

Electrolytic extraction of pure bismuth from an industrial residue from the treatment of an auriferous mineral

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A direct electrolytic extraction procedure for very pure bismuth (99.991%) from bismuthiferous dusts recovered following the industrial treatment of a gold-bearing mineral has been developed. An attack by nitric acid on these dusts leaves an insoluble residue containing the major part of the lead, antimony and silver. An hydrolysis of the solution in the presence of chloride ions precipitates an oxychloride of bismuth freed from iron and copper. A redissolution of the oxychloride of bismuth in chloride media followed by the boiling of the solution in the presence of a reducing agent eliminates arsenic.

As the electrochemical study had shown that traces of antimony still present in the electrolyte can deposit at the same time as the bismuth, they are complexed by an addition of tartaric acid (4 g. l⁻¹). The conditions of electrolysis ($C_{\text{Bi}^{3+}} = 30 \text{ g. l}^{-1}$, pH=0.7, $i = 3 \text{ A. dm}^{-2}$, $t = 70^\circ\text{C}$) are chosen in order to obtain, with maximum yield (95%), an adherent and well-crystalline deposit of bismuth.

The analysis of the metal produced by this procedure shows that the titre obtained is very superior to that of an industrial metal produced by a pyrometallurgical process (99.99.6%).

Introduction

The fusion in a water jacketed furnace of a concentrate of auriferous mineral, rich in bismuth minerals, allows the recovery of bismuthiferous powders in which the trioxide of bismuth is accompanied by a large number of elements of which the principal ones are Pb, As, Fe, Cu, Sb, Ag.

The recovery of bismuth, as it is carried out in the treatment factory, involves an attack stage on these bismuthiferous powders by hydrochloric acid. Hydrolysis of the resulting solution precipitates the bismuth oxychloride which remains contaminated by impurities. The reduction of the oxychloride by carbon in the presence of a flux leads to a metal that only contains 97% of bismuth. The quality of the metal thus obtained is not good enough for the great majority of applications, in particular for the preparation

of special alloys with low melting points, and pharmaceutical derivatives that necessitate low concentrations of antimony and arsenic. Chemical dissolution by the action of chlorine and of caustic soda increases its purity to 99.6%.

As the equipment of the factory permitted treatment in acid solution, it was interesting to study a hydrometallurgical procedure for extracting the metal by electrolysis; such a procedure also offers the advantage of avoiding the loss of bismuth by volatilization which is inherent in the pyrometallurgical treatment. Finally, an electrolytic procedure may allow the direct production of a metal purity at least equal to 99.99%.

Preparation of the Electrolyte

The bismuthiferous powder, recovered in the exit cyclones of the water-jacketed furnace, has

a complex composition. We have effected its analysis, after total dissolution in an HCl medium, then dilution, by determining the amounts of the major elements with the aid of an atomic absorption spectrophotometer Techtron '1000'. We have verified that the constituents of the solution submitted for analysis neither produce interferences, nor non-atomic absorption. In the case of arsenic, however, whose resonance wave-length is situated in the ultra-violet at 193.6 mm, we have had to make a correction for non-atomic absorption, which is intense at this wave-length, in measuring this by means of a hydrogen continuum lamp.

The composition of the raw material, given by the analysis, is shown in Table 1. The remainder

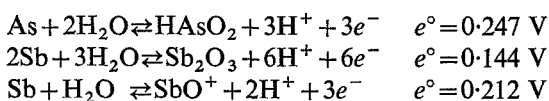
Table 1.

Element	Bi	Pb	As	Fe	Cu	Sb	Ag
Percentage content	30	5	5	4	0.25	0.16	0.04

up to 100% is composed of oxygen bound to the elements, of silica and of rare elements in low concentrations.

From an examination of the standard electrode potentials we can predict that the presence in the electrolyte even of very low concentrations of silver ions ($e^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.799$ V) and of Cu^{2+} ($e^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34$ V) would lead to a co-discharge of these elements with the bismuth ($e^{\circ}_{\text{Bi}^{3+}/\text{Bi}} = 0.277$ V). The total elimination of these two elements from the electrolyte is thus absolutely necessary.

