

DISPOSAL OF ELEMENTAL MERCURY VIA SULPHUR REACTION BY MILLING

F.A. LÓPEZ, F.J. ALGUACIL, C.P. ROMAN, H. TAYIBI AND A. LÓPEZ-DELGADO

Dept. of Primary Metallurgy and Materials Recycling. National Centre for Metallurgical Research, CENIM (CSIC). Avda. Gregorio del Amo, 8. 28040 Madrid (Spain)

SUMMARY: The formation of HgS (metacinnabar) from elemental mercury and pure sulphur, in non stoichiometric conditions, by means of the mechanical energy provided by a ball mill was studied. The effect of milling time in the completeness of the reaction was also studied. The formation of metacinnabar (HgS black) was observed even at short milling time (15 min), but several drops of un-reacted liquid mercury could be seen at that time. Liquid mercury was not detected for milling time of 90 min. The mechanism of the reaction was observed by SEM. This indicated that the reaction of formation of metacinnabar by mechanical dispersion starts with the diminishing of the size of the mercury drops; as reaction time increases the sulphur molecules form an interface with the microspheres of Hg and yield the formation of metacinnabar. The mercuric sulphide obtained passed the TCLP tests, yielded 2.0×10^{-3} mg/l of Hg in the leachate.

1. INTRODUCTION

Mercury, a liquid at ambient temperature, has a low but significant vapour pressure which causes its high toxicity. Mercury is generally less toxic and soluble in its elemental form than in several inorganic and organic compounds, but presents greater handling problems than the compounds of mercury which are fundamentally solid materials. Mercury is considered a Priority Hazardous Substance according to European Directive 2000/60/CE, due to the adverse effects on human health and on the environment. So, the actual EU policy is focused on controlling and restricting the use of Hg. This policy establishes 2011 as the cut off date for the utilization of Hg by Industry. As a result of this, any excess of Hg should be stored in safety conditions and in safe places until definitive policies on the stabilization or re-utilization are available. There is therefore a need for a process that effectively stabilizes elemental Hg, uses relatively inexpensive additives and/or operates economically both on small and large scales.

In the most extended processes, mercury reacts with powdered sulphur and/or liquid sulphur (polysulphide) to form mercuric sulphide, and this is considered the Best Demonstrated Available Technology (BDAT) (Gorin et al., 1994). Mercuric sulphide is the most stable compound formed between mercury and sulphur. According to the Gibbs free energy value (-11.1kcal/mol) the direct reaction of elemental mercury and sulphur ($S + Hg \rightarrow HgS$) is thermodynamically favoured. However, merely placing elemental mercury in bed of sulphur does not yield the desired mercuric sulphide reaction. Sufficient heat must be available to overcome the energy of activation for the reaction to occur. But problem can occur because the

dry powder obtained is susceptible to mechanical dispersion. To avoid some of mercury remaining occluded in the mercuric sulphide, surfactants can be used to disperse elemental mercury. Kaczur et al. 1989 describes a process for stabilizing "in situ" soluble mercury in deposits of mercury-containing materials which comprises treating the deposits with a stabilizing amount of an inorganic sulphur compound (sulphides, alkali metal thiosulphates and alkali metal dithionites). The inorganic sulphur compounds react with soluble mercury to convert it into insoluble mercury compounds and substantially inhibit its removal by leaching with water from the deposits of mercury-containing material.

Oji, 1998, describes a technique that use high-shear mixing to produce mercuric sulphide. Cinnabar is obtained at high shear (19,000 rpm) and at high temperature (<270°C) and metacinnabar at lower shear (1,060 rpm) and lower temperature (50°C). Experiments were performed in inert atmosphere.

Fuhrmann et al. 2002, studied the formation of mercury sulphide by stirring elemental mercury and mercury-mixed waste with elemental sulphur modified with organic compounds, in various proportions at 40 and 200 °C.

