Monitoring Sb in lead refining using advanced techniques in Industry 4.0

A. Van den Bulck[1], T. De Staercke[2], S. Zummar[3], and T. Van Rompaey[4]

1. Scientist, Corporate R&D Umicore, 2250 Olen, Belgium. Email: amy.vandenbulck@eu.umicore.com
2. R&D Project Chemist Adviser, Umicore, 2250 Olen, Belgium. Email: tinne.destaercke@eu.umicore.com
3. Process Engineering Manager, Umicore, 2660 Hoboken, Belgium: Email: shady.zummar@eu.umicore.com
4. Head of Research Operations & Technology, Umicore, 2250 Olen, Belgium. Email: tim.vanrompaey@eu.umicore.com

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ABSTRACT

An increase of 22 % in lead usage is expected in the European Union by 2050. During lead refining, the Harris process is a critical step in which a salt melt is used to remove arsenic, tin, and antimony. During this process, the caustic salt melt absorbs these impurities, requiring regular evacuation before saturation. Current metallurgical practices for 1) determining the end-point of the lead alloy involve time-consuming sampling and off-line analysis, and 2) determining the end-point of the caustic salt melt are based on subjective visual observations by the operator. In the context of Industry 4.0, automating these processes becomes desirable, as smart sensors systematically collect real-time data in an unbiased manner. This research focuses on monitoring the Harris refining process using objective methodologies. Two different methodologies are investigated. The first methodology focuses on electrical conductivity changes of the caustic salt melt as function of Sb content. For this study, synthetic and industrial samples are used. A lab-scale electrical conductivity set-up was built to accommodate the aggressiveness of the salt melt. Initial findings suggest a promising relationship between electrical conductivity and Sb content in the caustic salt melt. Although the results are preliminary, the study provides valuable insights by enabling real-time measurements. The second methodology focuses on measuring the electromotive force (EMF) in lead doped with Sb at pilot-scale. Multiple probes are reevaluated for their effectiveness in Sb measurement. Ultimately, a partially stabilized MgO probe with Ni as a reference, without cardboard and copper protection caps, yields promising results. A correlation between EMF and Sb content is observed. However, repeatability issues arise due to possible wire interference at low temperatures. The results underscore the potential of advanced measurement techniques in optimizing lead alloy production within the context of Industry 4.0.

INTRODUCTION

Lead (Pb) recycling has witnessed significant growth, rising from approximately 50% of total production output in 1990 to around 75% of current production (Roberts, 2020). The vital role of lead in the circular economy has been a point of discussion (Blanpain, Reuter, & Malfliet, 2019). As a 'carrier metal,' lead can dissolve or transport diverse materials—either directly or as compounds—into other processing pathways for subsequent recovery. Extensive studies have explored the thermodynamic relationships and limitations associated with lead, underscoring its critical importance within the metallurgical ecosystem. Despite efforts to reduce lead usage, such measures may adversely affect the recyclability of other materials, including Ag, Cu, Sb, Sn, Te, and Zn (Blanpain, Reuter, & Malfliet, 2019). Notably, if the European Union aims to achieve climate neutrality, it is projected that lead utilization will increase by 22% by 2050 (Gregoir, 2022). For these reasons, it is important to continue to improve lead operations by making them safer and more efficient. At Umicore's lead refinery, the Harris process is employed to extract arsenic (As), tin (Sn), and antimony (Sb). In this process, sodium hydroxide and sodium nitrate serve as sources of oxygen for the oxidation reaction, operating at temperatures exceeding 450°C (Sinclair, 2009; Lauterbach, 1931). The chemical reactions are as follows:

$$2[\mathrm{As}] + 2\mathrm{NaNO_3(s)} + 4\mathrm{NaOH(l)} \rightarrow 2\mathrm{Na_3AsO_4(s)} + \mathrm{N_2(g)} + 2\mathrm{H_2O(g)} \quad (1)$$

$$5[\mathrm{Sn}] + 4\mathrm{NaNO_3(s)} + 6\mathrm{NaOH(l)} \rightarrow 5\mathrm{Na_2SnO_3(s)} + 2\mathrm{N_2(g)} + 3\mathrm{H_2O(g)} \quad (2)$$

$$2[\mathrm{Sb}] + 2\mathrm{NaNO_3(s)} + 4\mathrm{NaOH(l)} \rightarrow 2\mathrm{Na_3SbO_4(s)} + \mathrm{N_2(g)} + 2\mathrm{H_2O(g)} \quad (3)$$

$$5[\mathrm{Pb}] + 2\mathrm{NaNO_3(s)} \rightarrow 4\mathrm{PbO} + 4\mathrm{Na_3PbO_2(s)} + \mathrm{N_2(g)} \quad (4)$$

