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T. T. Chen
CANMET

J. E. Dutrizac
CANMET

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APPLICATION OF ELECTRON MICROSCOPY TO THE ELECTROREFINING OF COPPER

T.T. Chen* and J.E. Dutrizac

CANMET, 555 Booth Street, Ottawa, Ontario, Canada K1A 0G1

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Abstract

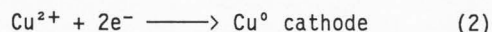
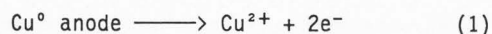
Electron microscopy was used to characterize the fine-grained products formed during the electrorefining of copper and to elucidate the chemical processes occurring during this metallurgical process. Copper anodes and the anode slimes from the electrorefining of copper at three Canadian refineries are studied to determine the behaviour of lead and selenium and the formation of various silver-copper selenides during the electrorefining process. Silver occurs in solid solution in the copper metal and dissolves with the copper. Silver then reacts with Cu_2Se to form Ag-Cu selenides. Lead is present in the anode mostly as complex Pb-As or Pb-As-Sb-Bi oxides. On exposure to the electrolyte, the lead is rapidly converted to insoluble PbSO_4 . Although most of the nickel in the anodes dissolves, some accumulates as NiO or Cu-Ni-Sb oxide inclusions in the anode slimes.

Introduction

Scanning electron microscopy is commonly used to characterize the composition and morphology of materials. It has been used widely in materials science, electronic engineering, biology, medical sciences, art and art history, food sciences, and physical metallurgy; the technique is of increasing importance in the mineralogical-extractive metallurgy field. Although most of the applications in mineralogy-extractive metallurgy so far have been limited to descriptive studies, the SEM technique also can be used to explore the reactions occurring during processing. To show how SEM examination can provide information beyond simple compositions and morphologies, this paper outlines the use of the SEM/EDX technique to characterize fine-grained metallurgical plant products, and to elucidate the chemical processes occurring during metallurgical treatment. The techniques are illustrated using, as an example, the copper anode slimes generated during the electrorefining of copper.

Electrorefining of Copper

Currently, most of the world's primary copper is produced by smelting. During smelting, many of the impurities originally contained in the copper concentrates are collected in the blister copper smelter product. Electrorefining in a $\text{CuSO}_4\text{-H}_2\text{SO}_4$ electrolyte is universally used to remove the impurities and to recuperate the valuable by-products such as silver, gold, tellurium and selenium (Table 1). The refining process involves the dissolution of impure copper at the anodes and the plating of high-purity copper at the cathodes:



Keywords: anode copper; anode slimes; electrorefining of copper; mineralogical characterization; behaviour of lead, selenium; formation of silver-copper selenides; scanning electron microscopy.

* Address for correspondence:
T.T. Chen
CANMET, 555 Booth Street
Ottawa, Ontario, Canada K1A 0G1
Phone No. (613) 995-9490

The impure anodes contain 99.1-99.8% Cu as well as trace amounts of O, Ni, Pb, As, Se, Sb, Bi, Te, Ag, Au, Fe, etc. (Table 1) [2,5]. After refining, the copper cathodes have purities higher than 99.99% Cu. The impurities originally

contained in the anodes dissolve in the electrolyte or remain as insoluble compounds, either on the anode face or at the bottoms of the electrolytic tanks. These insoluble compounds (i.e., the anode slimes) contain valuable metals (Table 2) and sometimes these metal values exceed that of the copper itself. For some large refineries, such as the CCR Division of Noranda Minerals Inc., Montréal, with a production of approximately 10 kg of slimes per metric tonne of anodes and with a refining capacity of over 370,000 metric tonnes per year [4,5], the valuable metals, Table 2, are a major economic consideration. For example, CCR recovers 933-1866 kg/month (30,000-60,000 troy ounce/month) of gold, and approximately 50,000 kg/month (1,600,000 troy ounce/month) of silver from their slimes [4,1]. The economic value of anode slimes is obvious. Detailed characterization of these slimes not only can assist process development for treating slimes to recover their metal values, but also can help to elucidate the chemical reactions occurring during electrorefining. For the latter application, the behaviour of selenium and lead during copper electrorefining is especially important and is presented as an example in this paper.

Experimental

Most of the anodes and anode slimes studied were supplied by Canadian Copper Refiners (the CCR Division of Noranda Minerals Inc.), Montréal, Quebec, and the Kidd Creek Copper Refinery, Timmins, Ontario; additional samples were obtained from INCO Ltd., Copper Cliff, Ontario. Despite some differences in the copper refining operations including anode casting methods and anode impurities, the constituents and morphologies of the anode slimes are generally similar, and the behaviour of the trace elements during electrorefining also is similar.

The as-received materials (both anodes and slimes) were first examined using a stereomicroscope to study their gross morphologies, and were subsequently examined in detail using a scanning electron microscope (SEMCO Nanolab 7) equipped with an energy dispersive X-ray analyzer (SEM/EDX KeveX 7000) and using X-ray powder diffraction instruments (Rigaku Rotaflex D-MAX B automated diffractometer and Debye-Scherrer camera) to determine their morphologies, qualitative compositions and phase identities. Polished sections were prepared from these materials; the sections were then analyzed using an optical microscope, SEM/EDX and electron microprobe (JEOL Superprobe 733 with Tracor Northern TN-5500 EDX System) to determine their constituents, morphological relationships among different phases, and the compositions of the phases. Detailed methods of sample preparation were given in a previous article [3].

Selenides and sulphides (e.g., Cu_2Se , CuAgSe , Cu_2S , PbS) are opaque under transmitted light, whereas sulphates, selenates and other oxidates (e.g., PbSO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSeO}_4 \cdot 2\text{H}_2\text{O}$,

CuSeO_4) are light transparent. That is, under the reflected light microscope, selenides and sulphides are bright in colour (e.g., white, bluish white, light yellow, etc.) whereas sulphates, selenates and other oxidates are dark (black) in colour. Similarly, under the reflected light microscope, lead oxides (e.g., PbO , Cu-Pb-As oxide, etc.) and copper oxides are dark in colour; CuO can be distinguished from Cu_2O as the former is grey in colour, strongly anisotropic and without internal reflection whereas the latter is grey with bluish tint, isotropic and with red internal reflection. The details of the ore microscopy of the various related phases are given elsewhere [6].

It was immediately noticeable, under optical microscopical examination, that the impurity phases in copper anodes are usually segregated together and occur along the grain boundaries of the copper matrix; only one selenide species (Cu_2Se) is present in the anodes. In the anode slimes, however, more than one selenide species is usually present in the same slimes. Under the reflected light microscope, Cu_2Se is bluish grey and easily tarnishes in air to dark blue; CuAgSe is pale yellowish white whereas Ag_2Se is grayish white; metallic silver is bright white and frequently tarnishes to yellowish or brownish white. Cu_2Se and CuAgSe both occur not only as discrete grains in the anode slimes, but also as intergrowths and gradational replacements. Intergrowths between CuAgSe and Ag_2Se are relatively difficult to recognize because of their fine grain sizes and rather closeness in colour under optical microscopic observation. Metallic silver is easily discernible due to its bright white colour, even in trace quantity. In general, the major differences in phase constituents especially the silver-bearing species, between different slimes samples can be easily detected through optical microscopic examination. Frequently, the regions of interest (e.g. textures of silver-bearing phases) in the polished sections were first located through optical microscopic observation, then examined in detail using SEM/EDX.