Litz, et al.2002 describe a process which includes the steps of: combining the mercury-containing feed material with a polysulfide and a reactive sulphur-containing compounds other than the polysulfide to form a composite feed material; and mixing the composite feed material to treat the reactive sulphur-containing compound with the mercury or mercury waste to form mercuric sulphide. According to the authors, the final product can pass the Toxic Characterization Leach Procedure or TCLP.

Riviere-Huc at al. 2006, provide a method for the stabilization of metallic mercury, by reaction with sulphur in the solid state. The reaction takes place in a hermetically sealed reactor and set in rotation.

Recently, Svensson et al. 2006 have studied the formation of HgS from HgO and elemental Hg elemental by mixing them with various sulphur sources (pirite, troilite) at different values of pH and aerobic or anaerobic media.

The aim of this work is to study the formation of metacinnabar from elemental Hg and elemental sulphur in non-stoichiometric conditions, at room temperature through the mechanical energy provided by a milling process. This work is a preliminary study which is a part of the European Project MERSADE (LIFE06 ENV/ES/PRE/03) for the design, construction and validation of a pilot installation for a safe deposit of surplus mercury from the European industry. This Project includes the development of a process for the stabilization of mercury and mercury-containing by means of the use of polymeric sulphur compounds.

2. EXPERIMENTAL

2.1 Materials and methods

The reaction between elemental Hg elemental and S in non stoichiometry conditions was carried out by means of the mechanical energy provided by a planetary ball mill (FRISTSCH mod. Pulverisette) containing four stainless steel balls. The size reduction principle in this mill is impact and friction. The grinding jar is arranged eccentrically on the sun wheel of the planetary ball mill. The direction of movement of the sun wheel is opposite to that of the grinding jars. The grinding balls are subjected to superimposed rotational movements (Coriolis forces). The difference in speeds between the balls and grinding jar produces an interaction between frictional and impact forces, which releases high dynamic energies. The interplay between these forces produces a high and very effective degree of size reduction of the sample.

Mixtures of elemental Hg (25 g) (MAYASA, Almadén, Spain) and S (99.4% wt, grain size <60 μm , type Rubber Sul 10, REPSOL IPF Madrid, Spain) in 1/1 wt/wt were carried out. This rate indicates an excess of 45% wt of S with respect to the stoichiometry amount. Several milling times ranging between 15 min and 3 h were studied. A grinding jar of 250 ml was used and the balls mass/mixture mass rate was maintained constant at 5/1. The milling rate was 400 rpm in all cases and the temperature in the grinding jar was measured at the end of each process.

To ensure that the reaction between S and Hg after milling time was completed, i.e, to determine the completeness of the reaction of stabilization of Hg, a simple method was used. Thus, the presence of elemental mercury was determined by centrifuging 15 g of the reacted mixture at 3,500 rpm for 1 h. Then the appearance of the conical wall of the centrifuge tube was observed by a magnifying glass (NIKON modelo SMZ 1500) provided with a capture image system.

2.2 Analytical procedures

The crystalline phases present in the samples were characterized by X-ray powder diffraction (BRUKER XRD Mod. D8 Discover, 0.03 2θ degrees step-widths and counting time of 5 s per step).

The morphology of the samples was observed by scanning electron microscopy SEM (HITACHI model S-2100) on as-obtained C-coated sample. A field emission microscope (JEOL JSM 6500 F) provided by energy dispersive analyzer (LINK OXFORD INCA, EDAX unit) was used to determine the composition of the samples. In this case, samples were embedded in a resin and C-coated.