The targeted elements are removed as sodium arsenate, sodium stannate, and sodium antimonate. Within the Harris cylinder, a layer of molten sodium hydroxide (NaOH) and sodium chloride (NaCl) floats atop the molten lead, called the caustic salt melt. The above compounds are present as a solid suspension in this molten caustic salt melt. However, a single Harris caustic salt melt is insufficient to eliminate all contaminants. As impurity concentrations rise in the caustic melt, its viscosity changes. When the melt reaches saturation and approaches excessive viscosity, it is evacuated from the cylinder. The melts can hold up to 20 wt.% of arsenic or tin, and 30 wt.% of antimony. Exceeding these limits results in overly viscous melts that cannot be evacuated from the cylinder (Lauterbach, 1931; Davey, 1980; Leroy, Lenoir, & Escoyez, 1970). While the Harris process recognizes viscosity as a limiting factor, the melt saturation level is currently assessed subjectively by the operator's visual judgment. Unfortunately, there are no recorded efforts to precisely measure the viscosity of the caustic salt melt; existing literature only provides information on saturation limits. In contrast to monitoring the Harris slag melt, attempts to monitor the lead melt have been done to determine when the impurities have been lowered to a desirable level. Traditionally, the end-point refining of lead alloys involves time-consuming sampling and off-line analysis. However, the use of electromotive force (EMF) of the oxygen potential has been demonstrated (Grange & Heerman, 1974; Kapusta, Meadowcroft, & Richards, 2002). In the first experiment (Grange & Heerman, 1974), a cell configuration involving Pt, Fe, Pb(l), PbO(s) | NaOH | Cu_2O(s), Cu(s), Pt is used to measure oxygen potential. The addition of different impurities to lead shows a clear effect on measured EMF. Industrial efforts were made where the tin concentration throughout the Harris process was compared to EMF measurements. A clear end-point of the refining process emerged when the EMF measure decreased by 215-220 mV and stabilised. These findings highlight the feasibility of using EMF measurements to monitor impurity levels during lead refining via the Harris process. However, challenges related to probe reliability exists, as specialized probes were required, and only 65-70% of them yielded successful measurements. In another attempt (Kapusta, Meadowcroft, & Richards, 2002), an oxygen probe is employed using a copper-copper oxide electrode within a cell configuration represented as: Fe (Stainless steel), Pb(l), PbO(s) | ZrO_2 doped Y_2O_3 | Cu_2O(s), Cu(s), Fe(stainless steel). The experimental approach mirrored the previous one, starting with laboratory tests to validate the probe's performance and followed by industrial monitoring of lead melts. The results show that utilizing oxygen activity EMF measurements to monitor the impurity content during lead softening is a viable approach. However, similar to the previous authors, probe construction challenges, particularly related to the thermal shock resistance of zirconia tubes, remains a major obstacle. The aim of the current study is two-fold. The first goal is to examine the electrical conductivity of the caustic salt melt as it relates to antimony (Sb) content. The hypothesis is that as Sb content increases, the presence of solid particles will alter the electrical conductivity path, resulting in changes to the overall electrical conductivity of the melt. The second part of the study focuses on testing new probes to address the existing construction challenges associated with the current probes. These new probes aim to enhance reliability and performance in measuring relevant parameters. By accomplishing these dual objectives, the way for automating the refining of the Harris process through the utilization of intelligent sensors is a possibility.

MATERIALS & METHODS

Materials

Industrial samples

The industrial caustic salt melt samples are directly obtained from the Umicore-Hoboken Sb-Harris cylinder at various points during the Sb removal process. The process operates within a 4-hour interval, commencing with a single pour of sodium hydroxide. This ensures a consistent rise in sodium antimonate content and prevents any dilution of the melt due to additional sodium hydroxide pours. Samples are collected at the 2-, 3-, and 4-hour marks, with the final sample taken just before cylinder evacuation. The samples are cast into round shapes with a diameter of 5 cm.

Synthetic samples

Pure anhydrous sodium antimonate is obtained from the Harris process wet plant at Umicore Hoboken and is used to create synthetic samples. These synthetic samples are prepared by mixing sodium antimonate with sodium hydroxide and sodium chloride, see the compositions outlined in Table 1. The quantities are calculated based on stoichiometry, assuming that the initial Harris salt melt has a 4:1 mass ratio of sodium hydroxide to sodium chloride, with only the former being consumed in the reaction to form sodium antimonate. Each sample weighs 250 g. To prevent exposure to ambient moisture, given the high hygroscopic nature of sodium hydroxide pellets, the preparation is conducted inside a glove box flushed with argon.