The arsenic and the antimony are present in solution essentially in the form of the species AsO_2H , Sb_2O_3 and SbO^+ . The potentials corresponding to the equilibria involved are the following: [1]



These potentials being all lower than that of the Bi/Bi^{3+} couple, the corresponding species are therefore not able, in principle, to discharge. However, one can predict that, in the course of the discharge of the Bi^{3+} ion, diffusion over-

potential will manifest itself owing to the faradaic depletion of the Bi^{3+} ions adjacent to the electrode; this overpotential may be written:

$$\eta_d = \frac{RT}{3F} \ln \left(1 - \frac{i}{i_1} \right)$$

i = cathodic current density

i_1 = limiting diffusion current density

The limiting diffusion current density i_1 , corresponding to a maximum concentration gradient in the neighbourhood of the electrode is given by:

$$i_1 = -zF \frac{D}{\delta} C$$

z = charge number of the ionic species

D = diffusion coefficient of the ionic species

C = concentration of ions in the bulk of the solution

δ = thickness of the diffusion layer (a function of the stirring and of the temperature of the solution)

F = Faraday's constant

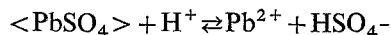
The diffusion overpotential affects the value of the discharge potential of the bismuth ion. A decrease of the concentration by a factor of a 100 in the diffusion layer, for example, causes a lowering of this potential by 40 mV. The discharge potential for the Bi^{3+} ion can then reach the equilibrium potential of arsenic and it is believed that it can even reach that of antimony. Under these conditions, there is a risk that the deposited bismuth may contain these two impurities.

In the case of lead ($e^{\circ}_{\text{Pb}^{2+}/\text{Pb}} = -0.126$ V) and iron ($e^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.441$ V) the risk of co-discharge with bismuth is low.

The attack on the powder by the hydrochloric acid cannot yet be held back, because all the elements present are taken into solution in the form of ions Bi^{3+} and BiCl_4^- [2], Pb^{2+} and PbCl_4^{2-} , AsO_4^{2-} , Fe^{3+} , Cu^{2+} , SbO^+ and SbCl_4^- [3], $(\text{AgCl}_2)^-$ [4, 5]. The hydrolysis of the solution at pH 1.5 involves, in addition to the precipitation of BiOCl , that of PbAsO_4 , PbCl_2 , SbOCl , $\text{Sb}_4\text{O}_5\text{Cl}_2$ [6] and AgCl . The elimination of these impurities therefore appeared to be impossible after hydrochloric acid attack.

To overcome this difficulty, we have utilized a nitric acid process for the solution of bismuth (Fig. 1) in the presence of a small quantity of chloride and sulphate ions. In these conditions bismuth goes into solution at the same time as AsO_4^{2-} , Fe^{3+} and Cu^{2+} . On the other hand, lead, antimony, and silver remain in the soluble part of the mineral in the form of PbSO_4 , Sb_2O_5 and AgCl (Fig. 1). This operation permits

affects the solubility of lead sulphate by displacing to the right the equilibrium



The solubility of lead sulphate increases rapidly [8] and already attains a high value ($0.0048 \text{ mole.l}^{-1}$) when the normality of nitric acid is 0.7.

The hydrolysis of nitrates (Fig. 1) in the presence of NaCl:



leads to the formation of bismuth and arsenic oxychlorides. The ions Fe^{2+} and Cu^{2+} remain in solution if the pH of hydrolysis does not exceed 1.5. Nearly all the copper is eliminated in this way.

The oxychlorides are separated by filtration, then redissolved in hydrochloric acid (Fig. 1). The elimination of arsenic in the form of AsCl_3 is then assured by boiling the solution in the presence of iron chloride in order to maintain the arsenic in a valency state of 3. A last hydrolysis permits the elimination of the Fe^{2+} ions thus introduced and the pure bismuth oxychloride, dissolved in hydrochloric acid, may then be submitted to electrolysis.