Although most of the constituents of the anode slimes could be easily identified using an optical microscope, phase identification in the present study was achieved mainly by SEM/EDX on polished sections as the energy-dispersive X-ray (EDX) analysis gave the specific elements present in that particular phase. One of the relatively difficult tasks involved in the phase characterization of the anode slimes using SEM was the determination of the existence of S in the presence of Pb using the EDX system (e.g., to distinguish PbO from PbS or PbSO_4). Fortunately, it was noticed that the position of the X-ray SK line and that of the PbM line were clearly discernible on the EDX systems (i.e., KeveX 7000 and Tracor 5500) used in the present study, and that the X-ray energy (peak) shift from the PbM line of the Pb "only" compounds (e.g., Pb^0 , PbO) to the combined PbM + SK peak of the lead sulphide or lead sulphate also was clearly resolved on the EDX systems. Some of the

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Table 1. Bulk Compositions of Some Commercial Anodes and Cathode Copper (in ppm or as shown).

Element	Anode Copper	CCR Anode*	Kidd Creek Anode*	Cathode Copper
Cu %	99.1 - 99.8	99.17	99.25	99.99
O	1100 - 1500	-	1500	-
Ag	350 - 3470	1489	1700	8 - 9
Pb	330 - 2700	600	2700	0.3 - 4.5
Se	120 - 2200	680	2200	0.3 - 2.2
As	40 - 390	390	40	<0.1 - 0.5
Sb	3 - 220	220	6	<0.1 - 0.6
Au	8 - 1100	47	-	-
Bi	5 - 170	70	5	0.2 - 0.33
Te	10 - 90	90	14	<0.1 - 0.2
Ni	200 - 6700	2100	200	0.4 - 5.5

Data from CCR, Kidd Creek and INCO Copper Refineries
* Typical tank house data

Table 2. Bulk Compositions of Some Anode Slimes (wt. %)

Element	CCR			Kidd Creek		INCO
	1	2	3	4	5	6
Ag	35.91	22.44	21.40	8.9	11.0	5.94
Se	7.72	16.10	11.80	24.8	19.5	6.68
Cu	17.8	32.1	18.70	40.8	26.8	16.6
Pb	10.7	3.61	10.10	14.3	21.7	1.08
As	1.56	1.22	1.14	0.4	0.45	0.83
Sb	0.81	0.11	1.68	0.1	0.05	-
Bi	0.68	0.18	0.77	0.25	0.24	-
Ni	0.57	0.12	0.67	-	<0.01	26.2
Au	0.63	0.61	0.60	0.009	0.038	-
Te	-	-	1.21	<0.01	0.04	1.66

All samples were water-washed.

Table 3. Electron Microprobe Analyses of Some of the Impurities Present in Anode Copper (wt. %)

Element	Copper Matrix	Cu ₂ Se*			Cu-Pb-As oxides**			
Ag	0.26	0.46	0.18	0.09	2.6	0.8	-	-
Se	nd	32.9	33.7	36.8	0.7	0.7	-	-
Cu	-	62.8	63.0	62.3	7.4	2.0	8.2	7.1
Te	nd	3.8	2.8	0.1	-	-	-	-
Pb	0.10	nd	nd	nd	38.3	62.6	26.1	57.3
Bi	nd	-	-	-	21.1	1.4	20.8	8.5
Sb	nd	-	-	-	6.8	14.6	12.3	1.5
As	0.06	-	-	-	4.5	3.6	23.1	16.8
Ni	0.135	-	-	-	-	-	-	-

nd - not detected.

* Analyses represent average compositions in different anodes.

** Analyses represent random individual particles.

particles of the anode slimes are very small, often less than 2 μm , and intergrowths of two different phases (e.g., Cu₂Se + CuAgSe) commonly occur within a single particle. EDX analysis in this case gives only the qualitative compositions of the phases. However, with the compliment of the backscattered electron image (i.e., Cu₂Se darker; CuAgSe lighter), X-ray image mapping on the SEM and the optical microscopy (i.e., Cu₂Se blue; CuAgSe yellowish white), as well as the electron microprobe analysis and XRD analysis, the constituents of the copper anodes and anode slimes were identified without difficulty.

Characterization of the Copper Anodes

Table 1 provides some insight into the compositions of the anodes studied. Basically, the anodes contain, in addition to Cu, various impurities such as Ag, Pb, Se, As, Sb, Te, Bi, Ni and Au. The total impurities, including O, are usually less than 0.9%. The impurities mainly occur as Cu₂O, Cu₂Se, Cu-Pb oxide, Cu-Pb-As oxide, or as a solid solution in copper. In anodes with high levels of Ni, Sb, and Bi, NiO, Cu-Ni-Sb oxide, and various Cu-Pb-Bi-Sb-As oxides may be present. Figure 1 shows the distribution of the impurities in a copper anode. The impurities occur mainly along the grain-boundaries of the copper matrix, and their distributions and morphologies seem to be controlled by the method of casting and the rate of cooling. Figure 2 and Figure 3 show the detailed structures of some of the impurities. The Cu₂O, Cu-Pb oxide, Cu-Pb-As oxide and Cu₂Se usually are very fine-grained, mostly less than 5 μm , and they commonly occur together. The Cu₂O, Cu-Pb-As oxide and Cu-Pb-Bi-Sb-As oxides usually occur as blebs or spheroids; Cu₂Se occurs as spheroids and as ring-like, rod-like or sponge-like structures enveloping the other impurities or filling the interspaces between these impurities. Table 3 shows some of the analyses of these compounds; Cu₂Se usually contains minor to trace amounts of Ag and Te in solid solution. The metallic copper matrix itself contains significant amounts of Ag, Ni, Pb and As in solid solution. In summary, the selenium and tellurium in copper anodes occur as a Cu₂(Se,Te) phase, and Pb, As, Sb and Bi are present mostly as complex oxides. Copper oxide (Cu₂O) always is abundant and NiO occurs in Ni-rich anodes. All of the impurity phases are present as complex inclusions concentrated at the copper grain boundaries. By contrast, most of the Ag and part of the Ni, Pb and As occur in solid solution in the copper metal matrix.

Characterization of the Anode Slimes

Table 2 shows the compositions of some commercial copper refinery anode slimes. Depending upon the source of the anodes (i.e., the copper ores), the compositions can vary significantly. For example, CCR anode slimes (No. 1-3) are relatively high in Ag and Au,

whereas Kidd Creek anode slimes (No. 4-5) are richer in Se and Pb. In most anode slimes, however, Ag, Se and Cu are usually present in major quantities, whereas As, Pb, Sb, Ni and Te are occasionally significant, and Bi, Au, Sn and Si usually occur in minor to trace amounts. Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, usually is present in major amounts in all the unwashed slimes as would be expected as the electrolyte contains $>100\text{g/L CuSO}_4$.

The slimes consist mainly of one or two of Cu_2Se , CuAgSe or Ag_2Se depending upon the Ag and Se contents of the anodes. The slimes also contain major amounts of PbSO_4 , variable amounts of a Cu-Ag-Se-As-Pb-O phase and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and minor to trace amounts of Cu_2O , Cu^0 , Ag^0 , silica gel, Cu-Pb-Bi oxides, Cu-Pb-As-Bi-Sb oxides, Cu-Cl oxide, Cu-Sb-As oxides, etc. Depending upon the source of the copper, other compounds such as NiO , Cu-Ni-Sb oxide, silicates, SiO_2 , SnO_2 , BaSO_4 , Cu-Sn-AsO_4 and Ag_2Te also may be present.