Samples were tested for Hg leachability using the TCLP (EPA Method 1311) test. Due to the fact that the extraction fluid to be employed in TCLP test is a function of the alkalinity of the sample, a preliminary evaluation of which extraction fluid was required, was carried out as follows: an aliquot of sample (5g) was transferred to a 500 mL Erlenmeyer flask, 96.5 ml of Milli-Q water were added and the suspension was stirred vigorously for 5 minutes using a magnetic stirrer. The test showed that fluid 1 (acetic acid and sodium hydroxide solution) was required as the extraction fluid. A modified version of the TCLP was conducted, using 20g of sample, instead of the prescribed 100g. Samples were extracted with an amount of extraction fluid 1 equal to 20 times the weight of the solid. Tests were performed in triplicate. Experiments were maintained in stirring for 18 h and after that the liquid and solid phases were separated by filtration using a suitable filter holder of 47mm size (Millipore Corp.) Glass fiber filters of 0.7 μm pore size were used. But the filtrates presented a light turbidity, thus 0.45 μm filter was employed. Filtrates were preserved by acidification with nitric acid to a pH < 2 and stored at 4°C until the performance of the Hg analysis in a Cold-Vapor Atomic Absorption LECO mod AMA 254. A sample of liquid Hg was also analyzed.

3. RESULTS AND DISCUSSION

All the samples obtained by milling the mixture of Hg and S consisted of black powers. By simple macroscopic observation, small spheres of elemental Hg could be seen in the 15 min milling sample, but not in samples obtained at longer milling times. The observations of samples after centrifugation (Figure 1) showed the presence of un-reacted elemental mercury for samples obtained at milling times shorter than 60 min. The presence of an important mass of un-reacted-Hg, segregated from the mass of HgS can be observed in Figure 1a. In Figure 1b only a small number of micro spheres of Hg are observed, but are not observed in Figure 1c which corresponds to the 60 min milling sample.

The formation of HgS (metacinnabar) takes place even at short milling time and so, DRX patterns showed that all the samples consisted of a mixture of the phases cubic metacinnabar (JCPDS 00-006-0261) and the orthorombic α -sulphur (JCPDS 00-008-0247). Other phases were not observed. The XRD intensities for all samples were similar. Figure 2 show the diffractograms corresponding to the 60 min milling sample and to the initial sulphur.