The analysis of the electrolyte obtained (Table 2) shows that the antimony cannot all be retained when one separates, by filtration, the insoluble part of the first matter from the attacking nitric acid solution which still contains 0.012 g.l^{-1} of this element. The conditions of electrolysis necessary to avoid the discharge of this residual antimony then have to be studied.

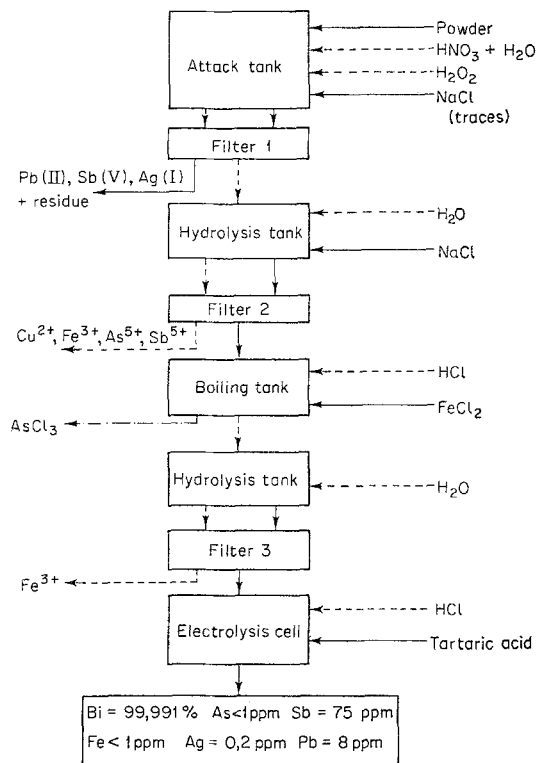


Fig. 1. Flow sheet for the preparation of the electrolyte.

————— solid phase
 - - - - - liquid phase
 - · - · - · gaseous phase.

the nearly total separation of silver because the solubility of silver chloride in nitric acid is low: $2.75 \times 10^{-5} \text{ mole.l}^{-1}$ [7]. One cannot eliminate the lead entirely because nitric acid markedly

Study of Electrolysis Conditions

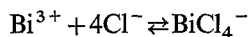
Influence of pH

As the pH for the commencement of hydrolysis of the ion Bi^{3+} is around unity, it is important that the electrolyte contains a high enough concentration of HCl. Now, in the presence of

Table 2.

Element	Bi	Pb	Sb	Fe	Ag	As	Cu
Concentration g.l^{-1}	30	280×10^{-3}	12×10^{-3}	0.6×10^{-3}	0.14×10^{-3}	—	—

chloride ions, one observes a complexation of the Bi^{3+} ion according to the equilibrium



The standard potential of the $\text{BiCl}_4^-/\text{Bi}$ couple, which is lower than that of the Bi^{3+}/Bi couple, is in the neighbourhood of -0.168 V [1]. An excess of hydrochloric acid then brings nearer the thermodynamic potential of the bismuth present in the electrolyte to that of antimony and can thus cause a contamination of the deposit.

Also, we have studied, as a function of the pH of the solution, the variation of the potential of a bismuth electrode in a solution in which the concentration of bismuth has been fixed at $30 \text{ g} \cdot \text{l}^{-1}$, and that of an electrode of antimony in two solutions in which the concentrations of antimony are respectively equal to $3.75 \text{ g} \cdot \text{l}^{-1}$ and $0.375 \text{ g} \cdot \text{l}^{-1}$. Fig. 2 summarizes the results. The curve a, relating to bismuth, has been traced between $\text{pH} = -1$ and $\text{pH} = 1$. The trace of the curves b ($3.75 \text{ g} \cdot \text{l}^{-1}$) and c ($0.375 \text{ g} \cdot \text{l}^{-1}$) relating to antimony has been limited by the hydrolysis which appears from the value $\text{pH} = 0$ for the concentrations studied, much higher than that of the electrolyte (Table 2). In order to compare them to that of bismuth, the curves b and c have been extended as far as $\text{pH} = 1$.