Figure 4 shows the general morphology of the anode slimes still attached to the face of the anode. The selenides usually occur as spheroids as well as ring-, sponge-, or rod-like structures; Cu_2O occurs as cubic crystals or as thin layers attached to the anode face. Lead sulphate is present as euhedral crystals attached to selenides or intergrown with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and metallic Ag occurs as tiny particles ($< 0.5 \mu\text{m}$) embedded in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ matrix. Copper sulphate seems to hold all the other slimes components together and to attach them to the anode. The slimes structure is shown in cross-section in Figure 5 where the hollow or solid spheroidal, or ring-like selenides are embedded in a bonding phase of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Fine particles ($< 1 \mu\text{m}$) of Ag^0 are visible in the matrix of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Lead sulphate either attaches to the ring-like selenides or partially fills the cores of the selenide spheroids. Not all the selenide spheroids, however, have a PbSO_4 core; some contain a Cu-Pb-As oxide or Cu-Pb-Bi oxide core instead.

The slimes collected from the bottoms of the electrolytic tanks have a slightly different composition from the slimes still attached to the anodes. In addition to the selenides and the various phases reported above, the slimes collected at the bottom of the tanks (Figure 6) also contain variable amounts of a precipitated mixture consisting of Cu, Ag, Se, Pb and As as major constituents and Bi, Sb, Ni, S, Te and Au as minor constituents. The composition of the precipitate is variable depending upon the source of the anodes. For example, some precipitates show a dominant Cu-Se-O constituent whereas others show a predominant Cu-Ag-Se-As-Pb-O phase. Electron microprobe analysis of a sample from CCR gave the approximate composition of Se 10.5, Pb 2.2, As 7.0, Cu 25.5, Ag 16.4, Au 1.7, Te 0.4, S 0.5 and Sb 0.06%. The remainder is mainly O and H_2O . Most of the Ag and Au in this particular sample is present as Ag^0 and Au^0 , and much of the Pb is believed to originate from enclosed PbSO_4 particles. In high-Ag and high-Au anode slimes, Ag^0 and Au^0 particles usually are visible in the matrix of these precipitates. In summary, most of the Ag, Se and Te present in the

Fig. 1. Optical micrograph showing the distribution of impurities (bright) in the anode copper (dark) from CCR. The impurities occur mainly along the grain-boundaries of the copper matrix (right-hand side); near the air face (left-hand side), the anodes usually show a concentration of copper oxide. Sample coated with carbon to enhance the contrast. (polished section).

Fig. 2. BSE image showing the detailed structure of the impurities in the anode copper (CCR). a- copper matrix, b- Cu_2O , c- Cu_2Se , d- Cu-Pb-As oxide. (polished section).

Fig. 3. BSE image showing the detailed structure of the impurities in the anode copper (CCR). a- copper matrix, b- Cu_2O , c- Cu_2Se , d- Cu-Pb-As-Bi oxide, e- Cu-Pb-As-Bi-Sb oxide. (polished section).

Fig. 4. General morphology of the slimes still attached to the anode (Kidd Creek). a- copper, b- Cu_2Se or $(\text{Cu,Ag})_2\text{Se}$, c- Cu_2O , d- Ag^0 , e- $(\text{Cu,Ag})_2\text{Se} + \text{PbSO}_4$, or $\text{CuAgSe} + \text{PbSO}_4$, f- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{PbSO}_4$. (loose powder mount).

Fig. 5. BSE image showing the general structure of the slimes still attached to the anode (Kidd Creek). a- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, b- $(\text{Cu,Ag})_2\text{Se}$, c- Ag^0 , d- Cu-Pb-As oxide or Cu-Pb-Bi oxide, e- $\text{PbSO}_4 + \text{selenide}$. (polished section).

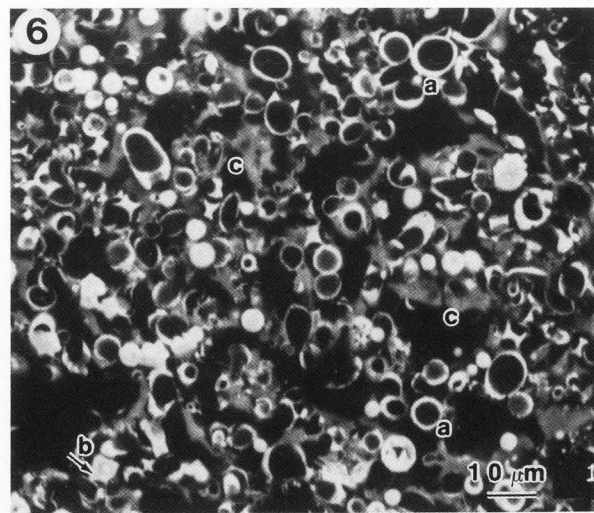
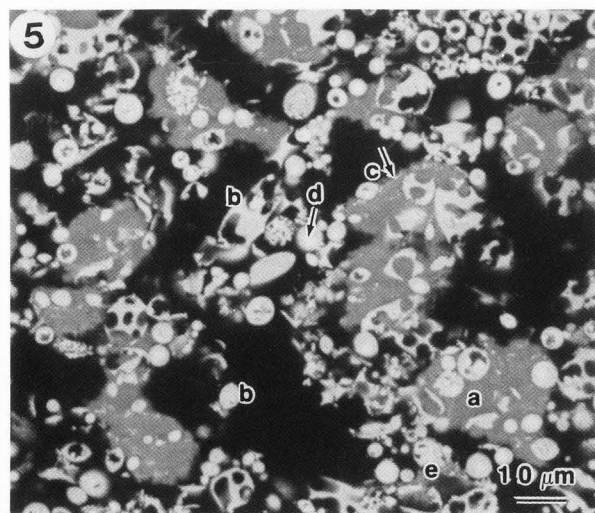
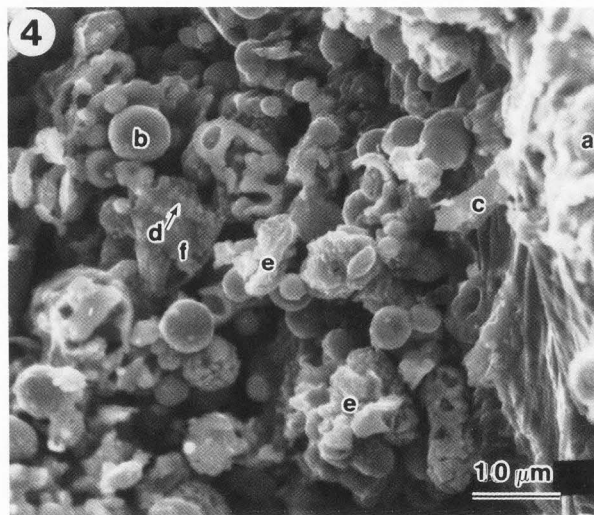
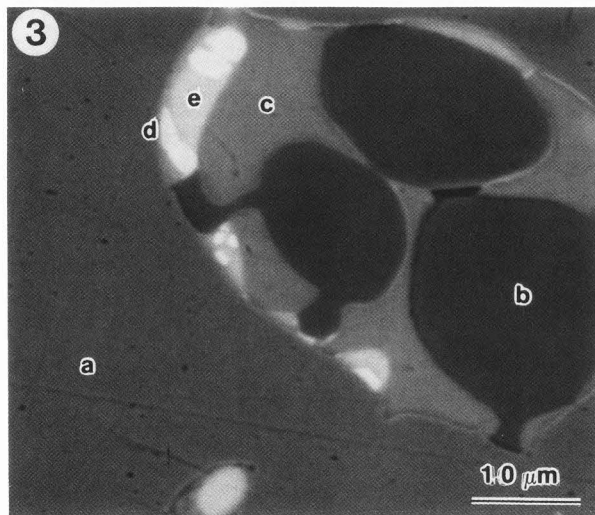
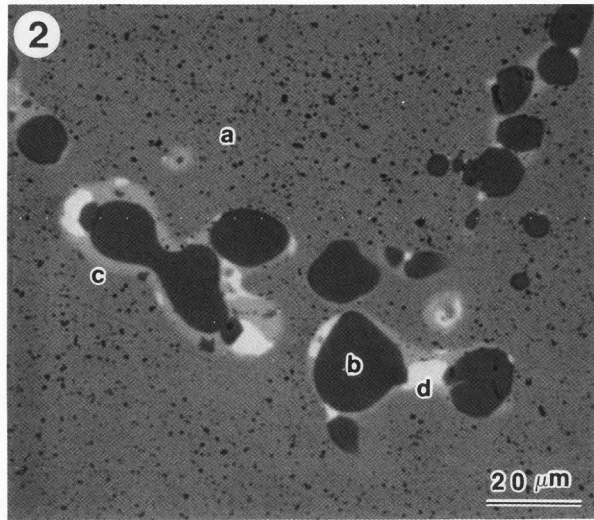
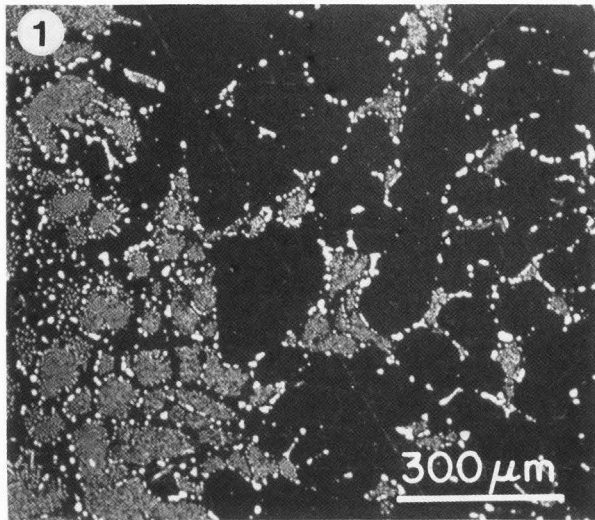
Fig. 6. General morphology (BSE image) of the slimes collected from the bottom of the electrolytic tank (CCR). a- AgCuSe or $(\text{Cu,Ag})_2\text{Se}$, b- Cu_2O , c- Cu-Ag-Se-Pb-As oxide. (polished section).

