M E R S A D E

MERCURY   SAFETY   DEPOSIT

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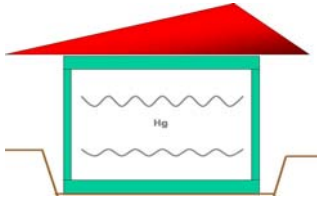## <MERSADE>

Task 1
State of Art

T1.3 y T1.4
Literature review concerning corrosion problems in mercury and stabilisation of liquid Hg

Status Report

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TASK 1. State of the art

Subtask. 1.3. Literature review concerning to mercury corrosion

Introduction

Concerns about corrosion of metals exposed to liquid metal environments dates from the earliest days of metals processing, when it became necessary to handle and contain molten metals. Liquid metals serve as high-temperature reducing agents in the production of meals and because their excellent heat-transfer properties, liquid metals have been used or considered as coolants in a variety of power producing system. Examples of such use are molten sodium for liquid metal fast breeder reactors and central receiver solar station as well as liquid lithium for fusion and space nuclear reactors. More recently liquid mercury has been selected as the target for the spallation neutron source (SNS).

Whenever the handling of liquid metals is required, either in specific uses as discussed previously or as melts during processing, a compatible containment material must be selected.

The forms in which liquid metal corrosion are manifested can be divided in several categories:

- Dissolution processes- in its simplest form, or through compound or complex formation with one or more impurities in the liquid metal-
- Impurity and interstitial reactions
- Alloying
- Compound reduction

If an element of the metal or alloy is soluble in the liquid metal, dissolution will occur until the liquid metal is saturated. At this point, dissolution would cease under isothermal conditions. Unfortunately, real systems almost always are submitted to temperature gradients leading not only to dissolution in the high temperature portions but also to a precipitation in colder areas. As consequence, the content of the element in the liquid metal decreases enabling additional dissolution[1].

A second mode of attack involves formation of intermetallic alloys of the solid metal with the liquid metal. If the intermetallic is poorly adherent, or if can be spalled off under mechanical or thermal stress, perforation can eventually occurs[1].

Liquid metal corrosion is also unique in the degree of selectivity with certain constituents of a metal. Liquid metals posses the ability to remove interstitials elements from depths and may, under severe conditions result in a breach of the containment.

Intergranular attack is another pernicious form of damage, penetration or dissolution by liquid metal might occurs with the additional shortcoming of no change of weight loss or appearance. Finally, liquid metal induced embrittlement (LMIE) is a phenomenon which reduces the fracture resistance of a solid material during exposure to liquid metal[2]. LMIE is not considered a corrosion problem it is worthwhile to mention it since might induce a catastrophic failure during service conditions. LMIE is not a dissolution or diffusion-controlled intergranular penetration process. It should be emphasized that gross amounts of liquid are not necessary. Besides, in most cases of LMIE, little or no penetration of liquid metal into de solid metal is observed, and also it does not depend on the time of exposure to the liquid metal before testing.
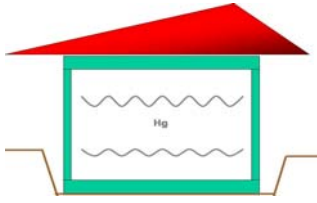
Many variables of the system may play part in the form and rate of corrosion established. There are several key factors that have major influence on the corrosion metals and alloys by liquid-metal systems or liquid-vapour metal coolants. These are:

- Composition, impurity content and stress condition of the metal an alloy
- Exposure temperature and temperature range
- Impurity content of the liquid metal
- Flow conditions: static or circulating conditions
- Heating and cooling conditions
- Liquid-metal velocity
- Exposure time
- Presence of corrosion inhibition elements
- Monometallic or multialloy system component

All these factors have varied influence, depending on the combination of the containment material and the liquid metal. For instance, in many cases the initial period of exposure (between 100-1000h) is a time of rapid corrosion that eventually reaches a much lower steady state. However, for the particular case of liquid mercury, its effects on aluminium or stainless steel or nickel-base alloys usually do not proceed automatically from the start of first exposure. This is consequence of the natural passive oxide layer on the aluminium and stainless steel that behaves as a natural barrier to liquid attack. It is only, when these films are penetrated, mechanically damaged, or chemically attacked by other species also present in the environment when liquid-metal corrosion takes place.