For a bismuth concentration of $30 \text{ g} \cdot \text{l}^{-1}$, the equilibrium potential for Bi^{3+}/Bi calculated

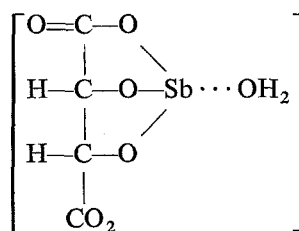
with the aid of the Nernst equation is equal to 0.260 V. Fig. 2 shows that, for $\text{pH} = 1$, the measured potential does not exceed 0.190 V. When the pH decreases, the rest potential of the bismuth electrode decreases more rapidly than that of the antimony electrode because of the complexation of the Bi^{3+} ion. It therefore appears necessary to effect the electrolysis at a pH as high as possible in order to avoid the discharge of antimony. However, this pH can be less than unity because of the hydrolysis of the bismuth ion; we have fixed the pH value equal to 0.7 .

The comparison of the curves b and c (Fig. 2) shows that for $\text{pH} > 0$, the potential of the antimony electrode depends little on the concentration because of the equilibria coming into play; one can then think that in the electrolyte studied, the potential of the antimony electrode, for $\text{pH} = 0.7$, is only less by about 20 mV than that of the bismuth electrode. We have seen that this difference is not sufficient to assure that the deposit be free from antimony.

We therefore have to introduce an addition agent into the electrolyte in order to complex the antimony.

Influence of the tartaric acid concentration

We have utilized tartaric acid which forms a complex with antimony of which the formula would be [9]:



However, hydrochloric acid partially destroys the complex. Therefore we have studied the variations of the antimony concentration in the electrolytic bismuth as a function of the quantity of tartaric acid introduced into the electrolyte. Fig. 3 shows the curve obtained. One sees that above a concentration equal to $4 \text{ g} \cdot \text{l}^{-1}$, the additions have practically no effect on the complexation of the antimony. Because of the cost of this product, we stopped at a value of $4 \text{ g} \cdot \text{l}^{-1}$.

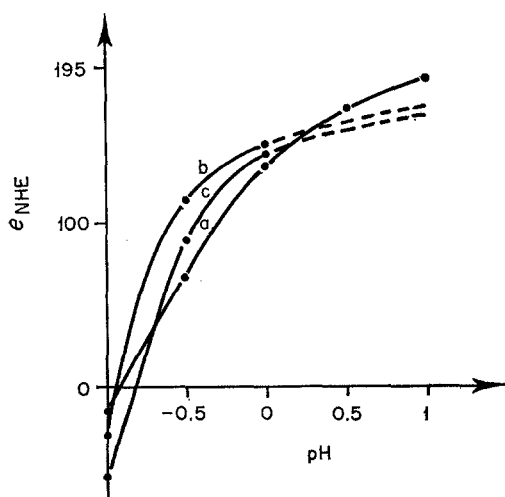


Fig. 2. Variation of the rest potentials of the couples Bi^{3+}/Bi and Sb^{3+}/Sb as a function of pH.

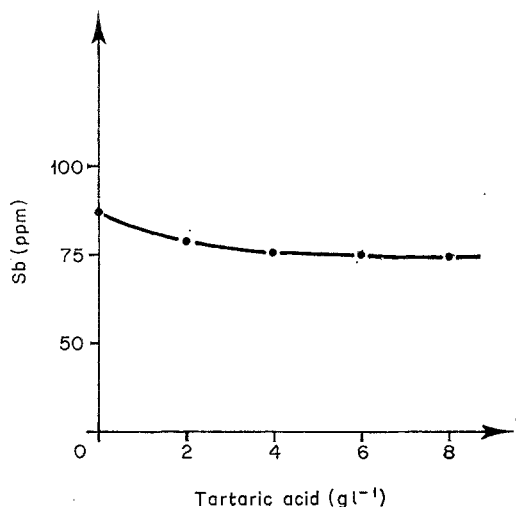


Fig. 3. Variation of the antimony content of electrolytic bismuth as a function of the concentration of tartaric acid in the electrolyte.

