JOURNAL OF APPLIED ELECTROCHEMISTRY 4 (1974) 279–288

Monitoring of impurities in molten lead by e.m.f. measurements. Application to the Harris process of lead refining

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Received 18 February 1974

E.m.f. measurements on the cell Pt, Fe, M(Pb)| NaOH| Cu_2O, Cu, Pt (M = As, Sn, Sb) at 450°C have shown the feasibility of using this system for direct monitoring of the impurity content of molten lead during the Harris process of lead refining. The reference electrode/electrolyte system described can be used to achieve the selective separation of antimony from the other impurities, arsenic and tin. Besides laboratory experiments, some tests of the system on an industrial scale are described.

1. Introduction

The Harris process of lead refining is widely used for removal of the arsenic–antimony–tin group of elements [1]. In a first step, lead bullion heated to a temperature (450°C) is circulated through a mixture of molten sodium hydroxide and an oxidizing agent such as sodium nitrate. The impurities are oxidized and form sodium salts, the lead remaining unaffected. In a second step the sodium salts suspended in the alkali mix are separated and recovered by a wet chemical treatment.

The continuous monitoring of the impurities in the molten lead would be interesting from the point of view of selectively extracting the impurities, allowing precise determination of the end of each refining step. The purpose of this investigation was the development of a probe which can be inserted directly in the molten lead in the Harris apparatus during its operation. An electrochemical method has been selected which is based upon the varying affinities for oxygen of the impurities. It essentially consists of the measurement of oxygen activity in the molten lead by e.m.f. measurements.

Over the last decade, solid electrolytes have been used with great success for oxygen activity measurements at high temperatures [2]. For several reasons, such as their rather low mechanical strength, and specially their relatively low conductivity at the temperatures of interest, these electrolytes were not used in this work. Instead research has been directed to the development of an oxygen concentration cell using molten sodium hydroxide as the electrolyte.

2. Experimental

2.1. *Chemicals*

Sodium hydroxide (p.a.*, UCB) was used as received. DTA experiments (Stanton Type Standata; nitrogen atmosphere; heating rate 15° min^{-1}) indicated that sodium hydroxide is stable in a temperature range from 318°C (melting point) to about 600°C. At higher temperatures, decomposition with loss of water starts to proceed at an appreciable rate. The influence of water in the electrolyte will be discussed below.

Nickel oxide; NiO, and copper oxide, Cu_2O, were used as received (p.a., UCB).

All the metals used in this work were furnished by Metallurgie Hoboken-Overpelt. Lead

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* p.a.=pro analysis, A.R. quality

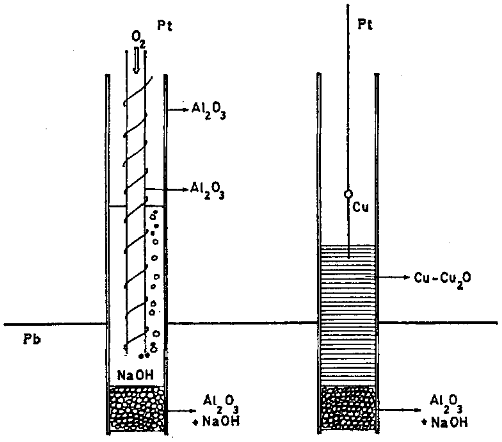
of purity 99·99% was used for the experiments. Tin and antimony were added to the molten lead as alloys of composition 85·64% Pb–14·36% Sn and 83·39% Pb–16·61% Sb (wt %). Arsenic was added as the element since the preparation of homogeneous solid arsenic–lead alloys encountered some difficulties.

Oxygen was dried by passing the gas through concentrated sulphuric acid and a tube filled with anhydrous magnesium perchlorate.

Pure argon gas was successively led over copper (450°C) and titanium (900°C) turnings.

2.2. *Reference electrode–electrolyte system (probe)*

A schematic representation of the probe used for the measurements, comprising the reference electrode and the electrolyte, is shown in Fig. 1.



(a) (b)

Fig. 1. Schematic representation of the probe used for the measurements, comprising reference electrode and electrolyte. (a) oxygen gas electrode, (b) metal–metal oxide electrode.

The reference electrode and the molten lead electrode are separated by a porous plug which was impregnated with the electrolyte.

The plug was made by introducing a paste of alumina powder (Alumina Prothermac STD) and water (90:10 wt ratio) into an alumina tube (Dégussit Al 23) and heating for about 2 h at 1100°C. The alumina powder used contains a relatively high amount of calcium oxide (95 wt % Al–2·7 wt % Ca) which probably serves as binding material (it was found impossible to make the plug with reagent grade alumina powder).