Table 1 - Synthetic caustic melt compositions for electrical conductivity measurements.

No.	Na_3SbO_4 (wt.%)	NaOH (wt.%)	NaCl (wt.%)	NaOH:NaCl ratio
1	0	80	20	4
2	32.5	52	15.5	3.4
3	44.0	42	14	3
4	53.0	34	13	2.6
5	31.0	27	12	2.3
6	73.0	17	10	1.7
7	0	60	40	1.5

Synthetic lead alloy samples are made by mixing pure lead (99.999 wt.%) coming from the end-product of Umicore's Hoboken lead refinery and fluxing with a Pb-65 wt.%/Sb-35 wt.% alloy during the EMF process. During the process samples are taken and sent for ICP-OES analysis.

Methods

Electrical conductivity measurements

A two-wire configuration is used to measure the electrical conductivity of both industrial and synthetic caustic melt samples. The setup includes 316L stainless steel crucibles with a volume of approximately 40 ml. For corrosion resistance, 1 mm diameter nickel wires are used as electrodes. These wires are enclosed in alumina tubes to enhance protection and rigidity, ensuring consistent cell geometry throughout the experiment. The electrodes protrude about 20 mm from the alumina tubes, maintaining a 6.2 mm distance between them. The electrodes are connected to a Keysight E4980A/AL Precision LCR Meter, which supplies an alternating current. The settings are set to 1 V and 100 kHz. A schematic of the setup can be found in Figure 1.

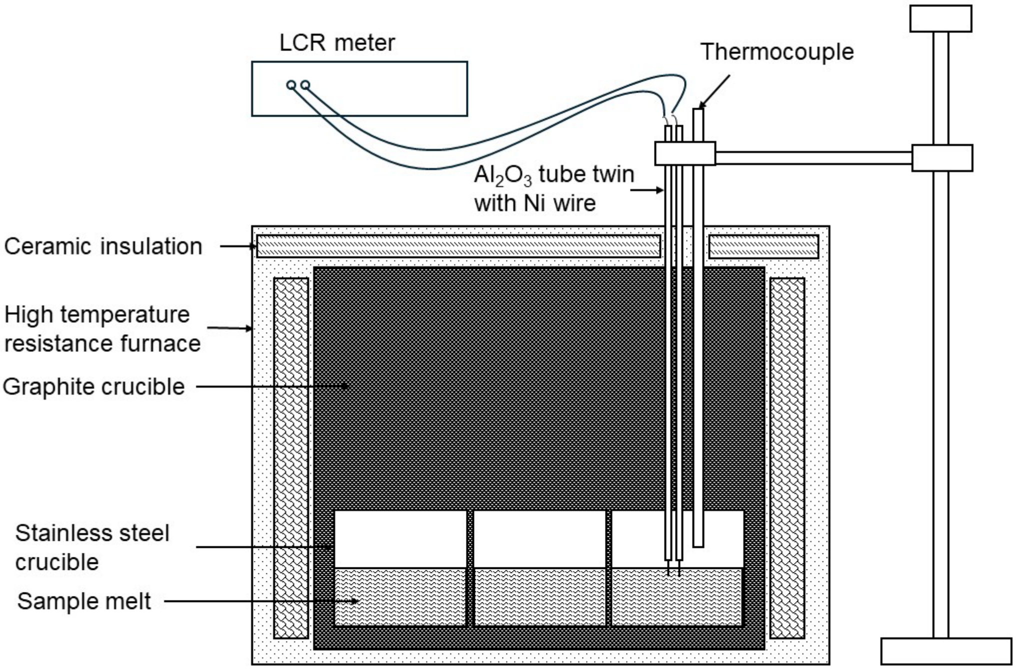

Figure 1 Schematic of setup for electrical conductivity measurement.

To maintain precise control, the setup is positioned atop a resistance furnace. Before conducting experiments, the cell constant is determined using 20 ml solutions of 0.01 M and 0.1 M potassium chloride. The electrodes are immersed to a depth of 4.5 mm, and the temperature-resistance data are used to derive the cell constant which is determined to be 1.41 cm^{-1}. Once the cell constant is established, crucibles containing the samples are placed in the furnace, raising the temperature to 485 °C. The estimated mass equivalent to 20 ml is carefully loaded into the crucible, avoiding direct exposure to ambient air. A nearby thermocouple ensures precise temperature control. Refractory bricks cover the furnace top, minimizing thermal fluctuations, while a continuous flow of argon prevents sample reactions with air. After reaching the target temperature, the samples are allowed to equilibrate for approximately an hour. A crucible containing material is positioned directly under the electrodes and the electrodes are lowered into the bath. As the electrodes lowered, a sudden decrease in resistance indicates contact with the melt's surface. At this point, the electrodes are further lowered by 4.5 mm and the resistance is recorded. Afterward, the electrodes are raised, and the crucible is replaced with the next sample. This process is repeated for each sample. Post-experiment, the distance between the electrodes is remeasured and no significant changes are observed, ensuring the cell's integrity.