Influence of temperature on the resistance

The conditions of pH being fixed, one can increase the conductivity of the electrolyte by raising the operating temperature. This temperature increase produces, in addition, a thermal agitation which has the effect of decreasing the thickness of the diffusion layer and thus of lowering the value of the overpotential arising from this phenomenon.

The curve in Fig. 4 shows the variations, as a function of the temperature, of the resistivity of a

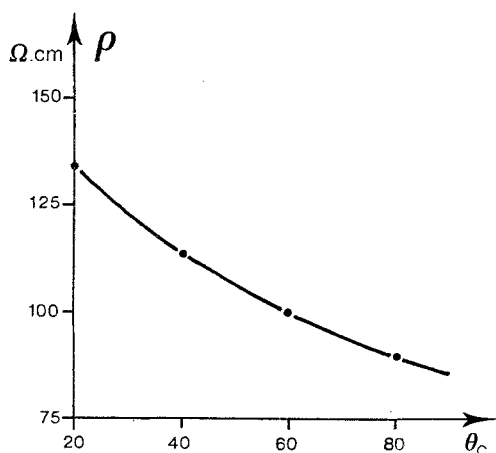


Fig. 4. Resistivity of the electrolyte as a function of temperature.

solution of pH=0.7, containing 30 g . l⁻¹ of bismuth. One sees that an increase of temperature of 50°C leads to a decrease of resistivity of more than 40 Ω cm.

We have adopted 70°C for the operating temperature. This corresponds to an optimum value; in effect, a higher temperature leads to too much evaporation and a depletion of HCl.

Influence of current density

A maximum current density increases the productivity of the installation. However, too high a current density leads to a powdery deposit and increases the irreversible character of the discharge. We have carried out a systematic study of this parameter.

The electrolysis cell, 600 ml capacity, is made of Pyrex glass. It consists of three compartments separated by fritted glass partitions of porosity 5. The electrodes are plates of platinum (35 mm × 25 mm). The anodes are situated on both sides of the cathode, parallel to it at a distance of 160 mm. The cell is placed on a magnetically stirred heater. The temperature is measured by means of a thermometer. The electrolysis is maintained at constant current by means of a potentiostat which maintains constant the voltage at the ends of a resistance placed in series in the circuit.

For each current density studied (1 A . dm⁻² < i < 5 A . dm⁻²) we have prepared a photomicrograph of the surface of the metal obtained. It appears that the most adherent and fine deposits are obtained for a current density equal to 3 A . dm⁻² at the temperature of 70°C (Fig. 5).

Influence of temperature on the current efficiency

Because of the high value of the Bi³⁺/Bi potential, the probability of hydrogen discharge is low in spite of the intervention of the diffusion overpotential of the Bi³⁺ ion. However, the activation overpotential decreases when the temperature increases and follows different laws for the H⁺ and Bi³⁺ ions in the presence of each other.

For control purposes, we have traced, for the electrolyte used (C_{Bi³⁺} = 30 g . l⁻¹, pH=0.7), the curve of the variation of current efficiency as a function of temperature, the current density being maintained at its optimum value i=

3 A . dm⁻² (Fig. 6). The efficiency values have been obtained by weighing the metal deposited for a constant quantity of electricity (5,000 coulombs), measured with the aid of an electronic integrator.

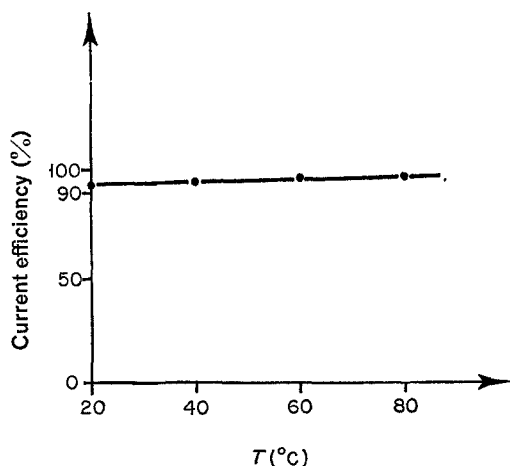


Fig. 6. Variation of the current efficiency as a function of the temperature of the electrolyte.