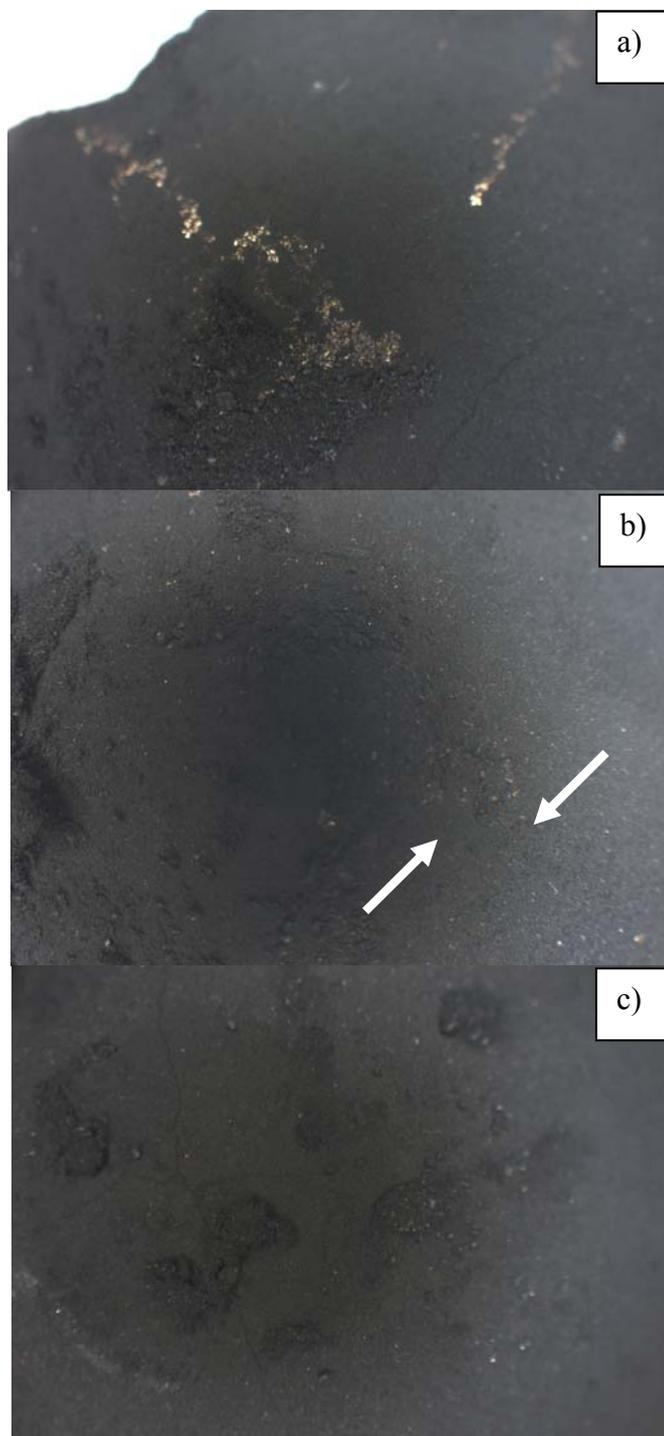


Figure 1. Macrophotographs of centrifuged sample, at: a) 15 min milling , b) 30 min milling and c) 60 min milling.

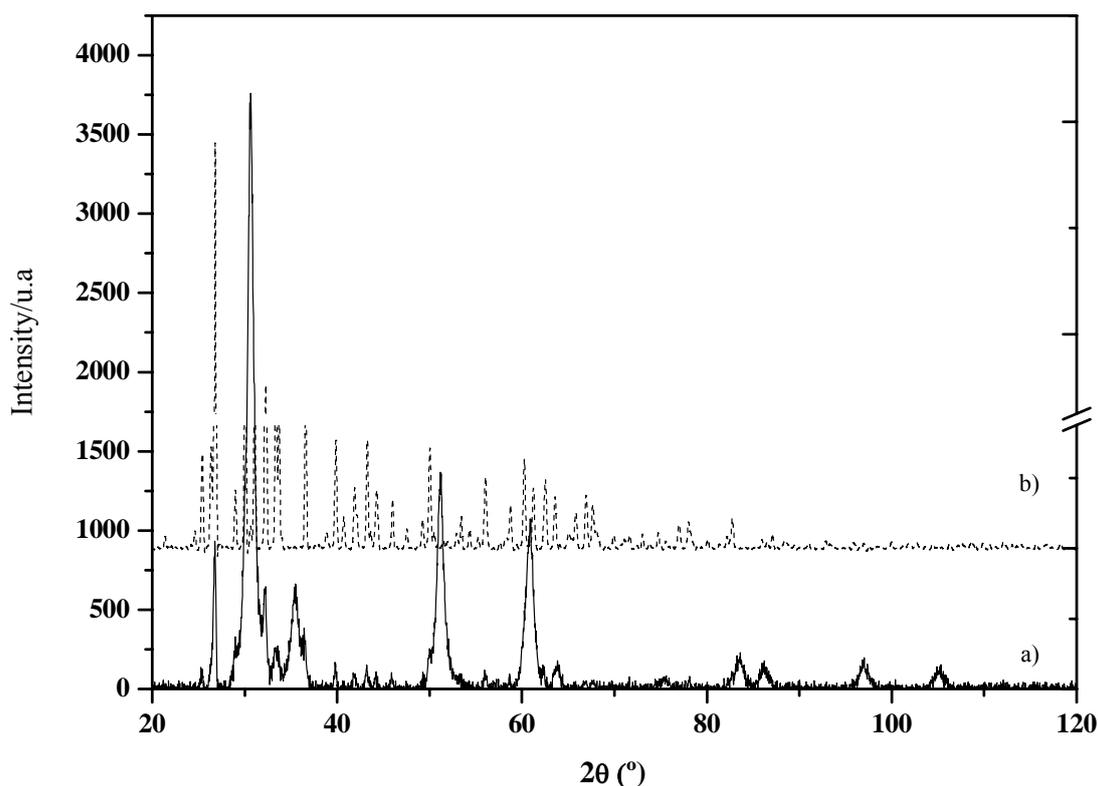


Figure 2. DRX patterns of: a) 60 min milling sample, and b) Initial Sulfur (Rubber Sul 10)

