Acid and Oxidizing Leaching of Chalcopyrite Concentrate by Ferric Sulphate and Fluorosilicic-Nitric Media

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ABSTRACT

A hydrometallurgical treatment was applied to the Hajar Mine Copper Concentrate (HMCC), Morocco, containing $\approx 28.1\%$ copper (the major copper mineral phase is chalcopyrite, $CuFeS_2$), $\approx 26.3\%$ iron, $\approx 5.8\%$ zinc, $\approx 1.9\%$ lead, $\approx 33.7\%$ sulphur, and small amounts of silver (269 g/t) and nickel (219 g/t). Three acid media were used: ferric sulphate in sulfuric acid, ferric sulphate in hexafluorosilicic acid, and a hexafluorosilicic acid–nitric acid mixture.

The results show that when a ferric sulphate reagent is used, in H_2SO_4, as well as in H_2SiF_6 media, dissolution of copper and iron do not exceed 30%, because of the formation of a passivation layer on chalcopyrite particles, whereas zinc is dissolved at about 90%. The final solid leachate residue represents 75% by weight of the initial

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solid and remains rich in copper ($\approx 28\%$) and iron ($\approx 25\%$). However, under strong acid and oxidizing conditions, in the hexafluorosilicic acid–nitric acid mixture, the dissolution of copper is more efficient, although it is nonselective, (92% Cu, 89% Fe, 98% Zn). The solid leachate residue represents only 40% by weight of the original sample, and assays 5.9% Cu, 7.3% Fe, 0.2% Zn, 4.1% Pb, and 56.4% S_{total}.

Mineralogical characterizations of the leachate solid residues show the formation of both elemental sulphur and a $Cu_{1-x}Fe_{1-y}S_{2-z}$ layer on the surface of the nondissolved chalcopyrite.

Key Words.   Copper; Chalcopyrite; Leaching; Ferric sulphate; Fluorosilicic acid; Nitric acid

INTRODUCTION

Chalcopyrite is the most abundant mineral phase in copper concentrates. It is classically treated by pyrometallurgical techniques that produce toxic gases such as SO_2, SeO_2, As_2O_3, and TeO_2. Much work has centered on hydrometallurgical routes (1–5). Most hydrometallurgical processing of chalcopyrite concentrates has focused on leaching; recovery of copper from solutions is common.

The leaching of chalcopyrite can be performed in sulfuric and chloride media (5–11). However, ferric chloride is considerably more efficient than ferric sulphate, which offers a slow-reacting kinetic and requires high temperatures. In spite of their efficiency, chloride-based processes have found few applications (because of high plant costs and corrosion) and few processes have progressed beyond the laboratory scale (12).

The aim of this paper is to develop another hydrometallurgical route for leaching chalcopyrite concentrates, based on acid and oxidizing conditions, by using hexafluorosilicic acid–nitric acid media, and to compare those media to H_2SO_4 and H_2SiF_6 media containing $Fe_2(SO_4)_3$. Tests were performed at the Hajar Mine Copper Concentrate (HMCC), Morocco.

Hexafluorosilicic acid, a strong and noncomplexant acid, was used in complex sulfide concentrate leaching (13). It was also used for the leaching of copper electrorefining anodic slimes for the dissolution of copper, silver, selenium, tellurium, and arsenic (14).

EXPERIMENTAL PROCEDURE

The leaching solutions were prepared using laboratory-grade products: hexafluorosilicic acid (H_2SiF_6, 31% by weight), nitric acid (HNO_3, 69% by weight), ferric sulphate ($Fe_2(SO_4)_3 \cdot 9H_2O$; 22% Fe^{III}, 21% H_2O), sulfuric acid (H_2SO_4, 95% by weight), and demineralized water.

The apparatus used consisted of a 250 mL erlenmeyer flask fitted with a magnetic stirrer. Leaching tests were carried out at atmospheric pressure with

a liquid-to-solid ratio of 11 : 1 by weight for nitrofluorosilicic media and 22 : 1 for sulfuric media, and for a leaching time of 3 h, unless otherwise stated. Stirring speed (300 rpm) was chosen for maintaining the grain particles in suspension. Tests at elevated temperatures were performed in a thermostated bath, where the chalcopyrite concentrate was introduced in the glass reactor containing the required volume of leaching solution at the leaching temperature.

After filtration, the solid residue was washed, dried at 60°C, and then analyzed for Cu, Fe, Zn, and S, which are the major chemical components of mineral phases in HMCC.

Particle size analysis was carried out by a laser granulometer (Malvern-Master Sizer). The specific surface was determined by BET and "t-point" methods (15–16). Mineralogical characterization was performed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The surface analyses of initial and residual unleached samples were performed by Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS), and X-Ray Photoelectron Spectroscopy (XPS). Chemical analyses were carried out by ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectroscopy) and atomic absorption spectroscopy (AAS).

