M.A. Rabah*, M.A. Barakat* and F.E. Farghaly*

EFFECT OF ADDITION OF CAUSTIC SODA ON DECOPPERING OF HARD LEAD USING PYRITE

[1]

The effect of caustic soda addition on the decoppering power of pyrite to decrease copper content in hard lead containing 0.56% weight percent copper has been studied. The process block diagram includes remelting of the hard lead samples, addition of pyrite and caustic soda. Experiments are conducted within the temperature range from 350 to 550 °C for a period of more than 1h. Factors such as stoichiometric ratio of pyrite, NaOH concentration, time, and temperature affecting the decoppering process, yield, and antimony content were studied. The results revealed that pyrite 2 stoichiometric ratio and 0.5 % caustic soda at 450 °C decreases copper content in the hard lead alloy from about 0.56% to 0.03 %. Decoppering time about 30 minutes affects both the yield and the quality of the product. Under these experimental conditions, decoppering efficiency amounts to 92% with a yield of 95%. A little decrease in antimony content from 2.77 % to 2.4 % was achieved. A model explaining the findings was suggested which assumes that chalcopyrite is the main product of decoppering reactions involved in the early period of the process. The chalcopyrite so formed goes into slag more readily as the alkalinity increase due to decreasing slag viscosity.
Key words: Decoppering, refining of lead, lead pyrometallurgy

INTRODUCTION

Hard lead bullion was freed from copper by pyrometallurgical treatment utilizing different sulphidizing agents. A continuous method for removing copper from hard lead was studied by Bowers (1983). The reaction of copper with sulphur occurred in a single stirred reaction vessel feeding sulphur into the stream of lead at the upper end of the reaction vessel, maintaining a dispersion of sulphur in the stream without substantial back-mixing. Reaction proceeded for sufficient time to affect reaction between them. Davey et al. (1980) studied the physical chemistry of lead refining under equilibrium conditions included copper drossing. The authors showed that kinetic consideration governed the operation of decoppering byincorporation sulphur into lead at low temperature or by stirring the melt with sulphur and pyrites at higher temperature. Hard lead containing tin could be decoppered by addition of 0.1 % sulphur at temperature ranging from 320-400 °C. While hard lead without tin could be decoppered with sulphur and pyrites better than with sulphur alone. The presence of antimony hindered the decoppering which was effective on lead with 5.5% antimony than with 2.3% antimony.

[1] *Industrial Wastes laboratory, Extractive Metallurgy Dept. CMRDI
P.O.Box 87 Helwan, 11421, Cairo Egypt. e-mail : rucmrdi@rusys.eg.net

Khodov (1982) presented a process of decoppering by centrifuging crude lead. The liquid crude lead had been primarily decoppered at 340-550°C. Copper content after filtration was 0.03-0.07 %. Kopylov (1982) studied the potential of centrifugal filtration for refining lead containing up to 6.6% copper, 2.8% arsenic and 1.9% antimony at various temperatures between 600 °C and 330 °C. The refined lead and dross were analyzed. Sulphides of copper and lead separated completely as solid phases at temperature of 500 -350 °C.

A process for refining lead, especially for removing copper, was studied by Lapain (1991). Molten lead was cooled to 900-600 °C in a such manner as to cause separation of the lead-rich phase and the impurities-rich phase. Continuous refining of secondary lead was investigated by Bowers (1984) whereby the process consisted of removal of copper. Kimura (1987) studied copper removal from lead by a dry method. An Al-Mg-Zn master alloy was added to molten lead containing ≥ 0.5 ppm of copper. The melt was mixed with alkali metal hydroxide and air blowing to form dross for removal. New decoppering method for lead bullion containing 0.02 % copper was studied (1980). NaOH and pyrite were used to reduce the copper content to < 0.005%. Dautov (1991) studied refining of molten crude lead in electric furnace. Removal of copper and other impurities increased when molten crude lead was treated with sodium sulphate as a sulphidizer. The associated addition of C-rich reducing agent at a C: Na_2SO_4 ratio of 1:5 at 900-1100 °C.

