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Acid and Oxidizing Leaching of Copper Refinery Anodic Slimes in Hexafluorosilicic Acid and Nitric Acid Media

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ABSTRACT

Copper refinery anodic slimes containing copper (23.8%), arsenic (2.9%), selenium 8%), tellurium (0.9%), antimony (3.2%), silver (8.3%), and gold (0.3%) were treated by acid leaching using hexafluorosilicic acid (first step) and by acid and oxidizing leaching using a mixture of hexafluorosilicic and nitric acids (second step). This treatment dissolved 99% of the Cu, Se, and Te, 97% of the As, 95% of the Sb, and 85% of the Ag. After these two leaching steps, the final solid leach residue, which represents about 28% in weight of the initial solid, is upgraded in gold (1.11% Au), containing only 0.06% Cu, 0.04% As, 0.3% Se, 0.02% Te, and 0.11% Sb, while still remaining high in silver (4.45%). The leach solutions obtained are concentrated in Cu (24.5 g/L) as the first step, and in Ag (15.3 g/L) and Se (15.5 g/L) as the second step, which is favorable for the selective extraction of metals.

INTRODUCTION

Copper refinery anodic slimes are of economic interest because of their precious metals content. However, environmental laws are becoming more restrictive, and these slimes are a source of toxic elements, mainly As, Se, and Te.

Actually, the principal objective of treating copper refinery anodic slimes is the recovery of precious metals and, sometimes, selenium and tellurium. This is achieved by using pyrometallurgical techniques (1–3) which, unfortunately, generally have high operating costs and produce pollutants such as SO_2 and arsenical compounds. In some cases hydrometallurgical techniques could be economically competitive and satisfy environmental requirements. Nevertheless, only a few methods involving these techniques have been studied: oxidizing leaching in a nitric acid medium containing sodium chloride (4), autoclave leaching under oxygen pressure in sulfuric acid media (5–7), and cyanidation of gold and silver (4).

The scope of this study is the development of another hydrometallurgical method based on both acid and oxidizing conditions, mainly for the dissolution of Cu, As, Se, and Te, by using a "hexafluorosilicic acid–nitric acid" media. Thermodynamic data (4, 8) show that Cu and As are easily soluble in acid solutions, but if the dissolution of Se and Te is also wanted, the leaching media must be both acid and oxidizing, and these conditions are correctly satisfied by "H_2SiF_6–HNO_3" media.

EXPERIMENTAL PROCEDURE

Samples of copper refinery anodic slimes were provided by Rio Tinto Minera (RTM), Spain.

The leach solutions were prepared from laboratory-grade concentrated hexafluorosilicic acid (H_2SiF_6, 31% by weight), nitric acid (HNO_3, 69% by weight), and demineralized water.

Leaching Tests

Leaching tests were carried out at room temperature with a liquid-to-solid ratio of 12/1, unless otherwise stated. The anodic slimes were added to the required amount of "hexafluorosilicic acid–nitric acid" mixtures and agitated for 3 hours except when the leaching time was being studied. The slurry was then filtered, and the solid residue was washed and dried at 70°C for approximately 5 hours. The filtrate and the residue were both analyzed for Cu, As, Se, Te, Ag, and Au. The dissolution rates of the elements ($T\%$) were determined by the following equation:

$$T\% = 100\ [(X_iP_i - X_rP_r)/(X_iP_i)]$$

where X_i is the metal content of the initial solid (%); X_r is the metal content of the solid leach residue (%); P_i is the weight of the initial solid (g), and P_r is the weight of the solid leach residue (g).

Analyses

Particle size analysis was carried out by a Laser granulometer (Malvern-Master Sizer). The specific surface was determined by the B.E.T. and by the "*t* point" methods (9, 10). Mineralogical characterization was performed by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Chemical analyses were by ICP-AES (atomic emission spectroscopy in plasma) for Cu, As, Se, and Te, and by ICP-MS (mass spectrometry coupled to plasma induced by high frequency) for Au and Ag. A materials balance was calculated to verify the results of the analyses, and an error of $\leq$10% was deemed acceptable.

RESULTS AND DISCUSSION

Characterization of Crude Copper Refinery Anodic Slimes

The anodic slimes produced by the Spanish copper refinery of Rio Tinto Minera (RTM) are particularly rich in copper and precious metals but, unfortunately, also contain such impurities as As, Se, Te, Sb, Ba, etc. Table 1 lists the mean chemical composition of these slimes.