Both oxygen gas and metal–metal oxide electrodes were used as reference electrodes.

To prepare metal–metal oxide electrodes, a mixture of the finely divided metal and its oxide was pressed on top of the porous plug and a connecting wire was inserted in this mixture. The alumina tube was then dipped for about 10 min in molten sodium hydroxide to impregnate the plug with the electrolyte and to ensure a good electrical contact between the solid mixture and the electrolyte. Oxygen gas electrodes were prepared in much the same way. Both types of electrodes had a good resistance to mechanical and thermal shock, whereas the internal resistance of the assembled cells never exceeded 10^3 Ω.

2.3. *Cells*

Two types of cells were used in this work. The first cell shown in Fig. 2 was used to test the behaviour of the reference electrodes and was designed for work with small quantities of lead (about 100 g for each run).

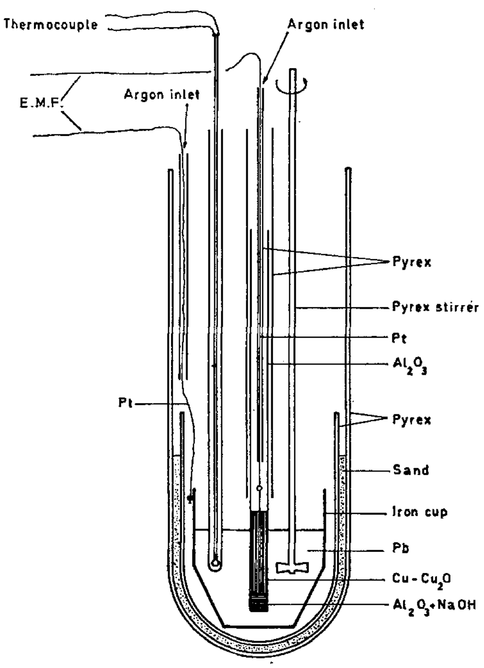


Fig. 2. Representation of the cell used for testing the behaviour of the electrode system, designed for work with small quantities of lead (about 100 g for each run).

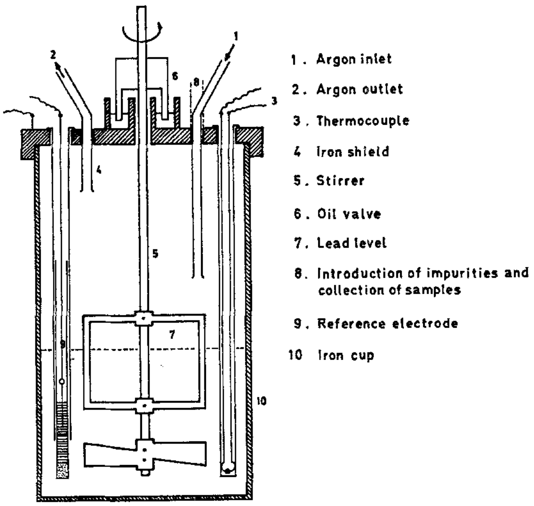


Fig. 3. Cell used for experiments involving impurities, designed to handle large quantities of lead (about 5–7 kg for each run).

The second cell, schematically depicted in Fig. 3 and designed to handle much larger quantities of lead (5–7 kg), was used for the main part of the experimental work involving addition of impurities to the molten lead. The cells were heated in an electric furnace, the temperature being measured with a Pt/Pt-Rh (10%) thermocouple. Temperature gradients were less than 2° for the first cell but were as high as 10°C for the second cell.

2.4. *E.m.f. measurements*

The e.m.f. values were measured ($\pm 0{\cdot}5$ mV) with a Philips PR 9403/01 high impedance voltmeter.

2.5. *Analytical methods*

The impurity content of the lead samples was determined by emission spectroscopy and X-ray fluorescence analysis, the first method being more sensitive, the second one however, being more precise.

3. Results

3.1. *Behaviour of reference electrodes. Oxygen activity in molten lead*

To test the behaviour of the reference electrodes a series of e.m.f. measurements was performed with the cell.

$$\text{Pt, Fe, Pb(l), PbO(s)}|\text{NaOH}|\text{Cu}_2\text{O(s), Cu(s), Pt} \qquad \text{I}$$

Before presenting the experimental results, the different electrodes used in this work are briefly discussed.

In molten sodium hydroxide one must consider the equilibrium

$$2\,OH^- \rightleftharpoons O^{--} + H_2O \qquad (1)$$

for which the equilibrium constant $K = (O^{--})(H_2O)$ has been determined as $10^{-7\cdot9}$ at 427°C by Antropov and Tkalenko [3].