The aim of this work was to evaluate decoppering of hard lead with pyrite in alkali medium to prepare lead antimony alloy meeting the standard DIN specifications as specified for the manufacture of battery grids. Evaluation is monitored in terms of the yield of the method.

EXPERIMENTAL

The experimental part of this work includes the preparation of the materials, execution of the experiments and measurement of the physico-chemical properties of the input materials, the products and the slag formed.

Materials:

The hard lead-antimony alloy. Commercial hard lead-antimony alloy sample weighing about 50 kg was obtained from the " General Metals Co. (GEMET)", El-Tebbin Cairo, Egypt. The sample was separated mechanically into small pieces of about 200 g each.

Decoppering agents. Pyrite, technical sulphur, caustic soda and sodium sulphide were utilized for decoppering of the hard lead alloy samples.

Acid leaching was performed by dissolving the formed slag in hydrochloric acid whereby the dissolved metal solution was freed from the excess acid by evaporation. Bidistilled water was used for analysis.

Method of decoppering:

Crucible furnace having 0.5 l capacity was used for decoppering experiments. After the furnace temperature reached the required level, the hard lead samples weighing about 200 g each were separately charged into the furnace with subsequent stirring. The mechanical stirrer was equipped with digital control device to adjust the rpm of the molten lead at the required rotational speed. Decoppering agent(s) was then added to the system and the process took place for different periods. At the end of each experiment, the slag so formed was skimmed and the molten lead alloy was poured in a receiver.

Methods of analysis:

Salts of slag recovered by acid leaching were dissolved in distilled water and the solutions were analyzed by atomic absorption spectrophotometer type 1000 SP Unicam.

Metals content in the input and obtained alloys were determined with the help of emission quantimeter type 3460-880 ARL, Seuces.

Yield percentage was determined according to formula:

$$\text{yield \%} = Wt_p / Wt_i$$

where Wt_p and Wt_i are the weight of product and input alloys, respectively.

Decoppering percentage was calculated gravimetrically from :

$$\text{decoppering \%} = WtCu_s / WtCu_i$$

where $WtCu_s / WtCu_i$ are the weight of copper went into the slag and in the input lead alloy respectively.

RESULTS

Table 1 shows the chemical composition of the used commercial hard lead-antimony alloy. It is seen that the percentage of copper and antimony amounts to ~ 0.56 and 2.77 respectively. Copper content in the alloy overweighs the standard level as specified by DIN for manufacture of battery grids.

Table1. The chemical composition of the used hard lead-antimony alloy
Tablica 1. Skład chemiczny stopu ołowiu antymonowego

metal ⟶	lead	antimony	tin	copper
weight %	94.67	2.77	2.00	0.56

Figure 1 shows the results of decoppering hard lead samples as affected by time at 450°C under stirring conditions. Decoppering agent used was pyrite (at pyrite to lead ratio equal to 1) together with 0.25 % sodium hydroxide. It is seen that the residual copper in the treated lead alloy decreases gradually with increase in time of treatment passing through a minimum after 25 minutes at 0.05% copper. With further increase in time of decoppering, the residual copper content in the lead alloy re-

increase passing through a broad maximum after 40 minutes. It is worthy to note that copper content approaches the lowest value 0.03% after 60 minutes of treatment.
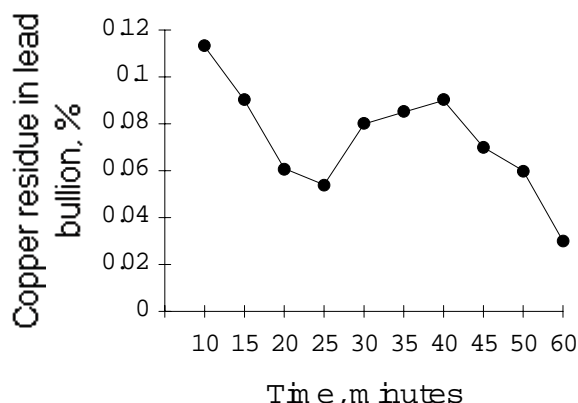