Electromotive force measurements

The Pb-65 wt.%/Sb-35 wt.% alloy is created by melting pure lead with 99.999 wt.% pure Sb in a lab-scale resistance furnace using a graphite crucible at 650 °C under a nitrogen environment. The EMF experiments are performed on a pilot-scale resistance furnace. Pure lead of 439 kg is loaded into the furnace and melted to a temperature of 450 °C in an air environment. Throughout the experiments, the Pb-65 wt.%/Sb-35 wt.% alloy is added every 30 minutes. To ensure mixing, nitrogen is bubbled through the melt. Before conducting the EMF measurements, a sample is taken for chemical ICP-OES analysis. The details of the added material and the targeted Sb content in the lead alloy are provided in Table 2.

Table 2 - Added material to pure lead and target Sb content for EMF measurements.

No.	Pb/Sb alloy (kg)	Sb (wt.%)
1	0	0
2	311	0.02
3	313	0.05
4	1249	0.20
5	4370	0.75

Several EMF probes are tested. At low temperatures, probes with protective cardboard and/or copper caps did not dissolve, so it was decided to avoid using any protective caps. Furthermore, the sensitivity to thermal shock prevents the use of yttria-stabilized probes. Ultimately, a partially stabilized MgO cell with a Ni reference and a celox insert is used. The analysis of the EMF measurements is performed by the supplier.

RESULTS & DISCUSSION

Electrical conductivity measurements

After reaching the target temperature of 485 °C, the samples are allowed to equilibrate for approximately one hour. Upon visual inspection, it is evident that the synthetic samples containing sodium antimonate did not fully melt; instead, they form a paste-like consistency. These synthetic samples differ significantly from the industrial samples, as confirmed by probing the melts with a stainless-steel rod. The material exhibits extreme stickiness and adhered tightly to the rod. To maintain the electrode integrity, measurements are excluded for the synthetic samples. Only the pure salt synthetic sample and the fully melted industrial samples undergo the measurement. The sample composed of a pure salt mixture exhibits an electrical conductivity of 2.3 S/cm—significantly lower than the theoretical value for pure sodium hydroxide (17.3 S/cm) (Marcus, 2016). However, this measurement aligns more closely with findings from a study on the electroconductivity of sodium and potassium hydroxide eutectics, which reported a value of 1.7 S/m at 450 °C (Glibert & Claes, 1979). The discrepancy likely arises from variations in melt compositions and higher temperatures. Subsequent measurements for the industrial samples reveal a notable increase in resistance and a corresponding decrease in conductivity with each additional hour of processing. Additionally, the magnitude of measured reactance increases over time. The detailed results of the conductivity measurements are shown in Figure 2.

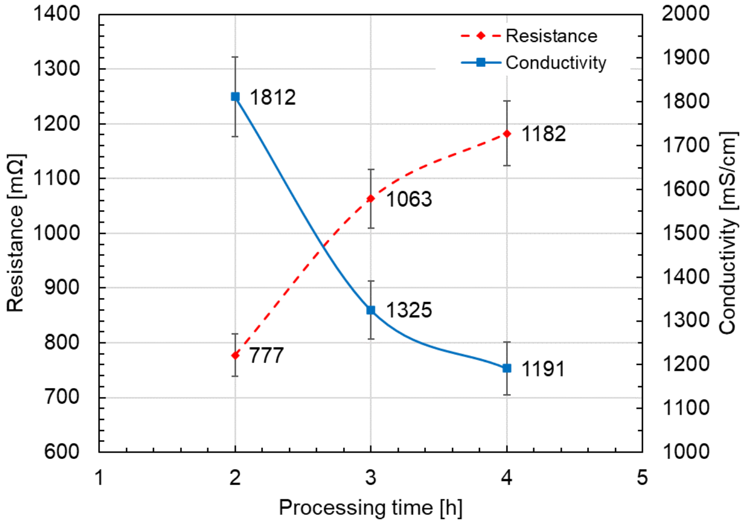

Figure 2 - Measured resistance and conductivity of industrial Harris caustic salt melt at 485 °C. The error bars indicate a 5 % error.

