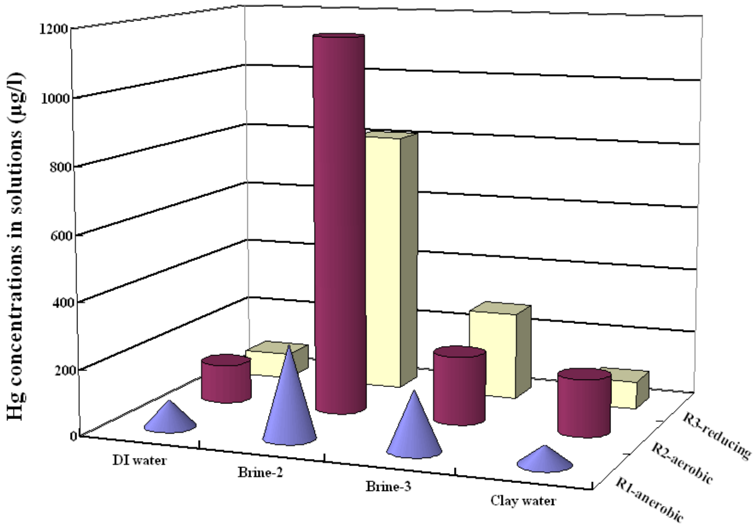
Figure 6. Schematics of a wet process for mercury solidification.



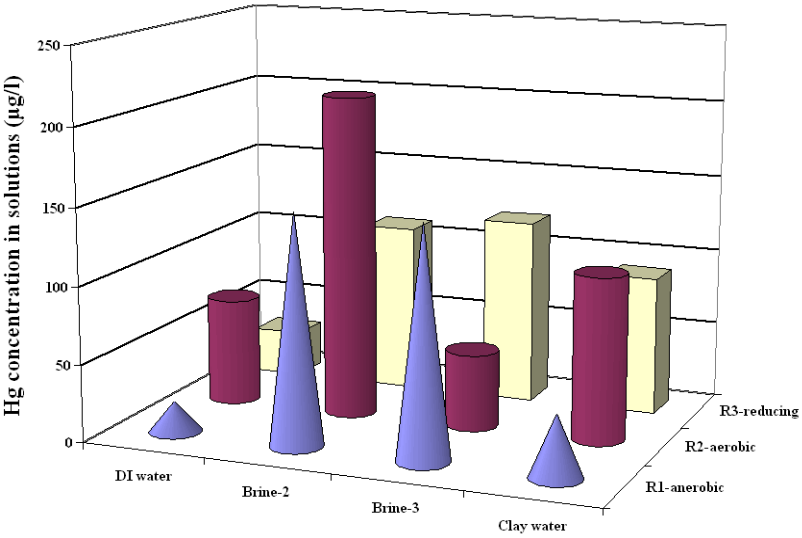
S. Chiriki et al., Figure 1



S. Chiriki et al., Figure 2

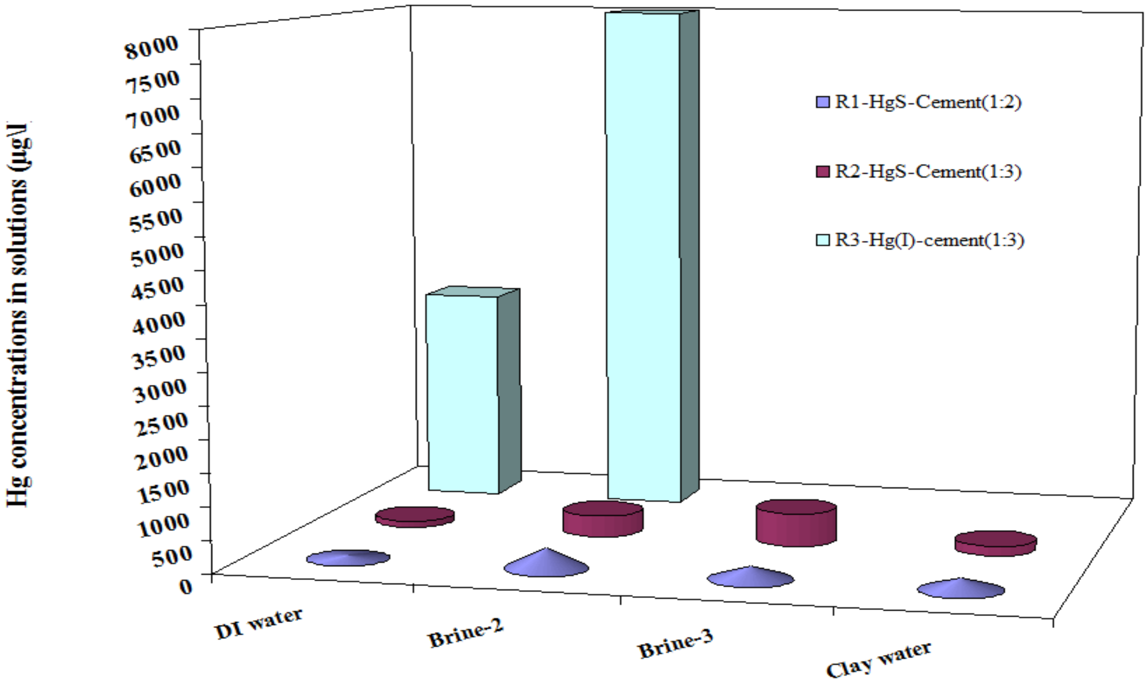

Hg concentrations in solutions (µg/l)
1200
1000
800
600
400
200
0
DI water
Brine-2
Brine-3
Clay water
R3-reducing
R2-aerobic
R1-anerobic