anodes occurs in the anode slimes as $(\text{Ag,Cu})_2(\text{Se,Te})$ particles whose morphology is that of the Cu_2Se grains in the anode. Much of the lead is present as tiny PbSO_4 grains although some also occurs in complex Cu-Pb-As-Bi-Sb precipitated oxides. The abundant Cu_2O blebs in the anode dissolve, but are replaced by rarer Cu_2O crystals or films. Copper sulphate is abundant in the slimes still attached to the anode and may help to attach the slimes to the anode face. The slimes collected on the cell bottoms differ in the presence of an abundant Cu-Ag-Se-As-Pb-O phase which seems to contain fine particles of Ag^0 and Au^0 .

The Behaviour of Selenium During the Electrorefining of Copper

Selenium occurs in copper anodes mainly as copper selenide (Cu_2Se). As was mentioned earlier, the slimes collected from the bottom of the electrolytic tanks contain a precipitated mixture of Cu, Ag, Se, Pb, As and O as major components, and Bi, Sb, Ni, S, Te and Au as minor constituents (Figure 6). Some of these precipitates are clearly Cu-Se-O in composition, and this means that at least a small amount of the selenium in the anodes dissolves and reprecipitates during electrorefining. Most of the copper selenide (Cu_2Se) in the anodes, however, remains undissolved and enters the anode slime layer directly during the electrorefining of the

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copper as is shown in Figures 7-9. Figure 7 shows an anode containing several clusters of selenide-oxide impurities that are present at or near the reaction interface between the anode and electrolyte. Inside the copper anode (a), the clusters (b) consist of Cu_2O (dark), Cu-Pb oxide or Cu-Pb-As oxide (bright), and Cu_2Se (grey). At the interface, the large cluster of selenide-oxides has just been exposed to the electrolyte and has changed to Cu_2Se (grey), PbSO_4 (bright) and CuSO_4 (dark). It seems that Cu_2O and Cu-Pb oxide have reacted rapidly with H_2SO_4 to form CuSO_4 and PbSO_4 , or have completely dissolved, thereby creating cavities in the remaining selenide structures.



Several spherical and porous selenide particles, with holes partially filled by PbSO_4 , are present at the lower right corner. Some of the selenides in the slimes layer are held together by a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ phase which, in turn, contacts directly with the electrolyte. The build-up of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ layer obviously will retard the electrochemical dissolution of the copper anode. Figure 8 and Figure 9 provide additional examples to show the general insolubility of copper selenide during electrorefining. In all cases, as soon as the Cu-Pb oxide or Cu-Pb-As oxide contact the electrolyte, they react with H_2SO_4 and either change to PbSO_4 or dissolve and leave holes in the original selenide-oxide structures. Figure 8 shows an elongate Cu_2Se particle at the reaction interface about to become completely detached from the anode. The selective dissolution of the copper at the inclusion-metal interface is apparent. Figure 9 shows another elongate Cu_2Se structure which has just been liberated from the copper anode and has passed into the anode slimes layer. The distribution of the anode impurities at the grain boundaries is clearly visible in Figure 8.

In summary, selenium in copper anodes occurs mainly as copper selenide in selenide-oxide clusters which consist of Cu_2Se , Cu_2O and Cu-Pb oxide or Cu-Pb-As oxide. During electrorefining, the selenide remains undissolved and enters directly into the anode slimes layer, whereas the oxides either completely dissolve or react with H_2SO_4 to form new compounds. The selenide-oxide clusters in the slimes consist of selenides (Cu_2Se , CuAgSe and/or Ag_2Se), PbSO_4 and cavities. Figure 10 shows the selenide structures in the slimes after washing with an ammonium acetate solution to remove the PbSO_4 . The cavities in the structures are formed by the dissolution of Cu_2O , Cu-Pb oxide and Cu-Pb-As oxide during electrorefining. Figure 7 to Figure 9 show that the morphology of the selenide particles in the slimes is a reflection of the morphology in the anode, and is controlled by the anode casting method.

The Behaviour of Lead During the Electrorefining of Copper

Lead occurs as a solid solution in the copper matrix and as inclusions of Cu-Pb oxide,

Fig. 7. BSE image of the anode-electrolyte reaction interface (Kidd Creek). a- copper, b- Cu_2Se (grey) + Cu-Pb oxide (bright) + Cu_2O cluster (dark), c- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, d- Cu_2Se (grey) + PbSO_4 (bright) + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. (polished section).