The mechanism of the formation reaction of mercuric sulphide is revealed by SEM study. Figure 3 shows SEM images of various specimens. Figure 3a shows a micro sphere of elemental mercury of 23 μm of diameter with small grains of sulphur adhered to its surface. This indicating that the movement of the balls into the grinding jar causes the massive liquid mercury fractures to micro spheres, accordingly the surface available for the reaction with sulphur, increases very substantially. Then an interface between microspheres of Hg and sulphur is formed which leads to the reaction and formation of HgS. Figure 3b shows a spherical particle of mercuric sulphide. The EDAX analysis of several sites of this particle yielded Hg content ranging between 73.3 - 78.2% and sulphur content between 26.8-21.8%. Taking into account the content of Hg in the stoichiometric HgS is 86.2%, the particle consists of a mixture of HgS and S. As the milling time increase the particles loss the spherical morphology and a transformation to irregular, prismatic, smaller particles can be observed. In samples obtained at milling time longer than 120 min, several particles containing Hg and oxygen were observed. These particles contain 89-98% of Hg and 2-15% oxygen, thus indicating the partial oxidation of mercury during the long timed milling process. Gibbs energy for the formation of HgO is -13.94 kcal/mol at 298 K, which is lower than that corresponding to formation of HgS. Several authors describe the use of inert atmosphere, (Riviere-Huc et al. 2006 and Oji 1998), the addition of sodium sulphides and other compounds (Fuhrmann et al. 2002) with the aim of avoiding the oxidation of mercury. In our case, oxidation of Hg was not detected for milling times shorter than 120 min.

The temperature inside the grinding jar after finishing the milling time is shown in Table 1. In this table is also showed the results of TCLP tests. A light increasing of temperature can be observed as the milling time increases. The low value of temperature obtained in all cases

(<45°C). This value of temperature is very much lower than the sulphur flash point temperature (207°C), thus, the potential for fire hazard is reduced. This low value can be due to the slow grinding rate used (only 400 rpm) and also to the excess of sulphur in the medium which can partially absorbed the heat generated by the reaction.