XRD characterization of the slimes shows they are slightly crystalline and contain the following mineral phases: Cu_7Te_5, AgCuSe, $AgAsSe_2$, Ag_2Se, $PbSO_4$, $BaSO_4$, Bi_2O_3, SiO_2. Furthermore, SEM characterization allows identification of such other phases as $CuSO_4$; Cu_2S and SnO_2; and some complex mixed phases composed of Ag-Se-Cu-S, Ag-Cu-As-Sb-S, and Cu-As-Sb-Se-S.

These anodic slimes are also characterized by 1) a high specific surface; the measurements made by the B.E.T. and by the "*t* point" methods show a surface area of 26.4 m^2/g. 2) A fine particle size, 80 μm; the d_{50} of the size distribution is close to 12 μm.

Leaching of Copper Refinery Anodic Slimes

Tests were performed using "hexafluorosilicic acid–nitric acid" mixtures. The parameters investigated were the acid composition of the leach mixtures, the leaching time, the leaching temperature, and the liquid-to-solid ratio.

Effect of Acid Proportions in Leach Mixtures

Previous tests performed with H_2SiF_6 2.3 M showed that this medium dissolve 99% Cu, 81% As, 37% Te, and 28% Se, while the dissolution

TABLE 1
Chemical Composition of RTM Copper Refinery Anodic Slimes

Element	Cu	Ba	Ag	Se	Pb	Sb	As	Te	Au
Content, %	23.8	11.8	8.3	8.0	3.7	3.2	2.9	0.9	0.3

rates obtained with HNO_3 3.5 M do not exceed 74% As, 69% Cu, 14% Te, and 9% Se. Hexafluorosilicic acid is therefore more efficient than nitric acid, although it is neither an oxidizing nor a complex-forming medium. However, when these two acid media are put to work simultaneously, dissolution rates of As, Se, Te, and Ag are enhanced, reaching (for H_2SiF_6 1.8 M and HNO_3 4.1 M) 89% As, 95% Se, 95% Te, and 89% Ag. The dissolution rate of Cu remains 99%. Various proportions of H_2SiF_6 and HNO_3 in the mixtures were therefore tested in order to determine the most adequate composition of the leach media which could lead to the best compromise among the dissolution rates of Se, Te, As, Ag, and Cu, and reduce the consumption of hexafluorosilicic and/or nitric acids. Results are given in Table 2, which show that:

Whatever the H_2SiF_6 and HNO_3 concentrations, the dissolution of copper remains constant at 99%, whereas arsenic dissolution varies slightly between 77 and 86% for H_2SiF_6 concentrations ranging from 1.3 to 2.2 M. However, the dissolution rate of As seems to decrease for $HNO_3 \geq 3$ M and $H_2SiF_6 > 1.7$ M.

When the HNO_3 concentration is set at 2 or 3 M, an increase of H_2SiF_6 concentration will enhance the dissolution of Se, Te, and Ag. On the contrary, when the HNO_3 concentration reaches 4 M, the H_2SiF_6 concentration no longer has any effect on the dissolution levels of these elements.

The higher dissolution rates for all the elements are obtained at H_2SiF_6 1.3–1.7 M and HNO_3 4 M. Studies of the other parameters were therefore performed at H_2SiF_6 1.3 M and HNO_3 4 M.

Furthermore, analyses of gold in the leach solutions showed that whatever the composition of the leach media, it has no effect on the dissolution of gold, which always remains in the solid leach residue.

TABLE 2

Effect of the Mixture Composition in H_2SiF_6 and HNO_3 on the Leaching of RTM Copper Refinery Anodic Slimes; Room Temperature; L/S = 12/1; Conditioning Time 3 hours

	Dissolution rates (%) at H_2SiF_6 and HNO_3 concentrations of														
	HNO_3 (2 M)					HNO_3 (3 M)					HNO_3 (4 M)				
H_2SiF_6 (M)	Cu	Ag	As	Se	Te	Cu	Ag	As	Se	Te	Cu	Ag	As	Se	Te
1.3	99	24	78	31	29	99	58	83	58	60	99	77	86	94	96
1.7	99	45	79	45	43	99	68	84	83	86	99	77	84	95	97
2.2	99	64	80	71	74	99	73	77	85	90	99	77	77	89	93

TABLE 3
Effect of Leaching Time on the Leaching of RTM Copper Refinery Anodic Slimes by the Mixture "H_2SiF_6 1.3 M–HNO_3 4 M"; L/S 12/1; Room Temperature

Leaching time (hours)	Dissolution rates (%)				
	Cu	As	Se	Te	Ag
1	99	79	72	78	68
2	99	81	85	89	73
3	99	84	93	96	78
4	99	86	94	96	77
5	99	87	95	97	80

Effect of Leaching Time

Leaching time was varied from 1 to 5 hours. The results in Table 3 show that conditioning time has no effect on the leaching of Cu, whereas the dissolution rates of As, Se, Te, and Ag increase, reaching their maximum for 4 hours. However, a leaching time of 3 hours leads to relatively acceptable rates of dissolution for Cu (99%), As (84%), Se (93%), Te (96%), and Ag (78%).