Fig. 8. BSE image of the anode-electrolyte interface that presents an elongate selenide-oxide cluster about to become detached from the anode (Kidd Creek). The distribution of the impurities along the grain-boundaries of the anode is apparent (cf. the right-hand side of Figure 1). a- copper, b- Cu_2Se + Cu-Pb oxide + Cu_2O , c- $(\text{Cu,Ag})_2\text{Se}$ + PbSO_4 + holes, d- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. (polished section).

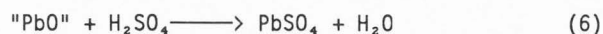
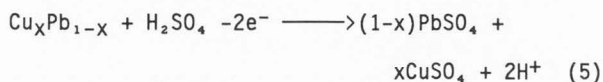
Fig. 9. BSE image of the anode-electrolyte interface that shows a selenide- PbSO_4 cluster just detached from the anode (Kidd Creek). a- copper, b- Cu_2O (dark) + Cu-Pb oxide (bright) + Cu_2Se (grey), c- $(\text{Cu,Ag})_2\text{Se}$ (bright) + hole + PbSO_4 (dark), d- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, e- PbSO_4 (core) in AgCuSe , f- $(\text{Cu,Ag})_2\text{Se}$ + PbSO_4 . (polished section).

Fig. 10. General morphology of the selenide structure (mainly AgCuSe) in an anode slimes sample from CCR. The raw slimes were washed with an ammonium acetate solution to remove PbSO_4 . The large round holes in the selenide structures were most likely formed by the dissolution of Cu_2O during electrorefining, whereas the small cavities originated from the dissolution of Cu-Pb-As-Bi-Sb oxides and Cu-Pb-As oxides. (loose powder mount).

Fig. 11. Morphology of PbSO_4 in the slimes (CCR). a- PbSO_4 , b- AgCuSe , c- Ag_2Se , d- $(\text{Cu,Ag})_2\text{Se}$. (loose powder mount).

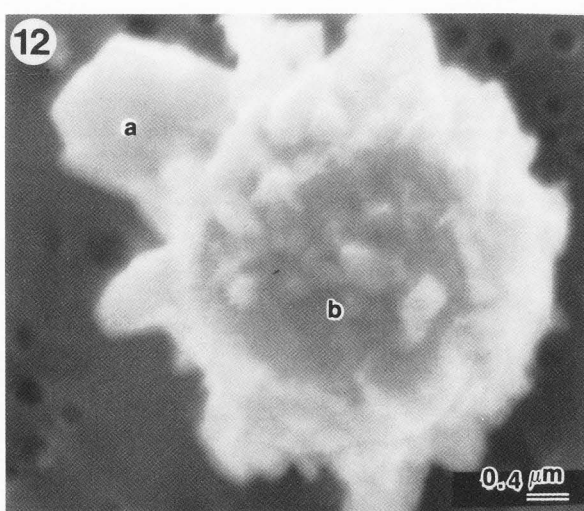
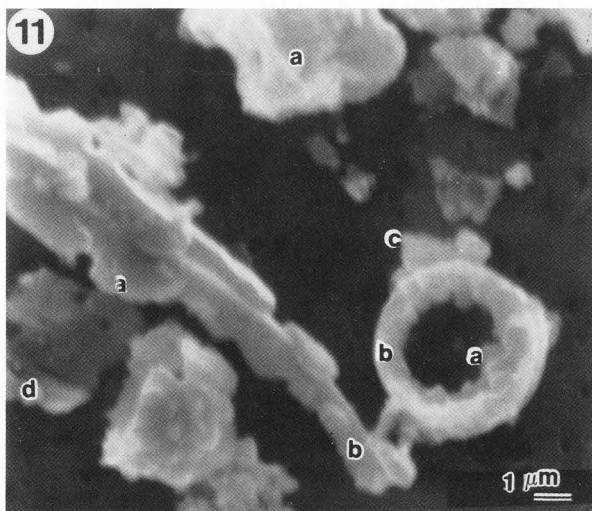
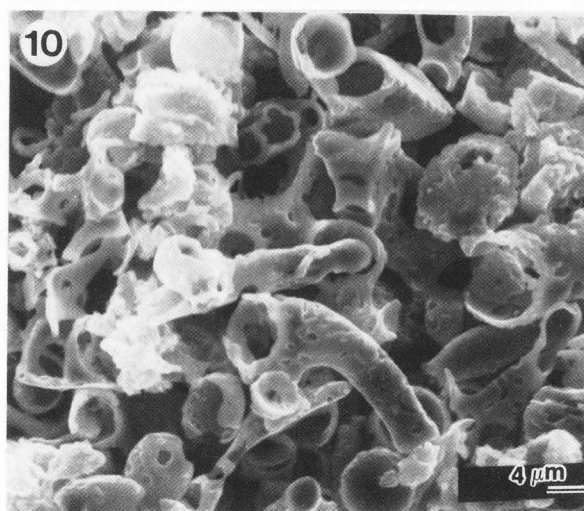
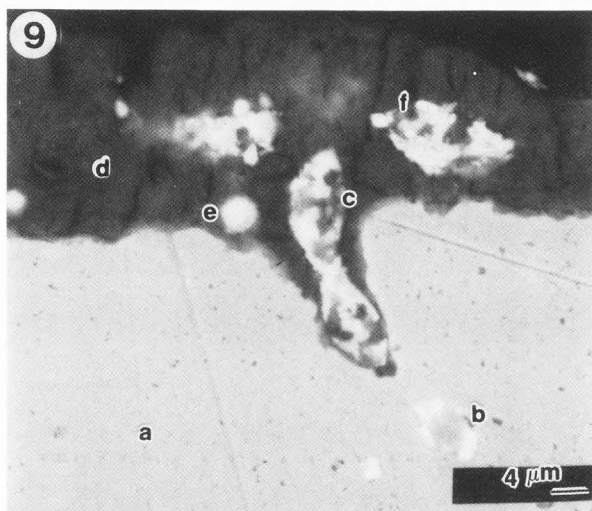
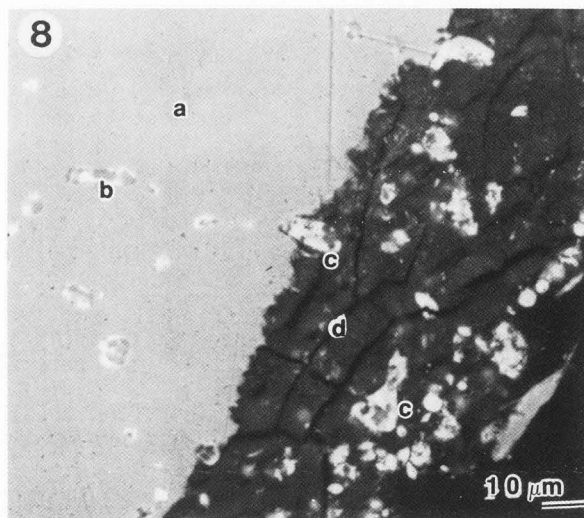
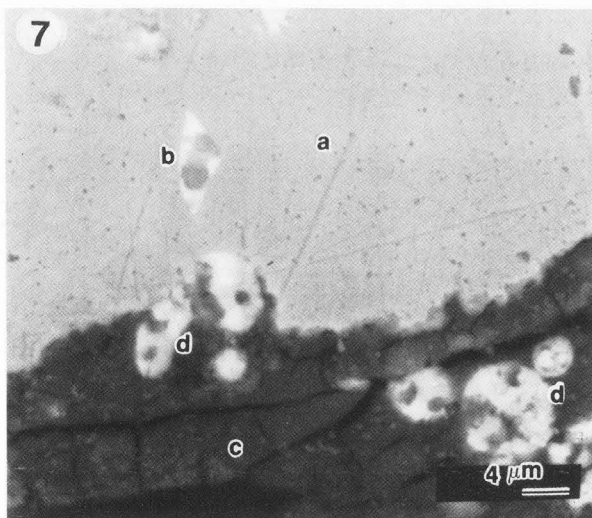
Fig. 12. Morphology of PbSO_4 (a) on a spherical AgCuSe particle (b) in the slimes from CCR. (loose powder mount).