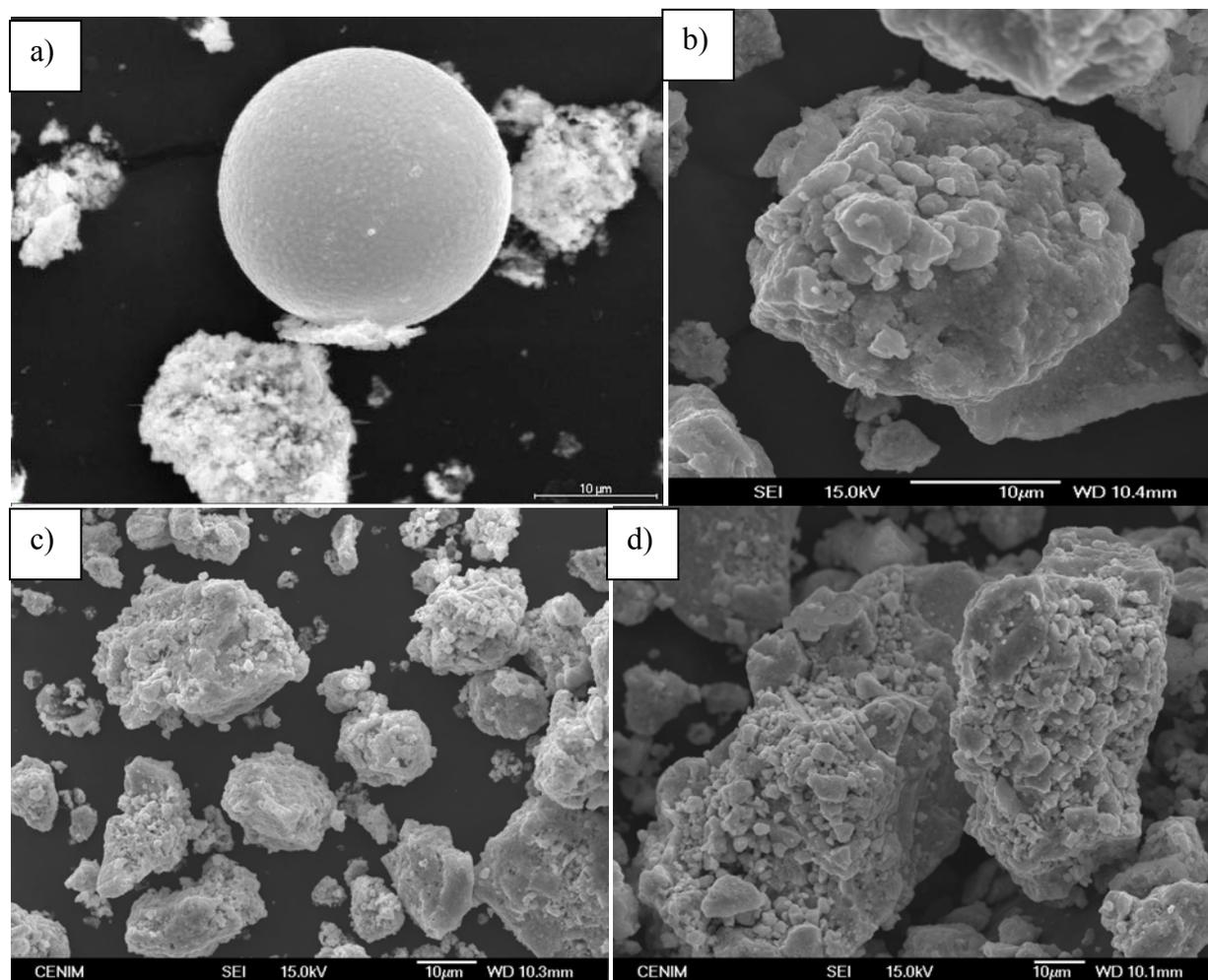


Figure 3. SEM images of: a) Hg sphere with sulphur grain adhered (15 min sample), b) HgS grain covered with sulphur (15 min sample), c) HgS grains covered with sulphur (60 min sample) and d) HgS grains covered with sulphur (180 min sample).

A decreasing of the value of mercury in the leachates (obtained by TCLP test) with the milling time is obtained for times shorter than 90 min. This sample yielded the lowest value. For longer time than that, the value of Hg in the leachates increases. This fact can be attributable to the content of un-reacted liquid mercury in samples obtained at short milling time and to the presence of mercury oxide in samples obtained at long milling time. The value obtained for the initial liquid mercury was 8,960 mg/l.

Table 1- Milling time, temperature and results of TCLP test.

Milling time (min)	T (°C)	TCLP Hg ($\mu\text{g l}^{-1}$)
15	29	5.1
30	32	3.7
60	35	3.1
90	37	2.0
120	39	4.7
180	41	4.3

4. CONCLUSIONS

The application of the mechanical energy provided by a ball mill to a non stoichiometry mixture of elemental mercury and sulphur permits the formation of metacinnabar as the only phase of HgS. The mechanism of the process, according to the SEM study, starts with the formation of micro spheres of Hg with an adequate superficial tension to favour the adhesion of the S particles. The micro spheres are produced by means of the impact and friction of the balls against the wall of the grinding jar. This mechanism required a determined level of solid inside the grinding jar, i.e. an optima mass of the balls / mass of mixture ratio. The kinetic of the reaction is rapid yielding mercuric sulphide at short milling time. The completeness of the reaction requires milling time longer than 60 min for milling speed of 400 rpm.

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