Fig. 1 Effect of decoppering time on copper residue in the treated lead-antimony bullion
(t= 450°C , 1 st. ratio of pyrite + 0.25 % NaOH)
Rys.1. Wpływ czasu trwania procesu na ilość miedzi pozostająca w stopie Pb-Sb

Figure 2 shows the residual percentage of metal antimony in the decoppered hard lead alloy. It can be seen that obtained curve has a parabolic shape with a broad maximum amounting to 2.4 after 30 minutes. The antimony percentage equals to 2.05 % after 10 or 60 minutes.
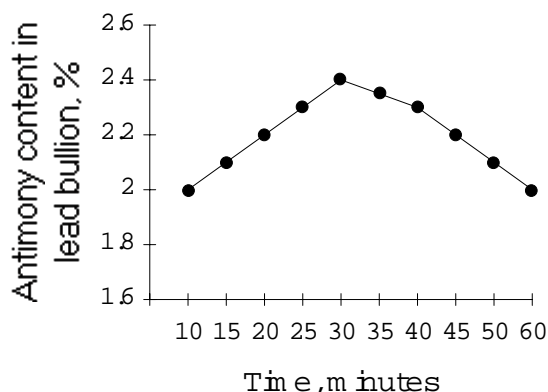

Fig. 2 Antimony content in the treated lead-antimony bullion as affected by decoppering time. (t= 450°C , 1 st. ratio of pyrite + 0.25 % NaOH)
Rys.2 Zawartość antymonu w stopie jako efekt czasu prowadzenia procesu usuwania miedzi

Figure 3 shows the yield of the decoppering process. It is seen that the yield decreases with increase in decoppering time to about 90 % after 40 minutes. With further increase in decoppering time and after 60 minutes, the yield decreases drastically to less than 40%. Figure 4 illustrates the efficiency of the decoppering process as a function of time under the same conditions whereby an opposite mirror image of Figure1 is attained. It can be seen that the decoppering efficiency value amounts to 76% after 10 minutes and then increases gradually with increase in time approaching a value of ≈ 90% after 25 minutes. After 40 minutes, the efficiency value decreases to about 84 % which is followed by an increase up to 96% after 60 minutes.
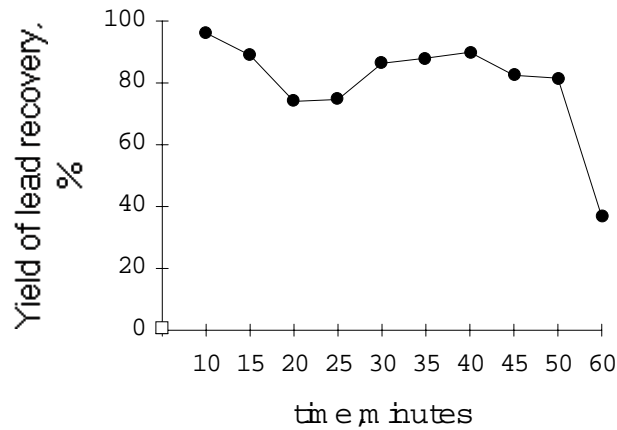
Fig. 3 Effect of decoppering time on the yield of the treated lead-antimony bullion
(t= 450°C , 1 st. ratio of pyrite + 0.25 % NaOH)
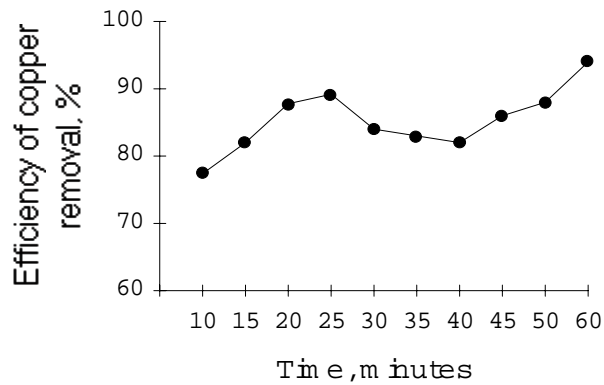Rys.3 Wpływ czasu prowadzenia procesu usuwania miedzi nawydajność uzyskania stopu Pb-Sb