The solubility of oxygen in molten lead has been determined by Alcock and Belford [4] and Richardson and Webb [5] as 0·00065 at% (0·000050 wt %) at 400°C and 0·0062 at% (0·00048 wt %) at 500°C. The partial pressure of oxygen in argon purified as described in the experimental section is of the order of 10^{-12} atm [6], much higher than the partial pressure of oxygen in lead at 450°C (about 10^{-20} atm). Therefore pure lead will be oxidized even under an argon atmosphere and some lead oxide will always be present. Coulometric experiments [7] have shown that lead in molten alkali hydroxides is oxidized to the bivalent state. Furthermore, lead oxide is only sparingly soluble

$$Pb^{++} + O^{--} \rightleftharpoons PbO\,(s) \qquad (2a)$$

$$\text{or} \quad Pb^{++} + 2OH^- \rightleftharpoons PbO\,(s) + H_2O \qquad (2b)$$

Experimental work by Speranskaya [8] and Slonimskii [9] indicated that reaction between lead oxide and molten sodium hydroxide

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O \qquad (3)$$

starts only at 800–830°C, in agreement with thermodynamic work of Lovchikov [10]. The electrode reaction at the molten lead–lead oxide electrode can thus be written as

$$PbO(s) + 2e^- \rightarrow Pb + O^{--} \qquad (4a)$$

$$\text{or} \quad PbO(s) + H_2O + 2e^- \rightarrow Pb + 2OH^- \qquad (4b)$$

Similarly the electrode reaction for the copper–copper oxide electrode can be written as

$$Cu_2O(s) + 2e^- \rightarrow 2Cu + O^{--} \qquad (5a)$$

$$\text{or} \quad Cu_2O(s) + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \qquad (5b)$$

Stern and Carlton [11] have shown that copper is not attacked by molten sodium hydroxide below 500°C. Furthermore it has been shown that copper oxide is sparingly soluble in acidic molten alkali hydroxides (relatively high water content) [12].

The cell reaction for cell I is then given by

$$Pb + Cu_2O \rightarrow 2Cu + PbO \qquad (6)$$

and the e.m.f. of the cell can be calculated from the standard free energy of the reaction at a given temperature. Since water does not take part in the cell reaction, the e.m.f. of the cell must be independent of the water content of the electrolyte. At 450°C, the experimental e.m.f. value is 162 (±3) mV. Experimental e.m.f. values as a function of temperature are compared in Fig. 4 with the values obtained by Alcock and Belford [4] with the aid of the cell

$$\text{Pt,Ir, Pb(l), PbO(s)} | ZrO_2\text{-MgO} | \text{CuO(s), Cu(s),Pt} \qquad \text{II}$$

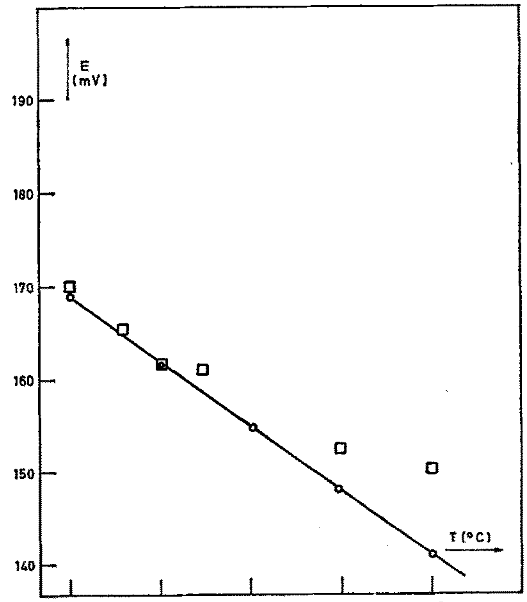


Fig. 4. Comparison of experimental e.m.f. values (-□—□-) as a function of temperature with data of Belford and Alcock [4] (-○—○-); see text.

The agreement is reasonable in the temperature range 400–550°C. At higher temperatures sodium hydroxide starts to decompose and copper metal is possibly slowly attacked by the electrolyte. In the lower temperature range, potentials reached a steady value within a few minutes after the system attained a constant temperature. Upon passing a small current through the cell once a steady potential was attained, the potential returned to this value within a few seconds after switching off the current.