Effect of Leaching Temperature

The leaching temperature was varied from 25 to 65°C for a leaching time of 3 hours. As shown by Table 4, increasing the temperature greatly enhances the dissolution rates of As but only slightly those of Ag, Se, and Te. At 65°C the dissolution of Cu, Se, Te, As, and Sb is almost

TABLE 4
Effect of Temperature on the Leaching of RTM Copper Refinery Anodic Slimes by the Mixture "H_2SiF_6 1.3 M–HNO_3 4 M"; L/S 12/1; Conditioning Time 3 hours

Temperature (°C)	Dissolution rates (%)				
	Cu	As	Se	Te	Ag
25	99	84	93	96	78
35	99	89	96	97	82
45	99	94	98	98	83
55	99	96	99	98	84
65	99	97	99	99	85

complete, exceeding 95%, whereas that of Ag reaches only 85%. Under these operating conditions the leach liquor contains 25.8 g/L Cu, 3.45 g/L As, 8.81 g/L Se, 1.3 g/L Te, 6.85 g/L Ag, and 3.1 g/L Sb, and the solid leach residue is composed of 0.02% Cu, 0.3% As, 0.1% Se, 0.05% Te, 4.64% Ag, and 0.6% Sb.

Effect of Liquid-to-Solid Ratio (L/S)

Experiments were performed at 35°C for 3 hours at varying liquid-to-solid ratios of 25/1, 18/1, 12/1, 10/1, and 8/1. The results are given in Table 5. The solid concentration in the slurry is practically without effect on the dissolution of Cu, Ag, Se, and Te, but the dissolution rate of As increases significantly when the L/S ratio exceeds 18/1, reaching 96% at 25/1. This phenomenon can be related to the solubility of some Sb–As compounds (11). In fact, the dissolution rate of antimony increases from 57% for $8/1 \leq L/S \leq 12/1$ to 89% for $L/S = 25/1$. Unfortunately, the use of a high liquid-to-solid ratio leads to a large consumption of hexafluorosilicic and nitric acids and to low concentrations of the metals in the leach liquor. Thus, an L/S ratio of 12/1 appears to be sufficient, because it dissolves over 95% Cu, Se, and Te, 81% As, and 78% Ag.

Outline of a Leaching Flow Sheet

The results obtained by using fluorosilicic acid and mixtures of this acid medium with nitric acid show that the best way to remove impurities and to recycle or to recover valuable metals is to use two steps for the leaching of copper refinery anodic slimes (Fig. 1).

In the first step, hexafluorosilicic acid media dissolves Cu, As, and Sb. Tests carried out with H_2SiF_6 1.5 M, at 65°C, L/S = 12/1, and a conditioning time of 3 hours gave the following average results:

TABLE 5
Effect of Liquid-to-Solid Ratio on the Leaching of RTM Copper Anodic Slimes by the Mixture "H_2SiF_6 1.3 M–HNO_3 4 M"; T 35°C; Conditioning Time 3 hours

Liquid-to-solid (L/S) ratio	Dissolution rates (%)				
	Cu	As	Se	Te	Ag
8	99	81	95	96	78
10	99	80	97	97	81
12	99	85	97	98	83
18	99	85	96	97	83
25	99	96	95	96	81