Therefore, compatibility of a liquid metal and its containment material varies widely[3]. In general, for a pure metal, surface attrition may proceed in an orderly, planar mode, being controlled by either dissolution or surface reaction. For a multicomponent alloy, selective loss of certain elements may lead to a phase transformation. For instance, loss of nickel in a stainless steel exposed to liquid sodium may result in the formation of a ferritic surface layer. A more dangerous situation can produce intergranular attack.

Aluminium alloys exposure to mercury lead to more complex process that can promote at least three forms of corrosion attack: **amalgamation**, a process by which aluminium and mercury form a liquid solution; **amalgamation corrosion** characterised by rapid weight loss, pitting, and intergranular corrosion and corrosion product formation in oxidising environments; and **cracking**, which involves rapid crack propagation and embrittlement at stresses substantially lower that the normal material yield strength[4]

Therefore, in order to evaluate the damage induced on a solid metal by liquid metal corrosion the three factors should be always evaluated collectively in any liquid metal system: surface damage, depth of depleted zone, and the presence of intergranular attack. This evaluation leads to an assessment of total damage, which may be presented either as a rate or as a cumulative allowance that must be made for the exposure of a given material over a given time.

Mercury corrosion

Literature exists in which relationships for numerous liquid-metal containment combinations have been established[5]. In many cases, particularly at low temperature and static conditions liquid metal corrosion is not a important factor, and many materials both metals and ceramics would suffice. This could be the reason why literature referring to corrosion problems occurred on metal containment used for the storage of liquid mercury is practically null.
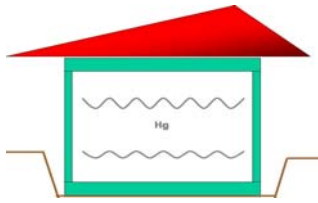
Plain carbon steel, are virtually unattacked by mercury under non flowing conditions or isothermal condition. This is the reason why it has been successfully used to contain mercury in temperatures up to 540ºC[4]. Additionally, the operating temperatures may raise up to 650 ºC by addition of 10 ppm of Ti. However, additions of other elements with a higher affinity for oxygen than titanium, such as Na or Mg, are required to prevent oxidation of the titanium and loss of its inhibitive action.

On the contrary, the presence of either a temperature gradient or liquid flow can lead to a drastic attack. Table I gathers the solubility change in ppm of iron nickel and chromium several metals in mercury[6].

Table I

	260ºC	538ºC
Iron	0.001	0.4
Nickel	7.0	80.0
Chromium	0.02	8.2

These values indicate that despite the increase of temperature the problem of mercury corrosion is still not severe. However, this may be true only for isothermal system where the saturated state is soon reached at a given temperature. But as solubility is an exponential function of temperature, dissolution rate increases rapidly with temperature above 500ºC. Although temperature does directly influence the susceptibility to corrosion in liquid mercury, this rate may also varies by other reasons such as the type of alloy, the heat treatment and the rate of diffusion of the alloying elements.

In this sense it has been demonstrated that the solubility of an element in liquid mercury is intimately linked to corrosion resistance, **Figure 1.** Thus, low solubility in mercury results in a low corrosion rate.
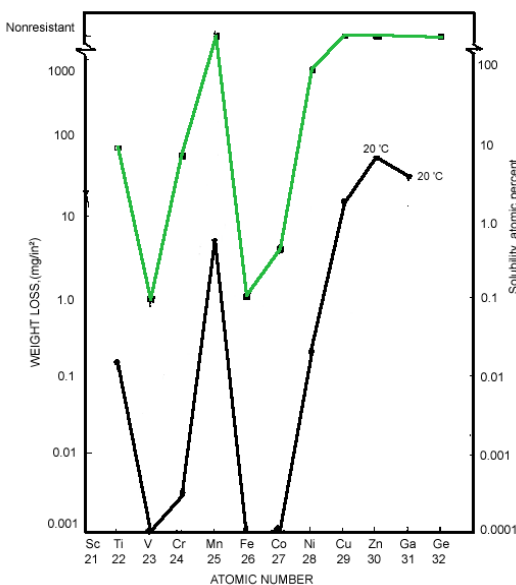

Figure1. Comparison of corrosion resistance in mercury with solubility data in Hg at 900ºF (482ºC)[3].