(a)

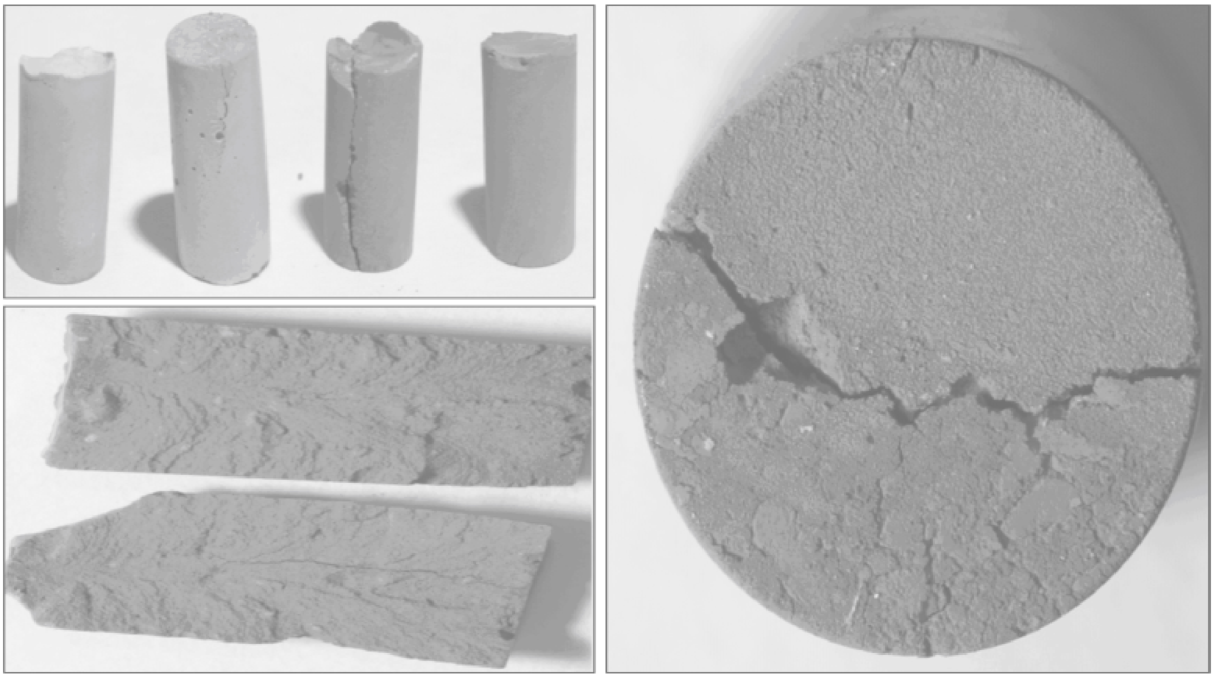


(b)

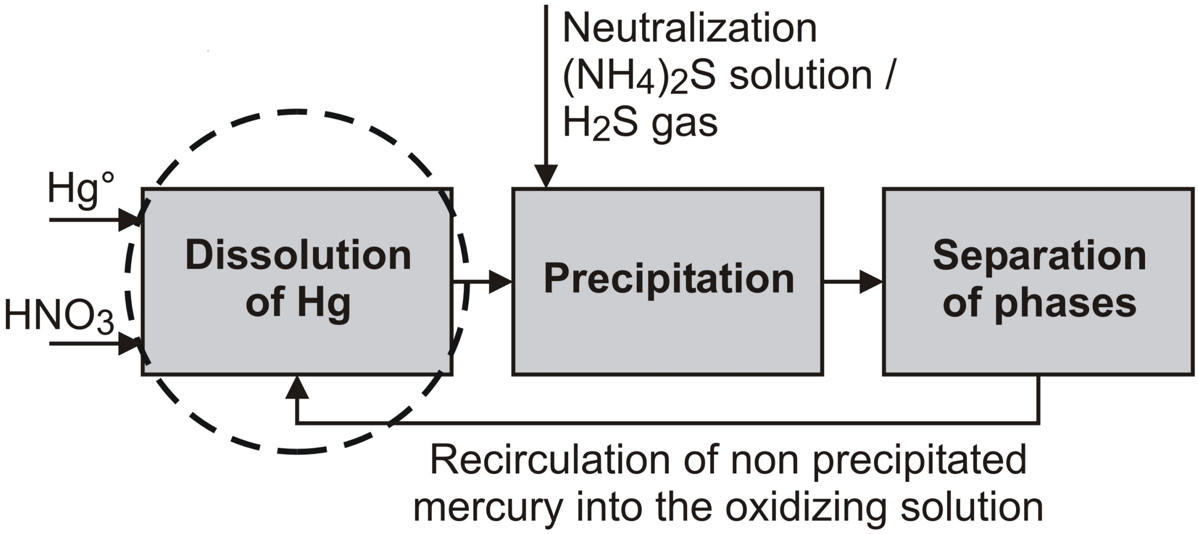
S. Chiriki et al., Figure 3



S. Chiriki et al., Figure 4



S.Chiriki et al., Figure 5



S.Chiriki et al., Figure 6