Similar results were obtained with the nickel–nickel oxide electrode and the oxygen gas electrode, although for both electrodes the standard deviations of the e.m.f. values were much higher (±10 mV for both electrodes). Therefore, only copper–copper oxide electrodes were used for the work involving impurities. The fact that even cells with an oxygen gas electrode give e.m.f. values in reasonable agreement with known thermodynamic data might be somewhat surprising in view of published data on the irreversibility of this electrode (at 450°C, the e.m.f. of the cell Pt, Fe, Pb(l), PbO(s)|NaOH|O_2 (1 atm), Pt was determined as 790 (±10) mV, whereas a value of 785 mV was calculated from the free energy of formation of lead oxide, $\Delta G_f^\circ = -72{\cdot}426$ cal mol^{-1} oxygen, given by Alcock and Belford [4].)* The results presented in this section by no means imply that sodium hydroxide is the ideal electrolyte for the precise determination of thermodynamic values from e.m.f. measurements on systems involving oxygen gas or metal–metal oxide electrodes. It must be stressed, however, that such measurements are apparently feasible, albeit with less precision than can be obtained

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* The oxygen gas electrode in molten alkali hydroxides has been studied by several authors [3, 13–16]. According to Krüger *et al.* [16], the overall reaction

$$O_2 + 4e^- \rightarrow 2O^{--}$$
$$\text{or} \quad O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

can be split up into two steps according to

$$O_2 \ + 2e^- \rightarrow O_2^{--}$$
$$O_2^{--} + 2e^- \rightarrow 2O^{--}$$

whereby the first step is potential-determining, the second step being slow. The apparent reversibility of the oxygen gas electrode in molten alkali hydroxides with a relatively high water content might be coupled with the finding of Antropov and Tkalenko [3] that O_2^{--} is not a stable species in such solutions. Increase of the water content also diminishes the concentration of O^{--} ions, see equilibrium of Equation 1. The electrode reaction might involve direct discharge of water molecules as was already suggested by the kinetic investigations of Agar and Bowden [13]. The experiments described in this paper were performed with sodium hydroxide containing about 5 g H_2O per kg NaOH.

with solid electrolytes. It would be interesting to investigate whether this also remains true in the lower temperature range where the low conductivities of solid electrolytes prohibit their use for e.m.f. measurements.

More kinetic information on the oxygen gas electrode in molten alkali hydroxides with relatively high water content would also be desirable. With respect to the kind of measurements involved in the main part of this work, it is clear that a large and well-defined potential jump at the end of the extraction is more important than the absolute potential values.

3.2. *Determination of impurities in molten lead by e.m.f. measurements*

The Harris process is based upon the varying affinity for oxygen of the different impurities—arsenic, tin and antimony—in the molten lead. Contrary to the case of lead oxide, the oxides of the impurities react with molten sodium hydroxide and are extracted as sodium salts.

Lauterbach [17] and Neumann and Knoblich [18] have studied the mechanism of the oxidation of arsenic, tin and antimony, and the formation of the corresponding sodium salts. The kinetics of these reactions was investigated by Behl *et al.* [19] and by Paschen and Winterhagen [20]. The thermodynamics of the reaction was studied by Lovchikov [10, 21], and the solubility of the sodium salts in molten sodium hydroxide was investigated by Lauterbach [17] and Lovchikov [22].

When the impurities are added to the molten lead, they react with the lead oxide and the oxygen dissolved in the molten lead phase. In view of the small quantity of lead oxide and the low solubility of oxygen in lead, the impurities are always present in large excess when compared to the available quantity of oxygen (even if only 0·1 wt % impurity is added) so that, at least in the beginning of the experiment, their concentration can be regarded as constant.

Under these conditions it is probably justified, taking tin as an example, to represent the cell by

$$\text{Fe, Sn(Pb), } Na_2SnO_3(s)|NaOH|Cu_2O(s)\text{, Cu(s), Fe} \qquad \text{III}$$

The cell reaction can be written as

$$Sn + 2Cu_2O + 2NaOH \rightarrow 4Cu + Na_2SnO_3 + H_2O \qquad (7)$$

and the e.m.f. of the cell is given by

$$E = E^{0\prime} + \frac{RT}{4F} \ln a_{Sn} = E^{0\prime\prime} + \frac{RT}{4F} \ln c_{Sn} \qquad (8)$$

since sodium stannate is insoluble in molten sodium hydroxide at 450°C [22]. The water content of the electrolyte and the activity coefficient of the impurity in the molten lead have been considered as constant. The oxygen activity is fixed by the formation of the insoluble tin compound. According to Equation 8, the e.m.f. of the cell should depend only on the concentration of the impurity in the molten lead and obey the normal logarithmic law.

