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Determination of arsenic(III) in caustic melts*

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Voltammetric and potentiometric methods were evaluated for the determination of As(III) levels in molten sodium hydroxide at 450° C. Because of the crystallization of As(V) salts on the working electrode, voltammetric measurements were limited to less than 3 wt % As(III) in melts containing up to 6 wt % total arsenic and only 2 wt % in melts containing up to 12 wt % total arsenic. Potentiometry had maximum sensitivity when the As(III)/As(V) ratio was near 1 : 1 at 12 wt % total arsenic. The applicability of the two methods for control of an As(III) to As(V) oxidation process was evaluated.

1. Introduction

In a variation of the Harris process for refining lead, arsenic is selectively extracted from de-copperized lead bullion into a stream of molten caustic soda at 450° C, viz:

$$2\text{As(bullion)} + 6\text{NaOH(melt)} \longrightarrow 2\text{Na}_3\text{AsO}_3\text{(melt)} + 3\text{H}_2\text{(g)} \qquad (1)$$

The caustic melt, containing the arsenic as the trivalent species, is separated from the bullion and fed to an oxidizer where controlled quantities of sodium nitrate are added to oxidize the arsenic to the pentavalent state, viz:

$$5\text{Na}_3\text{AsO}_3\text{(melt)} + 2\text{NaNO}_3\text{(melt)} \longrightarrow 5\text{Na}_3\text{AsO}_4\text{(melt)} + \text{Na}_2\text{O(melt)} + \text{N}_2\text{(g)} \qquad (2)$$

The caustic stream is then fed to a separating tank, where, on cooling to about 370° C, the arsenic crystallizes as $Na_3AsO_4 \cdot 2NaOH$, in which form it is subsequently recovered.

Lead bullion being fed to the process is expected to contain ~0.7 wt % As. After the molten caustic extraction stage, the residual level in the bullion is expected to be ~0.25 wt % As. The enriched caustic melt being fed to the oxidizer is predicted to contain about 5 wt % As(V) and 5.1 wt % As(III). This latter concentration will be lowered to about 1.5 wt % by the oxidation of As(III) to As(V), Reaction 2.

During the oxidation step, the addition of sodium nitrate must be controlled to ensure that it is not added in excess, since its presence in the recycled caustic phase would cause unwanted extraction of other elements, such as antimony and tin, from the lead bullion. Such control could be effected by monitoring the As(III) concentration in either the inlet or exit stream of the oxidizer.

This paper describes the exploration of two electrochemical methods for the determination of As(III) concentration in molten sodium hydroxide. An assessment is also made of their applicability as *in situ* monitoring techniques.

2. Experimental details

2.1. *Preparation of melts*

Analytical reagent grade sodium hydroxide (M&B Pronalys) (~110 g) was heated to ~450°C in a recrystallized alumina crucible (Haldenwanger Alsint 6A, 60 mm diameter × 70 mm long) enclosed in a stainless steel vessel and maintained under flowing high purity nitrogen. The lid of the vessel was equipped with gas inlets/outlets and access ports to enable the addition of reactants and the insertion of electrodes. Oxidation stability tests were conducted on separate melts in a 15 mm diameter × 400 mm long, closed-end Alsint recrystallized alumina tube, fitted with an end-cap which provided for evacuation. After allowing at least an hour for the melts to 'dry out' (i.e. attain equilibrium water concentration), sufficient arsenic metal was slowly added to give the required concentration (up to 12 wt % total As). Care was necessary in this operation due to the vigorous evolution of hydrogen during the dissolution reaction.

2.2. *Electrochemical measurements in the melt*

When required, the variation of the indicator reference potential was followed on a Yew model 3066 *Y–t* recorder via high input impedance (10 MΩ) buffer amplifiers constructed in this laboratory. Indicator electrodes were either platinum, nickel or tungsten wires. The reference electrode was sodium metal contained in an 8 mm diameter Alsint recrystallized alumina tube with a β-alumina plug [1]. Voltammetry was performed at a 0.68 mm diameter platinum wire working electrode inserted into the melt to a depth of 3 mm, giving a working area of ~0.07 cm. A platinum

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wire coil served as the counter electrode and the reference electrode was as above. A PAR model 173 potentiostat was driven by a Utah model 0151 sweep generator and the voltammograms were recorded on a Hewlett-Packard model 7035B X–Y recorder.