The current efficiency is sensibly independent of the temperature of the electrolyte. Its average value, 95%, is satisfactory.

deposited on the cathode. The last fraction of bismuth extracted has an insufficient purity and the electrolyte has to be recycled.

The finely crystalline deposit may be detached from the cathode by bending the latter. The determination of the impurities contained in the metal has been carried out by the atomic absorption technique already described; solution is effected by attacking the metal with the aid of nitric acid (Merck 'Suprapur'). The solution submitted to analysis contains 36 g . l⁻¹ of bismuth. This high concentration, which is necessary because of the very low scale of impurities in the metal, does not interfere with the determination of the elements.

The analytical results displayed in Table 3 give the concentrations of impurities contained on the one hand in the industrial metal obtained in the factory by pyrometallurgical processes and refined by chlorine and caustic soda dissolution and, on the other hand, in the electrolytic metal that we have obtained by the described method.

In addition to obtaining very pure bismuth, the proposed method also allows nearly all the foreign elements (Sb, Ag, Pb) to be left in a single

Table 3.

Elements		Bi	Sb	Pb	Fe	Cu	As	Ag
Impurity concentrations (ppm)	Electrolytic procedure	99.991%	75	8	< 1	< 1	< 1	0.2
	Pyrometallurgical and chemical refining	99.6%	90	1,900	22	17	200	1,500

Experimental Results

The electrolysis cell that we have already described permits us to effect the deposition of bismuth by fixing the parameters at values that we have determined ($C_{\text{Bi}^{3+}} = 30 \text{ g} \cdot \text{l}^{-1}$, pH 0.7, tartaric acid addition: 4 g . l⁻¹, $t = 70^\circ\text{C}$, $i = 3 \text{ A} \cdot \text{dm}^{-2}$).

We have continued the electrolysis till 66% of the quantity of bismuth initially in solution is

residue and to facilitate thereby their eventual recovery.

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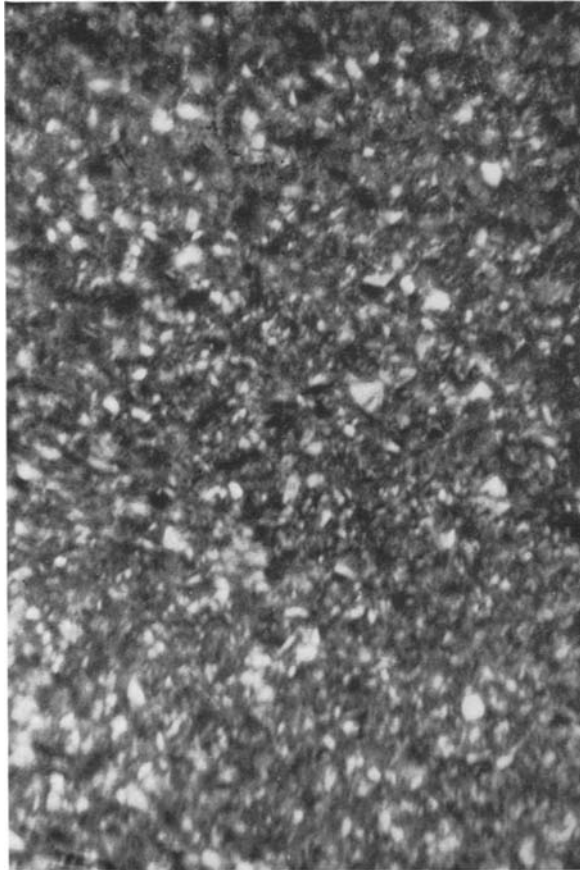


Fig. 5. Photomicrograph of the deposit ($i = 3 \text{ A} \cdot \text{dm}^{-2}$, $G = 750$).

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