In actual practice the e.m.f. of the cell reaches a steady value almost immediately after addition of the impurity to the molten lead. The e.m.f. then remains constant for a period ranging from some 30 min to several hours, depending on the impurity. Afterwards, as more and more oxygen diffuses into the molten lead, the impurity becomes increasingly oxidized and finally the

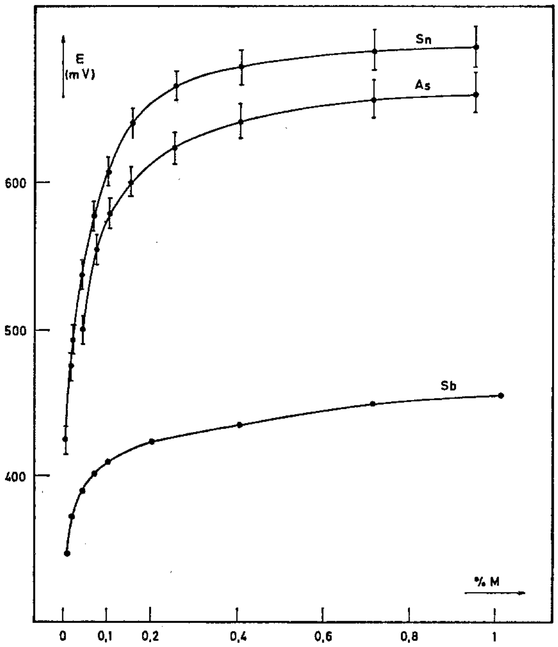

Fig. 5. E.m.f. of the cell Pt, Fe, M(Pb)|NaOH|Cu_2O, Cu, Pt as a function of the impurity content of the molten lead at 450°C for different impurities.

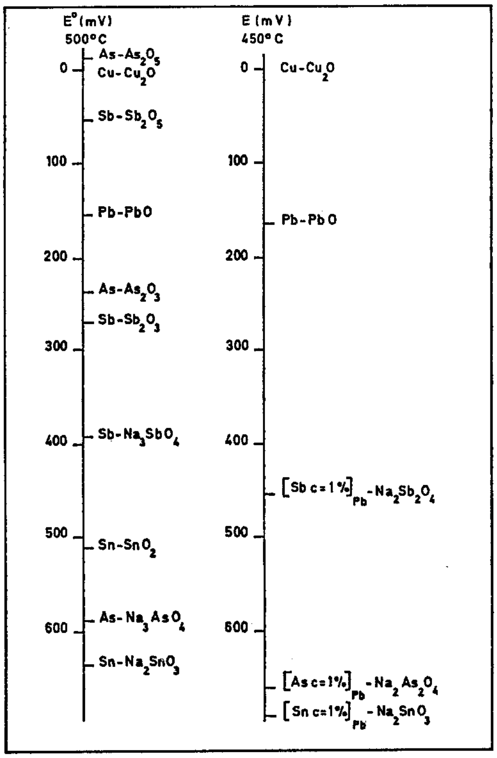

Fig. 6. Comparison of calculated (E^0) and experimental (E) e.m.f. values for the cell Pt, Fe, M(Pb)|NaOH|Cu$_2$O, Cu, Pt.

potential falls back to the value observed for the lead–lead oxide couple.

In Fig. 5, experimental e.m.f. values are shown for the different impurities as a function of their concentration.

In Fig. 6, e.m.f. values calculated for different oxides and their sodium salts are compared with the experimental values observed upon addition of 1% of the impurity to the molten lead. The formation of sodium arsenite and antimonite during the Harris process has been reported, but thermodynamic data are not available.

The precision of the data of Fig. 5 for tin and arsenic is not high enough to allow verification of the logarithmic law predicted by Equation 8, in sharp contrast to the very good reproducibility obtained for antimony. This difference probably is due to the fact that tin and arsenic are much easier oxidized than antimony as is also clear from the experimental and calculated e.m.f. values. A logarithmic plot of the data of Fig. 5 for antimony is shown in Fig. 7. Nernstian behaviour is observed with a slope of 45·8 mV per decade as calculated by least squares analysis. This might suggest that antimony is extracted as sodium antimonite, Na$_2$Sb$_2$O$_4$, for which the