2.3. *Analytical procedures*

In order to check on the As(III) level in the melt at any time, ~0.5 g samples were collected on a cold tungsten rod, weighed accurately, and then dissolved in 50 ml of distilled water. The analytical method involved the quantitative oxidation of As(III) to As(V) by coulometrically generated iodine from an iodide buffer solution, with potentiometric end-point detection [2].

An aliquot of the unknown solution containing up to 0.3 mg of As(III) was taken and added to 25 ml of phosphate buffer solution (0.05 M Na_2HPO_4, 0.05 M $NaH_2PO_4 \cdot 2H_2O$ and 0.1 M KI at pH 6.7–6.8). The iodine was generated at a current of 4.00 mA (Keithley Instruments, model 225 Current Source) between two 1 cm^2 platinum electrodes, and the end-point detected using a 0.25 cm^2 platinum flag indicator electrode with a saturated calomel reference.

The variation of the indicator electrode potential with time was plotted, via a buffer amplifier, on a Hewlett-Packard model 7045A X–Y recorder, with the x-axis set to time-sweep. The end-point for the titration was indicated by a sharp rise in the potential; the time at this point allowed calculation of the coulombs passed and hence, the amount of As(III) in the aliquot.

The method was calibrated using standard As_2O_3 solutions in NaOH; the titrations were found to be accurate and reproducible to within ±1%. Blank titrations performed on solutions prepared from melt samples, which did not contain arsenic, were within this limit.

3. Results and discussion

3.1. *Melt stability*

In order to determine the stability of the As(III) to aerial oxidation, a 6 wt % As melt was made up in a small diameter recrystallized alumina tube and maintained at 450° C. The melt was held under vacuum for 17 h by connecting this tube to a vacuum pump via a liquid nitrogen cold trap. Samples of the melt were taken at the beginning and end of this period, and then at three hourly intervals after re-exposure to the atmosphere. It was found that while under vacuum, the As(III) concentration decreased only from 3.4 wt % to 3.2 wt %. Three hours after exposure to the atmosphere, the concentration had dropped to 2.2 wt % and, after a further 3 h, was down to 1.2 wt %.

In melts prepared in alumina crucibles, by the time the arsenic additions (~12 wt %) had been completed (around 3 h), it was found that the As(III) concentration had dropped to around 8–9 wt %, i.e. 75% of the total. In spite of a continuous flow of nitrogen over the melt, there was apparently sufficient oxygen leakage to completely oxidize the remainder of the As(III) to As(V) overnight. Analysis of the melt at various times suggested that the rate of As(III) oxidation was approximately linear with time, apparently independent of its bulk concentration. Thus, oxidation of the As(III) by atmospheric oxygen, in molten NaOH at 450° C, was sufficiently rapid to permit measurements of the redox potential of the As(III/V) couple to be effected without the necessity of oxidant additions.

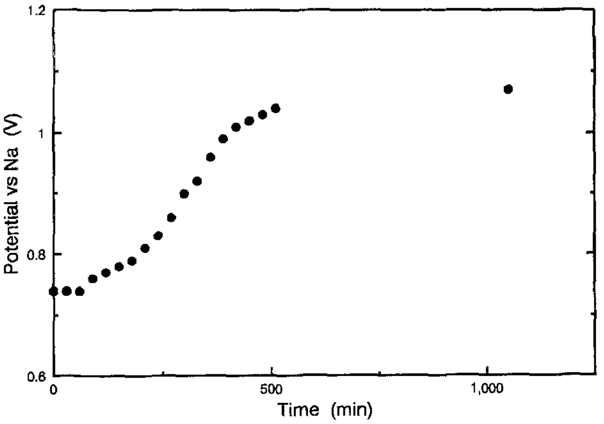

Fig. 1. Variation of potential on a platinum indicator electrode with time, due to the slow oxidation of As(III) to As(V) at ~450° C. (12 wt % As in NaOH melt, sodium in β-alumina reference electrode).