Fig. 4 Efficiency of copper removal from lead-antimony bullion as a function of decoppering time. (t= 450°C , 1 st. ratio of pyrite + 0.25 % NaOH)
Rys.4 Efektywność usunięcia miedzi ze stopu Pb-Sb jako funkcja czsu prowadzenia procesu

Another set of experiments was conducted to determine the effect of using different stoitiometric ratios of pyrite to the hard lead under treatment on the efficiency of decoppering and the yield of the process. Experiments were conducted decoppering the samples for 30 minutes at 450°C. The results are presented in figure 5. It is seen that both parameters increase with an increase in the stoichiometric ratio of pyrite whereby 92% and 95.3 % were recorded respectively.
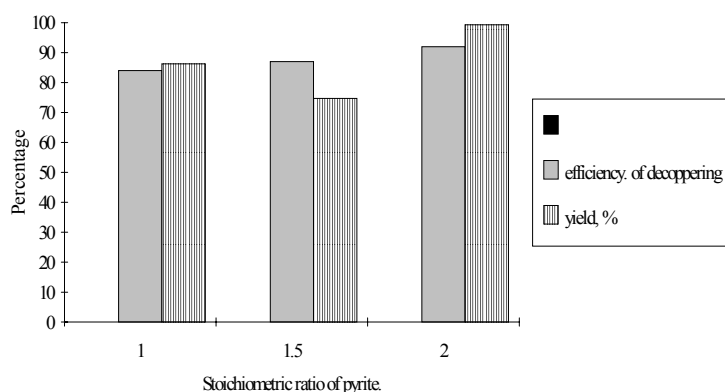
Fig. 5. Effect of stoichiometric ratio of pyrite on both the efficiency
of decoppering and yield percentage of the treated Pb-Sb bullion.
(t= 450°C , decoppering time, 30 min.)
Rys.5 Wpływ stosunku stechiometrycznego na wydajność i uzysk otrzymania stopu Pb-Sb

Fig. 6 shows the effect of addition of NaOH to pyrite on the yield using stoichiometric ratio of pyrite equals to 2. It is clear that the yield increases with the increase weight of NaOH reaching a value of 95.3 % at $\geq$ 0.5 % NaOH.

The effect of temperature on decoppering and antimony content of the hard lead alloy has been carried out (Figures not given). Results obtained show that after 10 minutes, residual copper percentage in the treated lead alloy does not change with increase in temperature from 350 up to 450 °C. However, with further increase in temperature up to 500 °C a minimum copper content in the product is attained. At higher temperature, 550°C, residual copper percentage increases. Antimony content acquires its lowest content at 400°C. At this temperature, the metal content is directly related to time of treatment. With respect to the yield of lead alloy, it decreases slightly with the corresponding increase in temperature
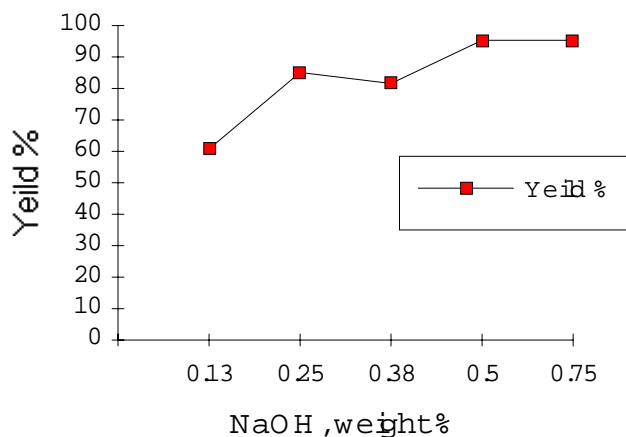

Fig. 6 Effect of NaOH on the yield percentage of lead
(t= 450°C , 2 st. ratio of pyrite)
Rys.6 Wpływ dodatku NaOH na uzysk ołowiu