Alloy additions of chromium, titanium, silicon and molybdenum, alone or in combination show resistance to 600ºC. Recently, 5% chromium steel and Si-Cr- Mo steels have replaced carbon steel because of their superior corrosion and higher rupture strength.

Nevertheless, the presence of some alloying elements in the solid metal might affect the alloy corrosion resistance.

In general, nickel content has an adverse effect on iron- base and cobalt-base alloys[7]. Nickel tends to form intermetallics compounds with mercury as well as with lead and bismuth. However, this effect appears to be more pronounced in the face centred cubic –FCC- structure than in the body centred cubic alloys -BCC-. In contrast, the effect on nickel on cobalt base alloys is small in absence of iron. But, for those cobalt base alloys containing relatively large amounts of iron, corrosion is similar to iron-base alloys corrosion.

For the BCC (martensitic and ferritic) iron-base alloys chromium contents in the 4-14% range are not deleterious and may be beneficial. Although the reasons for this behaviour are not clear[7]

However, Nejedlik et al.[7] have reported that corrosion of iron-base alloy corrosion is dependent on the total nickel, manganese and chromium content of the alloy. The corrosion resistance of iron-base alloys with a total Ni+Mn+Cr content below 15% is about the same as pure iron. Between 15 and 40%, corrosion rises sharply as a function of the alloy content, increasing 100-fold at 40%. Alloying additions of Ni +Mn+Cr over 40% have no further effect in corrosion. **Figure 2** plots this corrosion dependence on Ni+Mn+Cr content at 900ºF (482ºC).
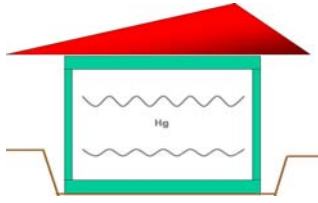
In severer working conditions, circulating mercury at temperatures higher than 540ºC an understanding of the various types of liquid metal corrosion is necessary to select or develop a compatible containment material[8-10].

Recently, many works have been published referred to corrosion problems appeared in 316L and 316LN stainless steel used as mercury vessels in spallation neutron sources. A large data bank include measurements of surface degradation by corrosion, mass transfer in liquid metal loops and effects of liquid interactions on mechanical properties such as fatigue and tensile properties[11-12].
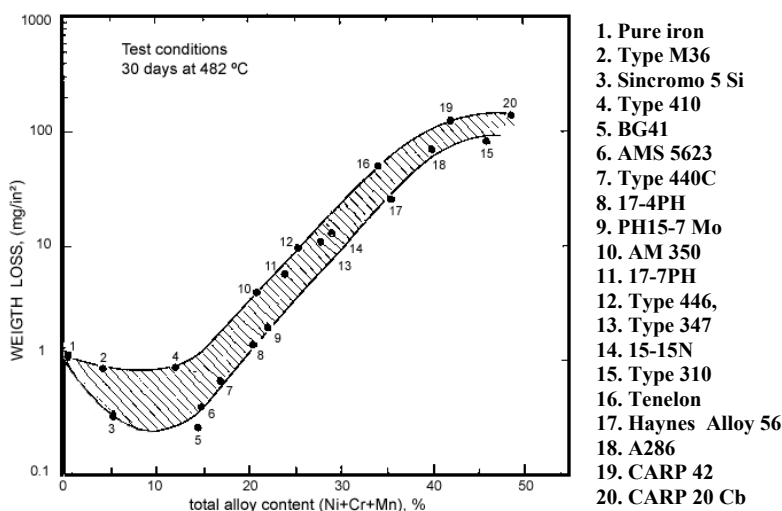