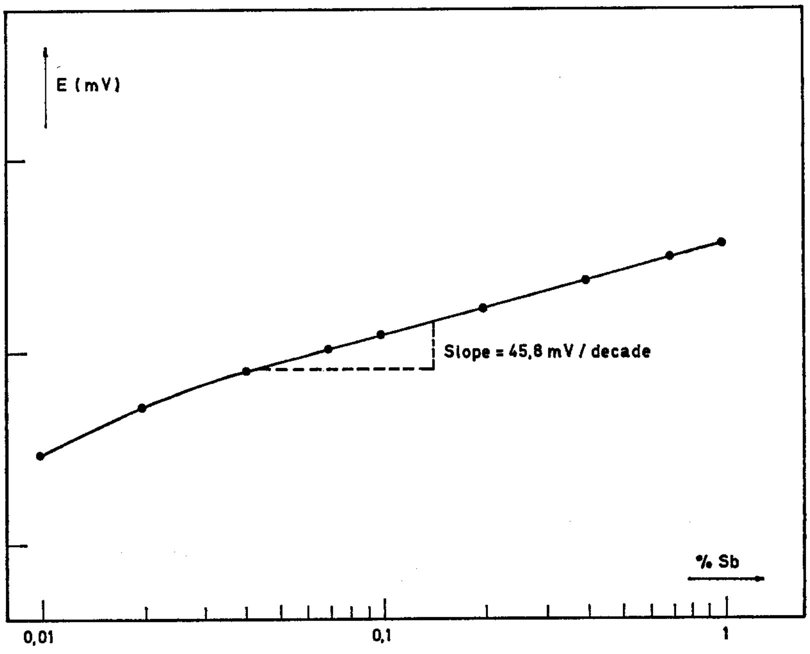

Fig. 7. Verification of the logarithmic Equation 8 for antimony in molten lead at 450°C.

theoretical value has been calculated as 47·7 mV per decade. Under the actual conditions of the Harris process, the antimonite may be further oxidized to the antimoniate due to the presence of sodium nitrate in the alkali mixture.

Finally, in some experiments several impurities were added successively to the molten lead. A typical curve is shown in Fig. 8. Upon successive addition of antimony, arsenic and tin to the molten lead (0·2 wt % for each impurity) the e.m.f. is determined successively by the couples lead–lead oxide, antimony–antimonite . . . as could be expected from thermodynamic data.

The results presented in this section clearly demonstrate the possibility of monitoring the concentration of impurities such as arsenic, tin and antimony in molten lead by e.m.f. measurements. To investigate whether this is also possible under the actual conditions of the Harris process, a series of e.m.f. measurements was performed on a laboratory and an industrial scale.

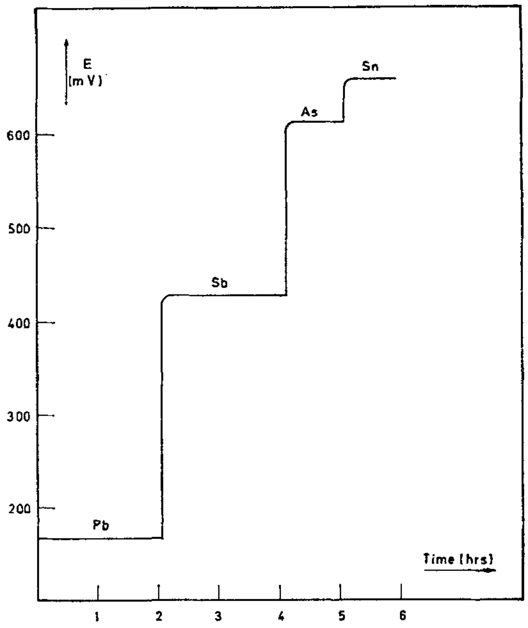

Fig. 8. E.m.f. of cell Pt, Fe, M(Pb)|NaOH|Cu_2O, Cu, Pt upon successive addition of various impurities (0·2 wt %) to the molten lead at 450°C.

3.3. *Monitoring of impurities in molten lead by e.m.f. measurements during their extraction on a laboratory and an industrial scale*

During the Harris process, arsenic (±0·04 wt %) and tin (±0·15 wt %) are extracted together but due to the difference in their concentrations, an appreciable quantity of tin remains in the molten lead when all the arsenic is already oxidized. The extraction of antimony (±1%) starts only after virtually all the tin has passed into the extractive phase. The end of the extraction of antimony can be determined visually by experienced workers. It would be interesting, however, to achieve the selective separation of arsenic and tin from antimony, i.e., to determine exactly the point where all tin is extracted. Therefore a series of experiments on a laboratory scale has been performed on the extraction of tin. The extractive phase consisted of 80 wt % NaOH–20 wt % NaCl, sodium nitrate being used as the oxidizing agent. The quantity of sodium nitrate added was calculated from the stoichiometry of the reaction

$$5Sn + 4NaNO_3 + 6NaOH \rightarrow 5Na_2SnO_3 + 3H_2O + 2N_2 \qquad (9)$$

The tin content of the molten lead was determined by analysis of samples taken at different times during the extraction. Although the logarithmic relation between e.m.f. and tin concentration could not be verified, as already noted in the previous section, the e.m.f. values recorded during the experiment exhibited a well-defined potential break at the end of the extraction.