A kinetic study of the decoppering process was carried out within the temperature range 350-550 °C for two minutes. Figure 7 illustrates Arrhenius plot

using pyrite with a stoichiometric ratio of 2. Activation energy of the decoppering process was computed and a value of 3.58 kJ/mole is obtained.
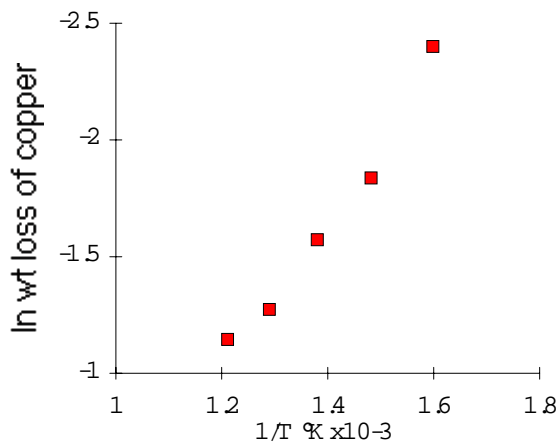

Fig. 7 The Arrhenius plot of decoppering process
Rys.7 Wykres Arrheniusa dla procesu usuwania miedzi

DISCUSSION

Pyrite (FeS_2) is conventionally used for decoppering of commercial hard lead-antimony alloys. The purpose of this work is to evaluate the decoppering efficiency of pyrite in alkali medium. When elemental sulphur is utilized for decoppering process, copper sulphide CuS is formed which may react further with Cu to form Cu_2S :

$$CuS + Cu \quad\quad Cu_2S \quad ....(1)$$

When pyrite is used instead of sulphur, no crystals of CuS or Cu_2S are formed. Instead, copper reacts with pyrite to give chalcopyrite $CuFeS_2$. It may further reacts with copper to give fornite according to :

$$3\ CuFeS_2 + 2Cu \quad\quad Cu_5FeS_4\ (\text{fornite}) + 2\ FeS...(2)$$

Since FeS_2 can be reduced to FeS, and it can react with PbS:

$$FeS + PbS + Cu \quad\quad CuFeS_2 + Pb.....................(3)$$
$$FeS + 4PbS + 5Cu \longrightarrow Cu_5FeS_4 + 4\ Pb...................(4)$$

The formed fornite do not appear to undergo to the backword direction of copper. Pyrite also enables lower copper content in lead at higher temperature.

The findings of this work can be explained according to the following model which assumes:

- chalcopyrite is the main product of reactions involved in the early stage of the decoppering process.

- formed chalcopyrite floats and goes into slag due to its relatively lower density and this is enhanced by decreasing the viscosity of the system
- diffusion of chalcopyrite into slag takes place more readily as the alkalinity increases.
- addition of alkali caustic soda decreases the viscosity of the system
- a far as sulphide formation is concerned, probably metals present in the system (lead, antimony and copper) are able to react with chalcopyrite

 $CuFeS_2 + M \quad\quad MS + FeS + Cu$ ....(5)
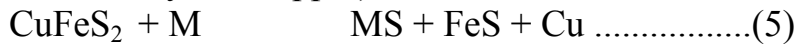
    where M is antimony or lead.
- from the thermodynamic properties of the involved reactions of the decoppering process, the activation energy of sulphide formation decreases in the order CuS > Sb_2S_3 > PbS interms of the slope of the curves of Arrhenius plot study (Figures not given).
- antimony sulphide is a thermally less stable compound as compared to lead sulphide. Antimony sulphide decomposes to antimony and nascent sulphur :

    $Sb_xS_y \quad\quad xSb + y\,S$ ....(6)

The liberated sulphur re-reacts with the more susceptible metal in the order given above.
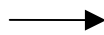
It is thus seen that copper content in hard lead-antimony alloys decreases within the early period of treatment with pyrite. After long periods, copper content re-increases satisfying reaction (5). With further time of treatment copper may re-decrease again via formation of copper sulphide. It is a cycle of copper content that is related to time.

CONCLUSION

The findings of this paper can be concluded as follows. Addition of sodium hydroxide to pyrite helps a removal of copper via decreasing the viscosity of the formed molten slag. It also decreases return of chalcopyrite going into molten lead and backward reaction liberating metal copper. Addition of sodium hydroxide also helps decoppering process with highest yield percentage as compared to the same reagents without alkali addition.