	1. Pure iron
	2. Type M36
	3. Sincromo 5 Si
	4. Type 410
	5. BG41
	6. AMS 5623
	7. Type 440C
	8. 17-4PH
	9. PH15-7 Mo
	10. AM 350
	11. 17-7PH
	12. Type 446,
	13. Type 347
	14. 15-15N
	15. Type 310
	16. Tenelon
	17. Haynes Alloy 56
	18. A286
	19. CARP 42
	20. CARP 20 Cb

*Figure 2. Effect of Nickel, Manganese and Chromium alloy content of iron base alloys on mercury corrosion[7].*

Cavitation erosion has arisen as an important problem, still not well understood, for this type of stainless steel[13,14]. This type of damage is consequence of a thermal-shock pressure wave produced by an extreme heating rate.

Obviously these are not the working conditions of material used for mercury storage. However, some of the results obtained by the researchers when they have attempted to simulate the working conditions in laboratory might be quite useful for storage conditions. For instance, G.A. Greene et al[15] have evaluated several alloys –Inconel 718, AISI 316L SS, TiAlV, Copper, Aluminiun, Inconel 600, etc – in circulating mercury at room temperature to investigate the short term metallurgical effects of mercury on the alloys to evaluate their suitability for service in a mercury –wetted environment. After 50 hours of immersion in mercury flowing at 55cm/s no weight loss was detected for both Inconel, or 316L SS. On the other hand, Cu and Al exhibited a mass loss of about 22% and 19% respectively.

Conversely, Pawel et al[16] measured the mass loss of numerous test coupons after exposure to flowing mercury at temperatures between 250-310ºC up to 5000h. The authors observed surface depletion of chromium and nickel from 316L stainless steel, while no corrosion was observed for Inconel 718. They concluded that surface wetting is a necessary condition for metallurgical attack by mercury.

This disagreement remarks that the results reported in literature for the specific test conditions should be considered strictly valid for such test conditions and extrapolation to static or dynamic conditions, other temperature or long mercury service conditions, is not recommended.
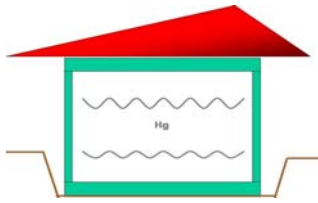
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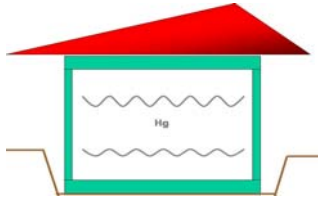
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Subtask 1.4. Literature review concerning stabilization of Hg.

Mercury, a liquid at ambient temperature, has a low but significant vapour pressure which originates its high toxicity. Mercury is generally less toxic and soluble in its elemental form than several inorganic and organic compounds, but presents handling problems rather than compounds of mercury which are fundamentally solid materials. There is therefore a need for a process for stabilizing mercury that effectively stabilizes both elemental and speciated mercury, uses relatively inexpensive additives and/or operates economically both on small and large scales.

Technologies developed to achieve safety disposal of mercury and mercury-containing wastes aim to the immobilisation of mercury to reduce the mercury mobility towards the environment. These technologies can be grouped herein three types: amalgamation, stabilization and encapsulation.

a. Amalgamation

Amalgamation is defined as the combination of mercury with metallic reagents such as copper, gold, zinc, aluminium, nickel, tin, gold, silver or sulphur that result in a solid, non-volatile product. In fact, amalgams consist of semi-solid solutions obtained by dissolution of mercury in the solid metal. Although amalgamation is a relatively inexpensive and speedy process for the treatment of liquid mercury, disadvantages come from the difficulties to scale up and the needing of using dilute nitric acids to achieve high efficiency. The method commonly is unable to stabilize adequately instable forms of mercury in the hazardous waste material.

b. Stabilization

To stabilize means to convert to a solid, hard, non-flowable mass or a solid, inert particulate material which resists common solvents and retains the materials contained therein when subjected to leaching conditions.