In view of these promising results, a limited number of experiments has been performed with the reference electrode/electrolyte system on an industrial scale, i.e. in the Harris apparatus during its operation (experiments were performed at the Hoboken plant of Métallurgie Hoboken-Overpelt; the quantity of lead involved in each run is about 200 ton). The experimental set-up used for these measurements, with the electrode system floating on the molten lead, is shown in Fig. 9.

The electrodes were shielded by an iron tube, which also made contact with the molten metal, to protect them from the important quantity of lead oxides (dross) formed on the surface which could lead to mechanical damage of the electrodes. The results obtained during a typical run are shown in Fig. 10. A striking feature of the results in Fig. 10 is the e.m.f. break of about

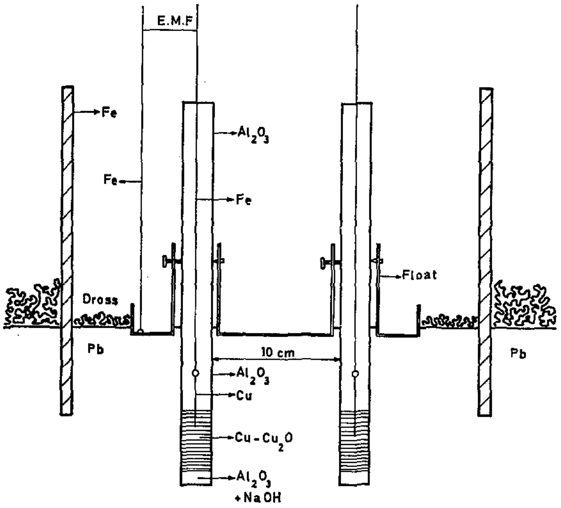

Fig. 9. Experimental set-up for experiments on an industrial scale.

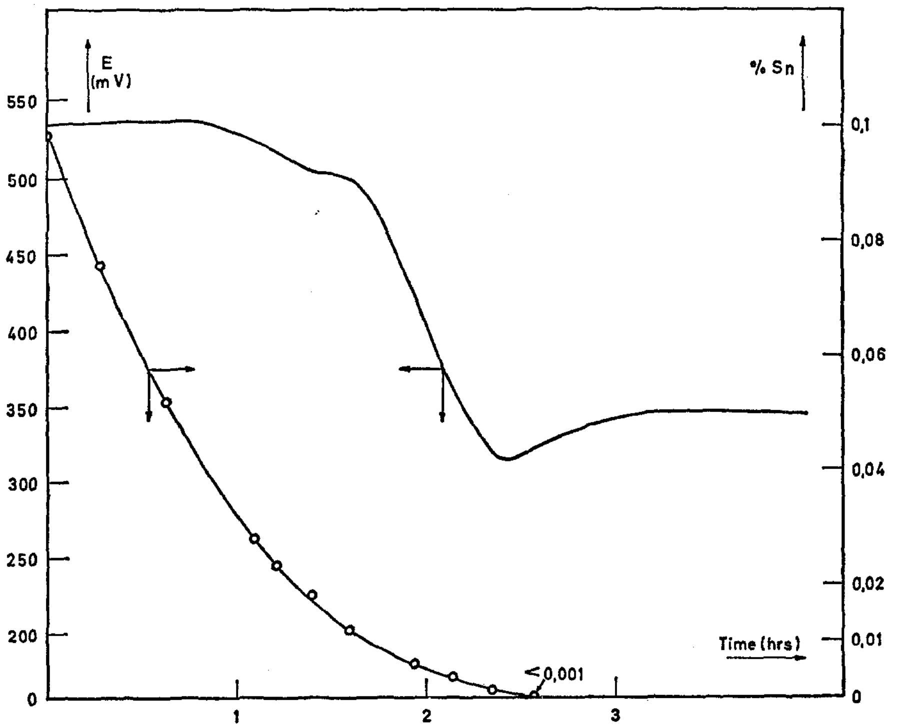

Fig. 10. Evolution of tin concentration in molten lead and e.m.f. during extraction on industrial scale.

215–220 mV at the end of the extraction of tin (and arsenic).