Cu-Pb-As oxide, or Cu-Pb-As-Bi-Sb oxide in the copper anodes. All the lead reacts rapidly during the electrorefining of copper and most reports as PbSO_4 .



The various Cu-Pb oxides or Cu-Pb-As oxides, etc. react with H_2SO_4 as soon as they contact the electrolyte; the lead either forms PbSO_4 in situ (Figures 7,8,9) or dissolves in the electrolyte and subsequently re-precipitates as PbSO_4 . A small amount (< 2%) of the Pb, however, seems to dissolve and remain in the electrolyte [2]. Figure 11 shows PbSO_4 crystallized as platy rhombic crystals (a) on the various selenide structures or as aggregates in the slimes. Figure 12 shows the morphology of the PbSO_4 on the surface of a spherical AgCuSe particle, and Figure 13 shows another view of a PbSO_4 cluster in the anode slimes. Many of the PbSO_4 particles exhibit crude crystallographic shapes.

Electrorefining of Copper



Some of the Cu-Pb oxide, Cu-Pb-As oxide, etc. is completely enveloped by Cu_2Se , particularly Cu_2Se spheroids, in the copper anodes. Since the selenide remains insoluble during electrorefining, these oxides remain unaffected and, consequently, enter the anode slimes layer directly. Figure 14 shows a Cu-Pb-Bi-Sb-As oxide grain (a) which is completely protected by a Ag_2Se shell (originally Cu_2Se), and remains unattacked during electrorefining. A Cu-Pb-Bi oxide particle which is completely enveloped by a selenide spheroid, $(\text{Cu,Ag})_2(\text{Se,Te})$, is illustrated in Figure 15. The Pb-bearing oxide phase has remained unaffected during the electrorefining process because of its protective shell.

In summary, most of the lead in the copper anodes reacts rapidly with H_2SO_4 to form PbSO_4 , which occurs as a filling in selenide spheroids or as free grains. Some of the PbSO_4 dissolves and subsequently reprecipitates as platy rhombic crystals on selenides or other phases. Only the lead entirely protected by complete selenide spheroids passes into the anode slimes as a lead oxide phase.

The Formation of Various Silver-Copper Selenides During the Electrorefining of Copper

Cu_2Se is the only selenide phase present in the copper anodes although some of the Cu_2Se particles contain a trace amount of Ag in solid solution (Table 3). In the anode slimes, however, various silver-copper selenides such as Cu_2Se , $(\text{Cu,Ag})_2\text{Se}$, CuAgSe and Ag_2Se occur. Usually more than one species is present. It is also observed that the higher the Ag/Se molar ratio in the anode, the more silver-rich are the selenide species present in the slimes. That is, Cu_2Se and $(\text{Cu,Ag})_2\text{Se}$ are the dominant selenide species in the anode slimes (Figures 4,5) from the low Ag/Se ratio anodes, whereas Ag_2Se and AgCuSe are the major selenide species in the slimes (Figures 6,10,11) from the high Ag/Se ratio anodes. Obviously, the silver originally contained in solid solution in the copper matrix dissolves and reacts with Cu_2Se to form silver-copper selenides during electrorefining.

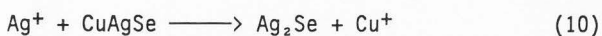
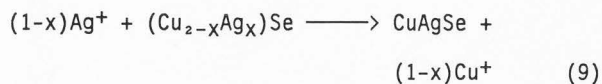
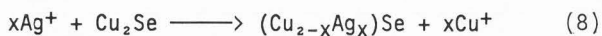
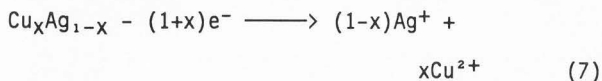


Figure 16 shows that the substitution of Cu by Ag in the selenide starts from the outer edge of the Cu_2Se grain and proceeds inward. Approximately

Fig. 13. Morphology of PbSO_4 clusters (a) in the anode slimes from CCR. The large porous tube-like, and broken hollow spheroidal structures (b) are AgCuSe . (loose powder mount).

Fig. 14. General slimes morphology illustrating an unattacked Cu-Pb-As-Sb-Bi oxide (a) which was completely protected by a Ag_2Se shell (originally Cu_2Se) during electrorefining (CCR). b- SnO_2 , c- Ag-Se-Cu-Pb-Bi-O precipitate, d- Ag_2Se . (loose powder mount).

Fig. 15. BSE image showing a Bi-Pb-Cu oxide grain which was completely protected by a $(\text{Cu,Ag})_2(\text{Se,Te})$ shell during electrorefining and remained unaffected in the slimes (INCO). a- Cu-Bi-Pb oxide, b- $(\text{Cu,Ag})_2(\text{Se,Te})$, c- AgCuSe , d- NiO. (polished section).

Fig. 16. BSE image of selenide grains in the anode slimes from CCR that shows the substitution of Cu by Ag starting from the outer edge of the selenide grain. The lighter areas are AgCuSe (a) whereas the darker areas are $(\text{Cu,Ag})_2\text{Se}$ (b). (polished section).