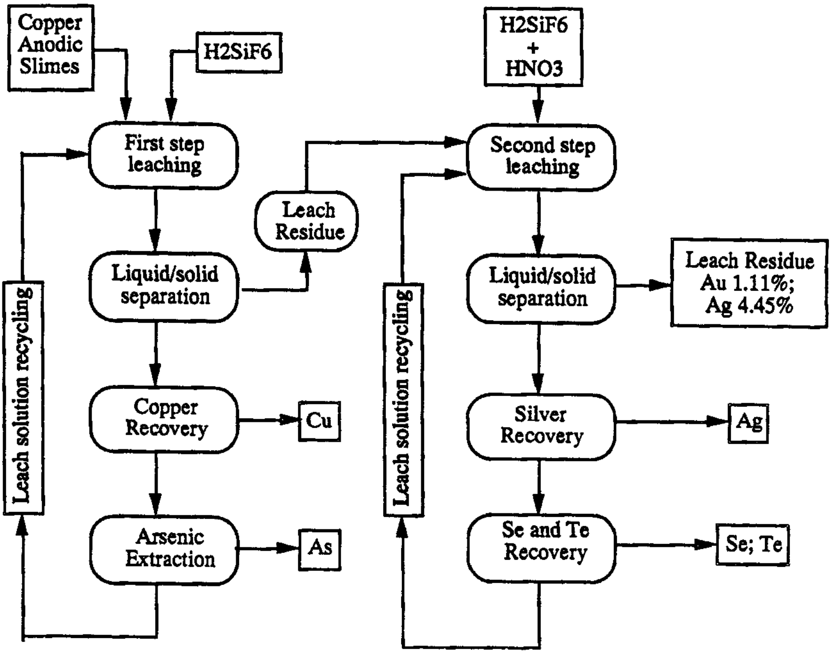

FIG. 1 Simplified flow sheet for the leaching of RTM copper refinery anodic slimes by hexafluorosilicic acid and by hexafluorosilicic–nitric acids media.

Dissolution rates: Cu 93%, As 90%, Sb 80%, Te 41%, and Se 11%. Silver and gold remain in the solid leach residue.

Composition of the solid leach residue: Cu 3.7%; As 0.7%; Sb 1.4%, Te 1.2%, Se 15.5%, Ag 17.8%, and Au 0.65%. This residue represents 46% by weight of the initial solid.

Composition of the leach solution: Cu 24.5 g/L; As 2.9 g/L; Sb 2.8 g/L; Se 1 g/L, and Te 0.4 g/L.

In the second step, the solid leach residue of the first step is leached again, this time by the "H_2SiF_6 1.3 M–HNO_3 4 M" mixture. Then, if it is assumed that the dissolution rates of the elements remain close to those obtained during direct leaching of the copper refinery anodic slimes, by using this mixture at 65°C, L/S = 12/1, and a conditioning time of 3 hours (i.e., Cu 99%, As 97%, Se 99%, Te 99%, Ag 85%, and Sb 95%), the following results should be obtained:

Composition of the final solid leach residue, representing about 28% by weight of the initial solid (feed of the first step): Cu 0.06%; As 0.04%; Se 0.3%; Te 0.02%; Sb 0.11%; Ag 4.45%; and Au 1.11%.

Composition of the leach solution: Cu 3.7 g/L; As 0.7 g/L; Se 15.5 g/L; Te 1.2 g/L; Ag 15.3 g/L, and Sb 1.3 g/L.

Thus, it appears from this leaching procedure that the final solid leach residue is upgraded in gold, and the solutions obtained in the two steps are mainly concentrated in copper during the first step and in selenium and silver during the second step. The advantage of the proposed flow sheet is therefore the selective dissolution of Cu and As previous to that of Se, Te, and Ag, allowing for easy extraction of the valuable metals. In fact, copper can be easily recovered by solvent extraction from the leach liquor of the first step with LIX 622 (Henkel) or Cyanex 301 (Cyanamid) extractants, and the removal of As can also be achieved by the same technique, using TBP as extractant (7). From the liquor of the second step, silver can be precipitated as AgCl, and Se and Te can be cemented on iron powder (7). Finally, gold and silver can be extracted by cyanidation from the ultimate solid leach residue after an alkaline wash of this residue.

CONCLUSION

Copper refinery anodic slimes from Rio Tinto Minera (Spain) have an average content of 23.8% Cu, 8.3% Ag, 7.2% Se, 3.7% Pb, 3.2% Sb, 2.9% As, 0.9% Te, and 0.3% Au. These elements are present in several amorphous and crystalline mineral phases, oxidized and nonoxidized, and particularly as mixed phases composed of Cu-Te, Cu-Se, Cu-Ag-Se, Cu-Sb, Cu-As, Ag-Te, Ag-As-Se, As-Pb, and As-Sb. It is therefore difficult to obtain a selective lixiviation. The dissolution of a given element depends both on the nature of the leaching medium and of the mineral phases in which it occurs.

However, the results obtained by acid leaching in hexafluorosilicic acid medium and by acid and oxidizing leaching in a mixture of this acid and nitric acid show that when these media are used consecutively in two steps, it is possible to achieve selective dissolution of various components. In fact, hexafluorosilicic acid, used alone in the first step, dissolves copper, arsenic, and antimony, and the use of the "H_2SiF_6–HNO_3" mixture in the second step dissolves selenium, tellurium, and silver. Thus, in the solid leach residue the silver content remains high (4.45%) and the gold content is multiplied by a factor of 3.7, reaching 1.11%. Furthermore, the selectivity offered by this two-step process makes it easier to recover the dissolved metals and the precious metals remaining in the final solid leach residue.

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