Stabilization is a chemical method which attains to the chemical immobilization by the formation of stable compounds or water-nonsoluble compounds. Stabilization reduces or eliminates the possibility of vaporization or leaching to the environment.

In the most extended processes mercury reacts with powdered sulfur and/or liquid sulfur (polysulfide) to form mercuric sulfide. Mercuric sulfide is the most stable compound formed between mercury and sulfur. It exists in two stable forms. Ones in the black cubic tetrahedral form (metacinnabar) and the other stable form is the red hexagonal form found in natures as cinnabar. Both forms are insoluble in water and in acidic solutions. In alkaline solutions with excess of sulfur anions HgS is solubilized.

According to Gibbs free energy value (-11.1kcal/mol) the direct reaction of elemental mercury and sulfur is favoured. However, merely placing elemental mercury in bed of sulfur or in a volume of polysulfide does not yield the desired mercuric sulfide reaction. Sufficient heat must be available to overcome the energy of activation for the reaction to occur. Intensive mixing provides the necessary energy activation for the reaction to take place.

The application of this method on soils and sludge spiked with elemental mercury yield low success because the heat provided by mixing action or generated from the mercury-sulfur reaction quickly dissipates throughout the surrounding matrix materials and so it is difficult to overcome the energy of activation to initiate the mercury-sulfur reaction throughout the entire reaction mass. Beside mercury in soils is not a continuous phase. Chemical stabilization of mercury in solid materials is difficult because of the dispersed nature of the contaminant within the solid matrix and the consequent problem of contacting a stabilizing agent with the widely dispersed contaminant.

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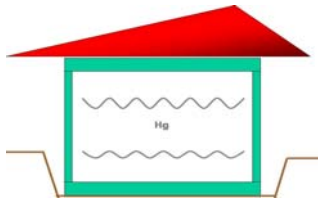
Sulfides compounds with high solubility in water are employed to react with mercury compounds. Inorganic sulfur compounds which include oxygen (thiosulfates and dithionites) react with mercury compounds in the same manner than sulfides compounds.

In the stabilization of soluble mercury in mercury-containing materials by the formation of insoluble mercury sulfides, it is desirable to minimize the formation of mercury polysulfide complexes which can be eluted or leached from deposits in effluents which would contain Hg concentrations higher than desired. This can be accomplished by the selection of the inorganic sulfur compound. Mercury polysulfide formation may also be minimized or eliminated by the addition of a polysulfide inhibitor (alkali metal sulfite, alkali metal bisulfite and alkali metal metabisulfite).

Similarly, to prevent or minimize the formation of hydrogen sulfide by limiting the amounts of hydrogen-containing sulfur compounds present as impurities in the inorganic sulfur compounds or by limiting the exposure of the stabilizing inorganic sulfur compounds to air and sunlight. The use of antioxidants (ascorbic acid, citric acid, phosphoric acid, butylated hydroxyanisole and butylated hydroxytoluene) will also reduce hydrogen sulfide formation.[1-9]
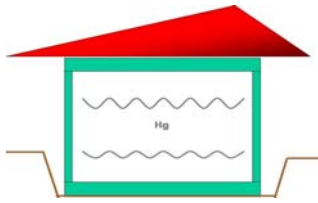
c. Encapsulation

To encapsulate means to embed within a stable matrix. Molten and casting are part of the encapsulation process. The objective of these methods is to seal the mercury waste from the surrounding environment.

Cement, concrete or concrete like products are commonly, used for wastes encapsulation, due to their hardness, very long life and the capacity to be mould prior to setting. But in some cases, the success of the procedure is limited because the presence of contamination negatively affect to the binding stage.

Methods for encapsulation of mercury wastes can be classified in two categories depending on the use or not of pozzolanic materials in the process.

c.1 Encapsulation without pozzolanic materials.