The tin-controlled e.m.f. values measured during extraction are systematically too low when compared with the results of Fig. 5. Furthermore, the final e.m.f. in Fig. 10 is 350 mV whereas the results of Fig. 5 suggest that the antimony-controlled e.m.f. should be about 450 mV in typical Harris metal. In the preceding section it was explicitly assumed that the available quantity of oxygen in the experimental cell used for laboratory experiments was very small when compared to the concentration of impurities in the molten lead. Thus, the e.m.f. of the cell was controlled only by the couple tin–stannate, arsenic–arseniate or antimony–antimonite—or, if several impurities are present at the same time, by the couple involving the impurity with the greatest affinity for oxygen—while no lead oxide is present. The assumption made, however, is no longer valid under the conditions of field experiments. Considering the case where antimony is the only remaining impurity in the molten lead, the e.m.f. is then determined both by the antimony–antimonite and lead–lead oxide couples, resulting in a shift towards lower e.m.f. values. In other words, a mixed potential exists for which the net chemical reaction taking place at the electrode can be written as

$$2Sb+3PbO+2NaOH \rightarrow Na_2Sb_2O_4+3Pb+H_2O \qquad (10)$$

This effect is not really important with regard to the practical applications of this work although, of course, the end-point in Fig. 10 is less well-defined.

It must be noted that absolute e.m.f. values measured with different electrode systems during the same run differed by as much as 40 mV, but the magnitude of the e.m.f. break was nearly the same. The obvious explanation for this fact is the existence of large concentration gradients in the bulk of the molten lead and at the surface.

Some laboratory experiments have also been successfully performed on the extraction of antimony, the e.m.f. of the cell after extraction dropping to the value characteristic for the lead–lead oxide couple. These experiments have not been extended on an industrial scale, however, since they were considered unnecessary in view of the visual criterion mentioned above for the determination of the end of the extraction of antimony metal. It is not expected, however, that there would be any practical problems in determining the end of the extraction of antimony metal by electrode measurements if desired.

4. Conclusion

In conclusion it can be stated that the reference electrode/electrolyte system described in this paper can be effectively used for the monitoring of impurities in molten lead under the conditions of the refining of this metal by the Harris process. A word of warning is needed, however, with regard to the actual fabrication of the measuring probes in the sense that it needs an experienced worker in order to obtain a high degree of reliability (with some practice, some 90–95% of the probes behaved well during laboratory experiments, but only 65–70% could be successfully used for experiments on an industrial scale). Therefore, some more research on the practical aspects of this work is certainly desirable. The principle of the method, however, seems to be well-established although it might certainly be interesting to clarify some questions of a more fundamental nature.

Acknowledgement

The authors wish to express their sincere thanks to Professor Dr R. Breckpot for his advice and encouragement during this work.

References

[1] W. H. Dennis, 'Metallurgy of the non-ferrous metals', Pitman, London, 1961, p. 264.

[2] C. B. Alcock, Ed., 'Electromotive Force Measurements in High Temperature Systems', The Institute of Mining and Metallurgy, London, 1968.

[3] L. I. Antropov and D. A. Tkalenko, *Elektrokhimiya*, **6** (1970) 595; *ibid.* **6** (1970) 1557.

[4] C. B. Alcock and T. N. Belford, *Trans. Faraday Soc.*, **60** (1964) 822.

[5] F. D. Richardson and L. E. Webb, *Trans. Inst. Mining Metallurgy*, **64** (1965) 529.

[6] F. D. Richardson, Private communication.

[7] A. Eluard and B. Trémillon, *J. Electroanal. Chem.*, **30** (1971) 323.

[8] E. I. Speranskaya, *Russ. J. Inorg. Chem.*, **6** (1961) 1000.

[9] B. I. Slonimskii, *Tsvetn. Metal* (1961) 226.

[10] V. S. Lovchikov, *Tsvetn. Metal* (1964) 64.

[11] K. H. Stern and J. K. Carlton, *J. Phys. Chem.*, **58** (1954) 965.

[12] A. Eluard and B. Trémillon, *J. Electroanal. Chem.*, **18** (1968) 277.

[13] J. N. Agar and F. B. Bowden, *Proc. Roy. Soc. London*, A **169** (1939) 206.

[14] A. S. Afana'ev and V. P. Gamazov, *Russ. J. Phys. Chem.*, **38** (1964) 1537.

[15] J. Goret and B. Trémillon, *Bull. Soc. Chim. France* (1966) 67.

[16] H. J. Krüger, A. Rahmel and W. Schwenk, *Electrochim. Acta*, **13** (1968) 625.

[17] H. Lauterbach, *Metall und Erz*, **28** (1931) 317.

[18] B. Neumann and G. Knoblich, *Metall und Erz*, **31** (1934) 121.

[19] M. Behl, J. Gerlach and F. Pawlek, *Erzmetall*, **21** (1968) 411.

[20] P. Paschen and H. Winterhagen, *Erzmetall*, **21** (1968) 14.

[21] V. S. Lovchikov, *Tsetvn. Metal.* (1964) 88; (1969) 38, 56.

[22] V. S. Lovchikov, *Tsvetn. Metal.* (1964) 125.