3.2. *Potentiometry in the melt*

3.2.1. The change in potential on a platinum wire electrode with time, due to the slow oxidation of the As(III) to As(V) in molten caustic containing 12 wt % total As at 450° C, is shown in Fig. 1. (The gap in this plot was due to the failure of the reference electrode during overnight operation, but the change in potential over this time was only about 30 mV.) Assuming a linear decrease in the As(III) concentration in the melt with time (see Section 3.1), its calculated concentration was then correlated with the indicator electrode potential (see Fig. 2). Tungsten and nickel indicator electrodes were also briefly evaluated, but neither was particularly sensitive to changes in As(III) concentration and hence, were not used in the rest of this study.

From Fig. 2 it can be seen that the change in potential in going from zero to 8.5 wt % As(III) was ~330 mV, the largest change having occurred around the inflection at 6 wt % As(III) (i.e. an As(III)/As(V) ratio of 1 : 1). Thus, it should be possible to use potentiometry to monitor the As(III) concentration of the melt being fed to the oxidizer since it is expected to have an As(III)/As(V) ratio of 1 : 1. To control to 5 ± 0.5 wt % As(III) (10 wt % total As melt) a potential range of 150 mV is available. However, control of the As(III) concentration in the exit stream to 1.5 ± 0.25 wt % would not be possible since the variation of potential in this concentration range is only ~5 mV.

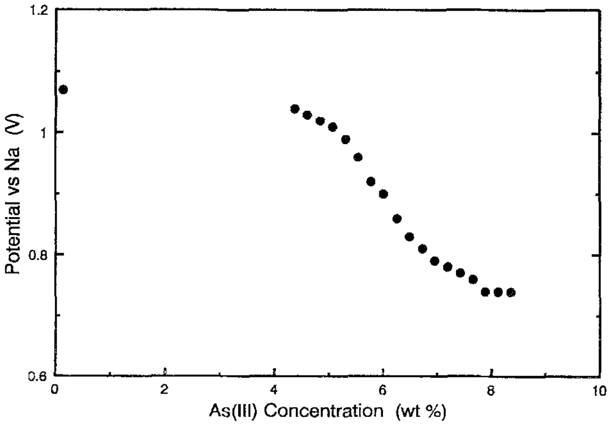

Fig. 2. Plot of potential on a platinum indicator electrode as a function of the calculated As(III) concentration. (12 wt % As in NaOH melt at ~450° C, sodium in β-alumina reference electrode).

3.2.2. A melt containing 13.5 wt % total As with 1.5 wt % as As(III) was prepared. Sodium nitrate was added to give ~15% excess over the stoichiometric requirement for complete oxidation of As(III) to As(V). The potential of the platinum indicator electrode increased by over 400 mV to around 1.4 V, signalling the presence of the excess sodium nitrate. This effect could perhaps be used in a plant to activate a 'cut-off' device to the oxidant supply.

An attempt to titrate a melt of similar composition with solid sodium nitrate, while monitoring the potential, failed due to crystallization of the $Na_3AsO_4 \cdot 2NaOH$ product on the indicator electrode. This may have been due to local cooling and/or supersaturation on addition of the nitrate. Laboratory determination of As(III) concentration by titration of melt samples with sodium nitrate may still be possible if an appropriately shielded electrode was used, and efficient stirring employed.

3.3. *Voltammetry in the melt*

The voltammogram for the oxidation of As(III) to As(V) at a platinum electrode exhibited what appeared to be a diffusion limited current plateau at potentials more positive than 1.2 V with respect to sodium. A typical example is shown in Fig. 3; presumably, the observed fluctuations in current were due to thermal convection effects. The height of the initial peak varied linearly with As(III) concentration up to about 3 wt % in a 0.1 to 6 wt % total arsenic melt and about 2 wt % in a 9 to 12 wt % total arsenic melt (see Figs 4, 5). The non-linearity at higher As(III) concentrations was probably caused by the observed build-up of $Na_3AsO_4 \cdot 2NaOH$ at the working electrode/melt-surface interface, which may have been due to localized As(V) saturation.