During the measurement, it is observed that resistance values exhibit continuous increase. However, after a few minutes, the resistance partially stabilizes. Although the rate of resistance increase becomes negligible, it never completely ceases. This fluctuation is likely attributed to the initial rapid corrosion of the electrodes, followed by a slower degradation. The degradation of the electrodes is visible notable. To assess the impact of corrosion uncertainty, the initially measured samples are retested, revealing an uncertainty of no more than 5%. Nonetheless, the electrical conductivity changes significantly as function of process time. The change in conductivity is likely attributed to 1) the presence of antimonate solids, and 2) the NaOH-NaCl ratio within the matrix. The overall outcome of this study is positive, but further optimization of the cell design is necessary. Nickel has been selected due to its high corrosion resistance in sodium hydroxide melts. However, it still experiences some attack during the measurements. The question remains whether the material will eventually form a passivating layer after initial exposure or continue to corrode.

Electromotive force measurements

Prior to conducting the EMF measurements, a representative sample for Sb content measurement in the lead alloy is taken. Subsequently, two EMF measurements are carried out for each fixed Sb content within the alloy. The resulting data is presented in Figure 3.

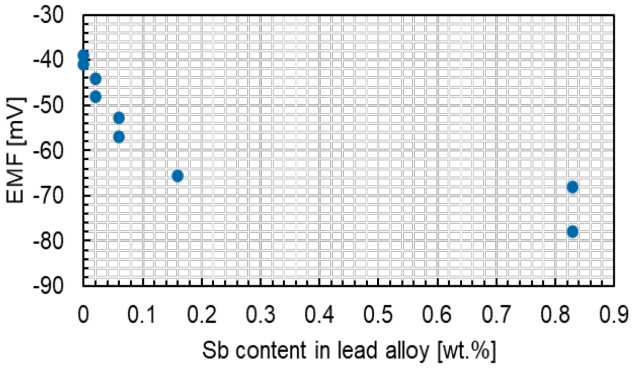

Figure 3 - EMF measurement as function of Sb content in lead alloy at 450 °C for one run. A second run could not yield the same results.

While the initial results indicate a positive outcome, a subsequent test repetition fails to reproduce the same findings. Specifically, these repeated tests reveal incomplete stabilization, which was attributed to the elevated resistance encountered due to the low temperatures of 450°C. The increased resistance may trigger other factors, including cable resistance, lance quality, and the overall measurement system. To address this challenge, ongoing efforts are focused on designing a specialized cell by the supplier. The primary goal is to minimize resistance during the measurement process.

CONCLUSIONS

Lead production volumes are projected to consistently increase, and lead's integral role within the circular economy is firmly established. Consequently, it remains critical to enhance lead operations by boosting efficiency and ensuring safety. In the context of Industry 4.0, it can be envisioned that the utilization of objective sensors and data-driven analyses can be made to draw informed conclusions. The objective of this study is to explore techniques for automating the Harris lead refinery process by incorporating real-time sensors in place of time-consuming analyses and subjective visual inspections of the Harris caustic salt melt saturation. In the first technique, the electrical conductivity changes as function of Sb content in the caustic salt melt that is investigated. This approach capitalizes on the interplay between chemical composition changes and the accumulation of particles within the molten material as the antimony concentration in the melt increases. The experiments focus on industrial caustic medium samples, exclusively containing antimony coming from Umicore's lead refinery, alongside to synthetic slags composed of pure materials to mimic the industrial composition. Interestingly, the behaviour of synthetic and industrial slags diverges significantly. While the former exhibits a thicker, paste-like consistency, the latter fully melts at operational temperatures. Unfortunately, a definitive explanation for this discrepancy could not be provided. Nevertheless, the insights primarily stem from the analysis of industrial samples. Given the plausibility of electrical conductivity as a reliable method, it is recommended to further refine this technique. Additional measurements using industrial samples can provide deeper insights into the relationship between electrical conductivity and antimony content. Additionally, the cell design must be investigated, as the nickel electrodes employed in the study suffer corrosive attack upon immersion in the melts. Aside its application in determining antimony saturation, it is suggested to investigate the impact of arsenic and tin on the electroconductivity of Harris slags as well. In the second technique, electromotive force measurements are reinvestigated. Unfortunately, akin to prior investigations, issues related to probe sensitivity hinders the attainment of satisfactory results. This challenge was attributed to the elevated resistance induced by the low operating temperature of 450 °C. To address this limitation, designing a specialized cell that can reduce resistance during measurements is proposed, thereby minimizing the impact of other artefacts.

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