REFERENCES

Bowers, J.E. and Johnston, R.D., 1984, "Continuous refining of secondary lead", Miner. Process. Extr. Metall. Int. Conf.(UK), 63-71.

Bowers, J.E., 1983, "Continuous method for removing copper from lead", patent US no. 4390363 (USA).

Dautov, R.S., 1991, "Refining of molten crude lead in electric furnace", U.S.S.R. Su 1,696,541,07, (45), 107.

Davey, T.R.A., 1980, "The physical chemistry of lead refining", Lead- Zinc- Tin 80, (Proc. Conf.) Las Vegas.

Davey, T.R.A., Jensen, G. and Segnite, E.R., 1980, "Decoppering of lead and hard lead by stirring with sulfur and pyrites", Extractive Metallurgy Symposium, Sydney, Australia.

Etsuji, K. and Hiromi, M., 1987, "Copper removal from lead by dry method", Jpn. Kokai Tokkyo Koho JP 62 33,728; 5pp.

Khodov, N.V., Suturin, S.N., Meshkov, E.I. and Dolgov, A.V., 1982, "Centrifugal crude lead decoppering), Tsventn. Metall [Russian], (6), 22-24.

Kopylov, N.I., et.al., 1982, "Decoppering lead by centrifugal filtration", Tsvetn. Met., (7), 19-21 (in metal abstract, 1983, vol. 16 43-0099).

Lepain, E., Sanchez, G., Chabry, P. and Kollar, R., 1991, "Process for refining lead especially for removing copper", Ausz. Eur. Patent No. EP0456528, 7, (46).

Matini, C. D. and ýLambert, R.F., 1980, "New detellurizing and decopperizing practices at Omaha refining of Asarco", Lead- Zinc- Tin, 80 [Proc. Conf.] Las Vegas; 333- 347.

FIGURE CAPTIONS

Fig. 1 Effect of decoppering time on copper residue in the treated lead-antimony bullion

Fig.2 Antimony content in the treated lead-antimony bullion as affected by decoppering time

Fig. 3 Effect of decoppering time on the yield of the treated lead-antimony bullion

Fig.4 Efficiency of copper removal from lead-antimony bullion as a function of decoppering time.

Fig.5. Effect of stoichiometric ratio of pyrite on both the efficiency of decoppering and yield percentage of the treated Pb-Sb bullion

Fig. 6 Effect of NaOH on the yield percentage of lead

Fig. 7 The Arrhenius plot of decoppering process

Rabah M.A., Barakat M.A., Farghaly F.E., Wpływ dodatku sody kaustycznej na obniżenie zawartości miedzi w ołowiu antymonowym (stop Pb-Sb) przy użyciu pirytu.

W pracy przestawione zostały wyniki opisujące wpływ dadatku sody kaustycznej na obniżenie zawartości miedzi w ołowiu antymonowym (stop Pb-Sb). Proces ten polega na ponownym stopieniu stopu wraz z dodatkiem sody kaustycznej i pirytu. Proces stapiana jest realizowany w temperaturze $350 – 550^0C$ przez okres około jednej godziny. Parametrami procesu są: stosunek stechiometryczny sklaników, stężenie NaOH, czas, temperatura, uzysk i zawartość antymonu w stopie. Zostało ustalone, że dla stosunku stechiometrycznego 2, przy 0.5% NaOH w temperaturze 450^0C można uzyskać obniżenie zawarości miedzi w stopie z 0.56 do 0.03%. Czs trwania procesu był około 30 minut. Efektywność usunięcia miedzi wyniosła 92% przy uzysku stopu 95%. Zanotowano niewielkie straty antymonu z 2.77% na 2,4%. Ustalono, że głównym produktem odpadowy procesu jest chalkopiryt. Powstały w procesie chalkopiryt tym łatwiej przechodzi do żużla im jest on bardziej zasadowy co jest sopwodowane obniżenie się lepkości żużla.