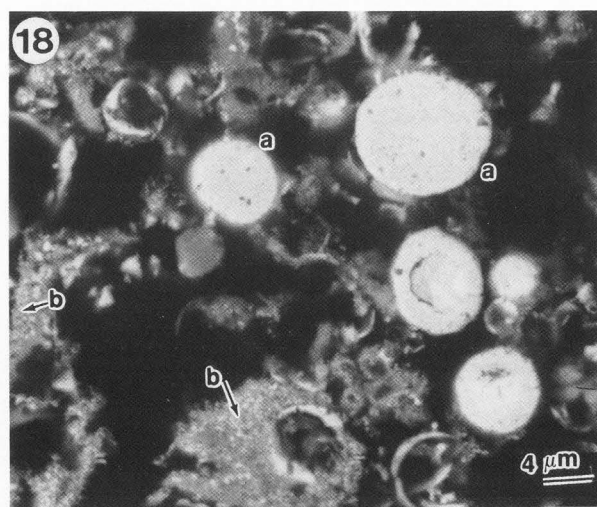
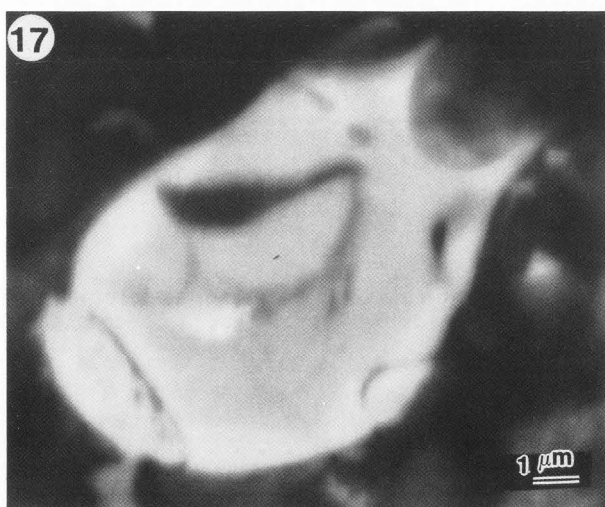
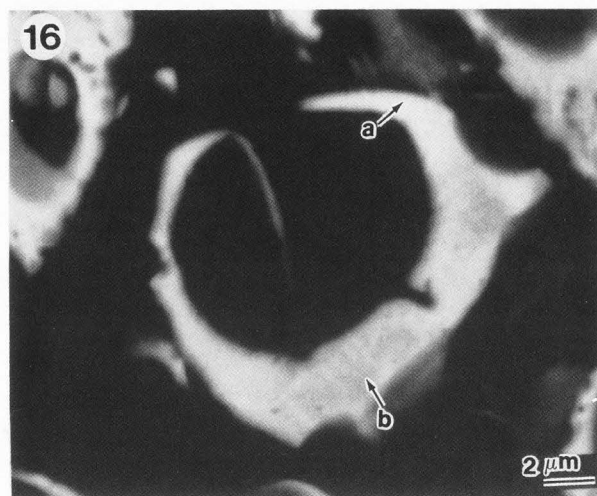
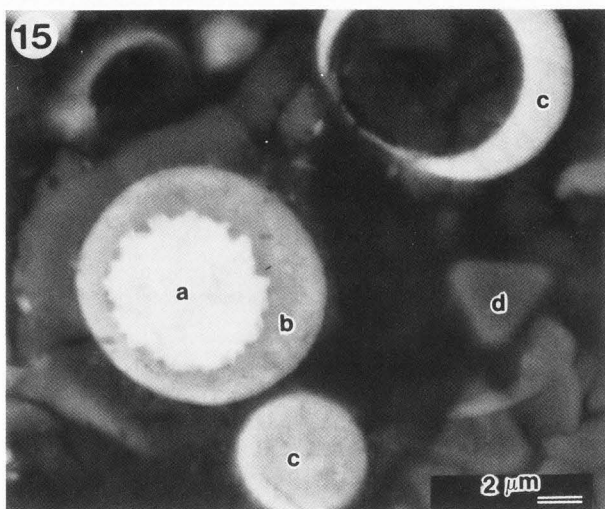
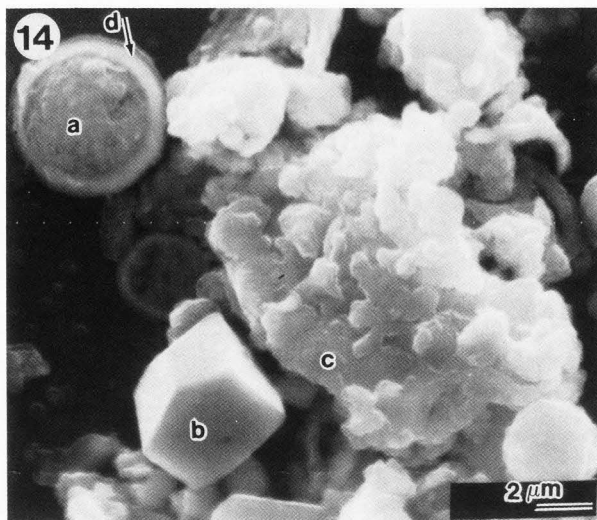
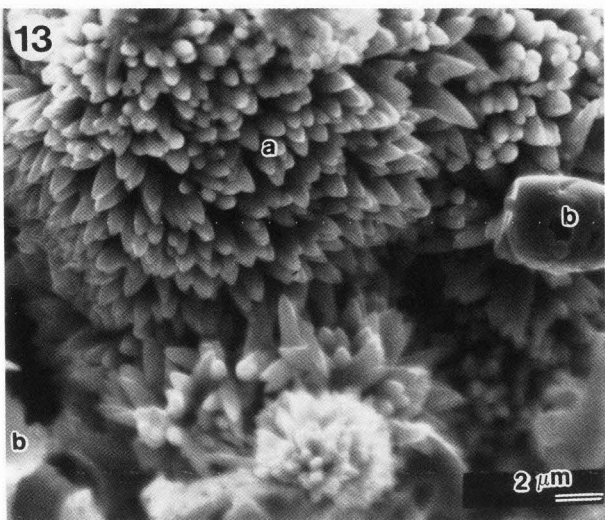
Fig. 17. BSE image of a Cu_2Se grain (grey) from the INCO anode slimes. The outer edge of the grain has been converted to AgCuSe (light). (polished section).

Fig. 18. BSE image of a Ag-rich anode slime from CCR that shows Ag_2Se (a) and Ag^0 (b) as the major constituents. (polished section).

one-half of the original Cu_2Se (grey) grain has been replaced by AgCuSe (bright); the remainder is mainly $(\text{Cu,Ag})_2\text{Se}$. Figure 17 shows another Cu_2Se (grey core) grain partially replaced by AgCuSe (light) on the edge. The presence of more than one selenide species in the same slimes is shown in Figures 11 and 15. For the Ag-rich anodes, the slimes produced usually contain major amounts of Ag^0 and Ag_2Se where the metallic silver may originate by precipitation with cuprous ion (Eq. 11). Figure 18 shows a silver-rich anode slime in which all the selenide grains are Ag_2Se , and a large quantity of Ag^0 also is present.

In summary, the silver, dominantly present in the anode in solid solution in the copper, dissolves during electrorefining and then either reacts with Cu_2Se particles or is precipitated as silver powder by cuprous ion or metallic copper. The reaction with Cu_2Se proceeds through $(\text{Cu,Ag})_2\text{Se}$ to AgCuSe and finally to Ag_2Se , and these reactions retain the morphology of the original Cu_2Se particles. One consequence of these sequential reactions is the presence of more than one selenide phase in the slimes. Because the reactions with selenide phases are rapid, the Ag/Se ratio of the anode strongly influences the selenide species in the anode slimes.

Electrorefining of Copper



Conclusions

The fine grained and complex products formed during the electrorefining of impure copper have been characterized using SEM-EDX techniques. The copper anodes subjected to electrorefining consist of a copper matrix containing numerous inclusion phases concentrated at the copper grain boundaries. Part of the Ag, Ni, Pb and As present in the anodes is in solid solution in the copper. Much of the Pb and As, however, is present as Cu-Pb-As oxide or Cu-Pb-Bi-Sb-As oxide inclusions at the copper grain boundaries. All of the Se and Te contained in the anodes is present as $\text{Cu}_2(\text{Se,Te})$ inclusions in the metal.