The method comprises the addition of the hazardous waste materials to a settable composition, which is prepared by using no-pozzolanic materials such as dolomite, calcium carbonate, magnesium carbonate, caustic magnesium oxide, etc, which forming slurry and allowing it to set to encapsulate the mercury or components thereof. Dolomite is a calcium magnesium carbonate found in nature. A true dolomite contents about 54% calcium carbonate and 43% magnesium carbonate. Natural dolomites contain impurities of various types which can include alumina, iron and silica. When dolomite is heated carbon dioxide is liberated and a mixture of calcium oxide and magnesium oxide is obtained. If dolomite is heated at 1500 ºC, all the carbonate is liberates as CO_2. These oxides are used in refractory material, but the oxides are not suitable for a cementitious material. By controlling the heating, magnesium carbonate is decomposed preferentially over calcium carbonate. The preferential decomposition of magnesium carbonate is attained between 500-800ºC, and then the dolomite is converted to a settable dolomite comprising caustic magnesium oxide. Aluminium sulfate or magnesium sulphate is used to enhance the preferential decomposition of magnesium carbonate. Various additives (organic fillers, inorganic fillers) can be added to accelerate the formation of strong binding agents, and assist in the recrystallisation of the composition to make it set. Other additives as sodium carbonate or carboxylic/polycarboxilic acids can be added to assist in the setting process by means of the liberation of carbon dioxide. Acidifying agents as citric acid, lemon acid, oxalic acid, etc, can be necessary. These agents can assist in the carbonisation of MgO and Mg(OH) to recrystallise the composition into a set material. Besides they can act as a ligand to form complexes around the fillers helping to trap them in the set matrix.[10]

c.2 Encapsulation with pozzolanic materials

Pozzolanas are defined as materials which combine with lime at ordinary temperature, in the presence of water, to form stable insoluble compounds possessing cementing properties. Pozzolanas can be naturally occurring materials such as volcanic ashes and tuffs, clays and synthetic materials such as fly ash, rice hull ash, silica fume, etc.

c.2.1 With cement or cementitious materials

Different methods are described to immobilize toxic waste materials by forming aggregate with certain cementitious materials (pozzolana, calcium hydroxide-containing materials such as lime, kiln dust, hydrothermal cement reactant such as zinc or aluminium oxide, anhydrous sodium silicate and hydraulic cement as Portland cement). The objective is to create a strong ceramic material by forming chemical or mechanical bonding. Metals in hazardous waste can affect negatively to the hardening of hydraulic cements. So additives or filler materials such as pulverised fuel ash, hydrated lime, finely divided silica, limestone flour and organic or inorganic fluidising agents, blast furnace slag and also previous steps to stabilize mercury waste are needed.[11-15]

c.2.2 Without cement

Different technologies have been develop to encapsulate mercury waste which use principally sulfur cement, polysulfide polymer, fosfated ceramic, or organic polymers such as polyethylene, polyesters and polyxilanes.

Sulfur polymer cement also known as modified sulfur cement, is usually formed by reacting sulfur with a hydrocarbon such as dicyclopentadiene, vinyl toluene, etc, to form a sulfur reaction product which is more amorphous in nature as opposed to being crystalline. Sulfur polymer cement is manufactures by several companies and is marketed under several tradenames.

These methods can includes several steps such as a first process to stabilize the waste with sulphur polimer cement, and a second one to encapsule the mixture to product a monolithic final waste form. Different additives as oxidative curing agents (MnO_2, PbO_2, calcium peroxide, zinc peroxide, sodium perborate, ammonium dichromate and cumene hydroperoxide), and/or stabilizing agents (sodium sulfide, triisobutyl phosphine sulfide, calcium hydroxide, sodium hydroxide, calcium oxide and magnesium oxide, are added to cause cross linking and hardening of the sulfide polymer.[16,17]

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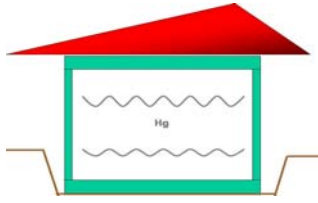
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