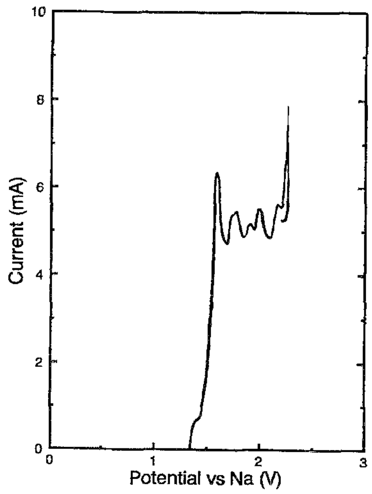

Fig. 3. Voltammogram for the oxidation of As(III) to As(V) in a NaOH melt at ~450° C. (0.63 wt % As(III)/4.5 wt % total As; Pt working, sodium in β-alumina reference electrode; sweep rate 20 mV s^{-1}).

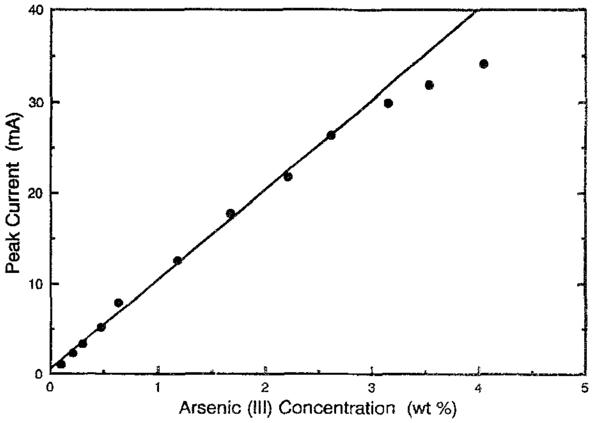

Fig. 4. Variation of initial peak current with As(III) concentration in a NaOH melt at ~450° C. (0.1–6 wt % total As; Pt working, sodium in β-alumina reference electrode; sweep rate 20 mV s^{-1}).

Based on the above data, voltammetry appears to be a promising method for monitoring the As(III) concentration in the outlet stream of the oxidizer. For a control range of 1.5 ± 0.25 wt %, the limiting current would be expected to vary by about 30%. However, to monitor the concentration of As(III) in the inlet stream (~5 wt %) would require operation in the non-linear portion of the calibration curve where the method is less sensitive.

4. Conclusions

This work has shown that the As(III) concentration in

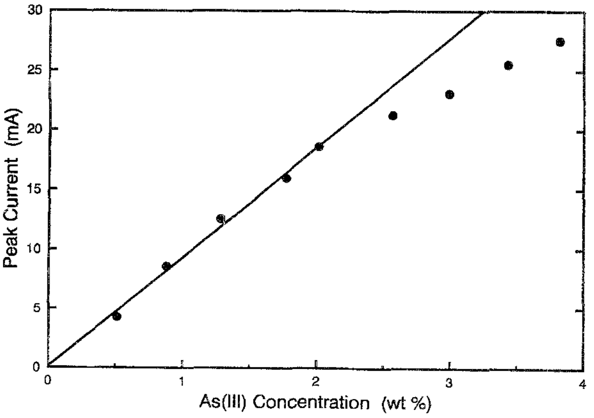

Fig. 5. Variation of initial peak current with As(III) concentration in a NaOH melt at ~450° C. (9–12 wt % total As; Pt working, sodium in β-alumina reference electrode; sweep rate 20 mV s^{-1}).

a caustic melt can be determined in the laboratory by potentiometry or voltammetry at a platinum electrode. The most suitable method was found to be dependent upon either the As(III) As(V) ratio or the As(III) concentration. For *in situ* monitoring, potentiometry seems more applicable for the inlet stream to the oxidizer where, the As(III) As(V) ratio is $\sim 1:1$ and the method has maximum sensitivity. It may also be possible to use this technique to provide a back-up warning signal indicating an over-supply of oxidant. The potentiometric method requires a reliable reference electrode, but should not be sensitive to variations in electrode area and mass transfer conditions. However, due attention would have to be given to maintenance of electrical connections, as corrosion and thermal effects could lead to significant changes in the observed potentials.

The laboratory results indicate that voltammetric analysis would be more appropriate in the outlet stream, where the As(III) concentration is ~ 1.5 wt %. In practice, measurement of the limiting current for the As(III) oxidation would probably be made at a pre-set potential. Successful implementation of this control method would require (i) a stable and durable reference electrode, (ii) invariance of the working electode area, and (iii) control of the mass transfer conditions. Maintenance would probably involve frequent cleaning and replacement of electrodes.

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