During electrorefining, the oxide inclusions react rapidly as soon as they contact the $\text{CuSO}_4\text{-H}_2\text{SO}_4$ electrolyte. The copper oxide forms copper sulphate which dissolves slowly in the electrolyte, and the lead oxide is converted to insoluble PbSO_4 . The associated As and Sb pass into solution, but may subsequently reprecipitate, in part, in the anode slimes on the bottom of the refining cells. The Cu_2Se inclusions do not dissolve during electrorefining, and they simply accumulate in the anode slimes layer as spheroidal or more complex particles. The silver in solid solution in the copper anodes dissolves during electrolysis, and the soluble silver ion reacts rapidly with the residual Cu_2Se particles to form Ag-bearing selenides. The reaction begins at the outer surface of the particles, and progresses inward forming, sequentially, $(\text{Cu,Ag})_2\text{Se}$, AgCuSe and Ag_2Se . Silver powder also is present, and this is likely precipitated by another reaction, possibly involving cuprous ion. It has been shown that the compositions of the silver-bearing products in the anode slimes depend on the Ag/Se ratio of the as-cast anodes, and this information is of some significance for the subsequent processing of the slimes to recover the precious metal values.

Acknowledgements

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Discussion with Reviewers

K.S. Chopra: Did you use a windowless detector to do the quantitative analysis job? How did you assign the phases to be oxides?

Authors: All the quantitative analyses were carried out by electron microprobe on polished sections, and not by SEM. The distinction between oxides, sulphides or selenides was made on the basis of ore microscopy; the details of the techniques are presented in the Experimental.

K.S. Chopra: How did you perform quantitative analysis on rough sample, such as the slime sample, Figure 4?

Authors: Rough samples were analyzed using XRD and SEM qualitatively. Quantitative analyses were all performed on polished sections of the same samples. For example, there is no difficulty to correlate the phases in Figure 4 (loose powder mount) with those in Figure 5 (polished section).

K.S. Chopra: Did you perform X-ray diffraction analysis to determine compositions such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?

Authors: Yes. Whenever possible X-ray diffraction was used to identify the phases like $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Also, hydrated minerals generally can also be recognized under the SEM or electron microprobe, as they gradually dehydrate/decompose under the bombardment of the electron beam under vacuum.

K.S. Chopra: Some of the assumptions such as cavities originated from the dissolution of Cu-Pb-As-Bi-Sb oxides, etc, should be considered purely speculative.

Authors: Although the conclusions are speculative, they are not purely so. For example, by comparing the morphology of the impurities of the specific anode casts with those

of the anode slimes, some interpretations can be derived with confidence. For example, the slimes shown in Figure 10 were produced from anodes fabricated using the mould casting/Walker wheel method, the anode cooling rate is relatively slow, the grain sizes of the impurities in the anode are fairly coarse, the segregation between the copper and the impurities was well developed so that the impurities occur primarily along the copper grain boundaries (Figure 1). As is shown in Figure 2, in these anodes, Cu_2O occurs as large blebs and spheroids, and the various Cu-Pb-As-Sb-Bi oxides occur as tiny blebs closely associated with Cu_2Se . The relative sizes and amounts of the oxides are controlled by the relative quantities of the impurities (such as As, Sb, Bi, O, etc) in the anodes. Since most of the Cu-Pb-As-Sb-Bi oxides usually occur as tiny particles attached to selenide (Figure 3) in these anodes, it is reasonable to interpret that the small cavities on the surface of the selenide particles (Figure 10) originated from the dissolution of Cu-Pb-As-Bi-Sb oxides. However, for anodes cast using a Hazlett continuous strip caster, the anode cooling rate is faster; the impurities in the anodes are very fine-grained, and the impurity clusters are usually irregular in shape. As a result, an interpretation such as the above is impossible. The interpretation also is impossible for anodes with high As, Sb, Bi contents as the particle sizes of the As, Sb, Bi bearing impurities in the anodes are much larger.

G. Remond: How is it possible that a thin rim like that of d in Figure 14 be positively identified, as these rims are very thin; e.g., less than 0.5 μm in thickness?

Authors: In a loose powder mount (Figure 14), the phases were identified qualitatively using SEM. However, the same phase assemblage can be identified in polished section (e.g., phase b in Figure 15). Some of the particles have thicker rims which can be analyzed more reliably using the electron microprobe. In addition, ore microscopy and XRD are always used to check the phase identifications wherever possible.

Reviewer II: Could the authors comment on the use of carbon coating in reflected-light optical microscopy (Figure 1). Why is it successful?

Authors: The success of carbon coating to enhance the phase contrast in reflected-light optical microscopy depends on the phase assemblages of the sample. For example, if only silicate and oxide phases are present, this technique will not work because all these compounds become white after carbon-coating. Metal phases and sulphide phases usually change colour after carbon coating, and the coated colour varies with the thickness of the carbon. Basically, the exact colour of the phase after the carbon-coating must be known before the application of this technique. For Figure 1, the authors used the characteristic phase assemblage of the copper anodes to apply this technique. That is, the anode consists of a minor amount of

oxide and selenide impurities dispersed in a predominantly metallic copper matrix. After proper carbon coating, the copper matrix becomes blue in colour whereas oxides and selenide become white in colour. Consequently, the phase contrast between the metallic copper and the impurities was enhanced, and the grain-boundary distribution texture of the impurities in copper anodes became obvious.

G. Bonifazi: Have the authors performed a statistical quantitative analysis in order to estimate, for example by means of image analysis techniques, the shape and the size of the impurities in a copper or/and in the anode slimes? Which have been the most recurrent structures found during the analysis?

Authors: Some image analyses on high Ni anodes have been done to determine the amounts of NiO in the copper anodes. However, analysis on the size and shape of the impurities have not been done, because the morphology of the impurities in the anodes is controlled by the anode casting condition, very much related to the cooling rate of the anode. Also, it is affected by the relative amounts of the different impurities in the anode; e.g. the morphologies of the Cu-Pb-As oxides and Cu_2Se in the high-Pb and high-As anodes are different from those in the low-Pb and low-As anodes. Similarly, the morphology of the Cu_2Se in the high-Se and low-O anodes is different from that in low-Se and high-O anodes. In anode slimes, the morphology of the selenides is inherited from the anodes.

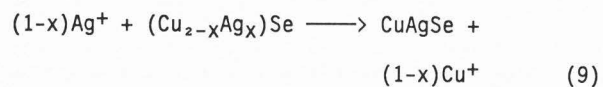
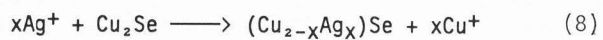
G. Bonifazi: Have the authors taken into consideration and examined samples taken during different intervals of time, inside the electrolytic tanks or have the researches been carried out always analysing the resulting products at the end of each process?

Authors: The mineralogical changes occurring during different time intervals of the electrorefining of copper have been studied. The changes between the slimes still attached to the anode face and those in the bottom of the electrolytic tank also have been studied. The results will be published shortly.

G. Bonifazi: How have the morphological data, together with the compositional ones, been used to elucidate the diverse reactions occurring during electrorefining? Are the obtained data related to a significant number of samples, in order to make them representatives of a phenomenology?

Authors: Using Figures 7, 8 and 9 as examples, it is obvious that the selenides remain undissolved and go into the anode slimes directly during copper electrorefining. Since (1) only Cu_2Se is present in the copper anodes, but various Cu-Ag selenides are usually present in the slimes, and since (2) Figures 16 and 17 show that the replacement of Cu by Ag in Cu_2Se starts from the surface of the particle and proceeds inwards, it

becomes obvious that the reactions:



have taken place during the electrorefining of copper.

A large number of samples from the three Canadian copper refineries, not only the industrial anodes and anode slimes but also test anodes and test anode slimes have been studied. The details will be published later.