MATERIALS

The sample of Hajar Mine Copper Concentrate (HMCC) used in this study was provided by Reminex society (Hajar Mine, Morocco). It is the same as that treated by ferric chloride (17). Mean chemical and mineralogical compositions are given in Table 1, which shows high levels of sulphur, copper, and

TABLE 1
Chemical and Mineralogical Compositions of Hajar Mine Copper Concentrate (HMCC)

Chemical analysis				Mineralogical analysis	
Elements	%	Elements	ppm	Minerals	%
Cu	28.1	Ag	269	Chalcopyrite ($CuFeS_2$)	70
Fe	26.3	Ni	219	Sphalerite (ZnS)	15
S	33.7	Sn	178	Galena (PbS)	2.2
Zn	5.8	Cd	116	Pyrrhotite (FeS)	4
Pb	1.9	Sb	108	Talc	7
				[$Mg_3Si_4O_{10}(OH)_2)$]	
MgO	0.3	V	88		
SiO_2	0.5	Ba	56		
Al_2O_3	0.06				

iron and low concentrations of Zn, Pb, and silver (269 ppm). Chalcopyrite ($CuFeS_2$) is the main component of the sample and is the only source of copper.

The material is also characterized by a small specific surface (0.653 $m^2 \cdot g^{-1}$) and a fine particle size ($d_{50} \approx 20 \ \mu m$), all grains being less than 100 μm. It is slightly hydrated and oxidized by its exposure to air. This superficial oxidation was determined by XPS and DRIFTS analyses, which indicate the presence of some sulphate ions and the formation of iron oxide species (Fe_2O_3 and FeOOH).

RESULTS AND DISCUSSION

The parameters investigated in this paper, for the hydrometallurgical treatment of HMCC were reagent concentration in leaching solutions (except for ferric sulphate medium), leaching time, leaching temperature, and liquid-to-solid ratio (L : S).

Leaching by Ferric Sulphate Media

Ferric sulphate was studied in the presence of sulfuric acid and hexafluorosilicic acid media to determine which is more effective for the dissolution of copper. The concentrations of reagents were fixed at 0.5 M of ferric sulphate, 0.5 M of sulfuric acid, and 0.5 M of hexafluorosilicic acid.

The results are shown in Tables 2, 3, and 4, and show that the behavior of HMCC is the same in H_2SO_4 and H_2SiF_6 media containing $Fe_2(SO_4)_3$. Dissolution of copper and iron are practically identical, not exceeding 28–30%, and show identical tendencies toward every studied parameter. However, the zinc dissolution kinetic is faster in $H_2SO_4 \cdot Fe_2(SO_4)_3$ medium than in

TABLE 2
Effect of Liquid-to-Solid Ratio on Leaching of HMCC by H_2SO_4 0.5 M$\cdot Fe_2(SO_4)_3$ 0.5 M and H_2SiF_6 0.5 M$\cdot Fe_2(SO_4)_3$ 0.5 M Media (T, 85°C; conditioning time, 3 h)

	Dissolution, %					
	H_2SO_4 0.5 M$\cdot Fe_2(SO_4)_3$ 0.5 M			H_2SiF_6 0.5 M$\cdot Fe_2(SO_4)_3$ 0.5 M		
L : S	Cu	Fe	Zn	Cu	Fe	Zn
22	24	26	97	23	28	96
18	19	22	96	22	28	97
15	19	22	96	21	26	97
11	18	22	96	19	24	96

TABLE 3

Effect of Leaching Time on Leaching of HMCC by H_2SO_4 0.5 M·$Fe_2(SO_4)_3$ 0.5 M and H_2SiF_6 0.5 M·$Fe_2(SO_4)_3$ 0.5 M Media (T, 85°C; L : S, 22 : 1)

| Leaching time, H | Dissolution, % | | | | | |
| | H_2SO_4 0.5 M·$Fe_2(SO_4)_3$ 0.5 M | | | H_2SiF_6 0.5 M·$Fe_2(SO_4)_3$ 0.5 M | | |
	Cu	Fe	Zn	Cu	Fe	Zn
1.5	19	23	93	18	21	79
3	24	26	97	23	28	96
5	23	29	98	25	28	98
7	26	31	98	31	35	99

$Fe_2(SO_4)_3 \cdot H_2SiF_6$ medium, and exceeds 90% at 90 min of conditioning time.

Furthermore, maximum dissolutions of chalcopyrite and sphalerite are obtained at L : S = 22 : 1, a temperature of 85°C, and for a leaching time of 3 h. Under these conditions:

- The undissolved solid from the $H_2SO_4 \cdot Fe_2(SO_4)_3$ mixture represents 74% by weight of the initial sample and assays 30.3% Cu, 28.1% Fe, 0.2% Zn, and 40.5% S. The leaching solution contains 3.2 g/L Cu, 3.5 g/L Fe, and 2.7 g/L Zn.
- In the $H_2SiF_6 \cdot Fe_2(SO_4)_3$ media, the leachate solid residue assays 25.2% Cu, 23.9% Fe, 0.1% Zn, and 38.5% S. It represents 72% of the initial sample and is enriched in sulphur. The composition of the leaching solution is 4.2 g/L Cu, 4.7 g/L Fe, and 2.8 g/L Zn.

TABLE 4

Effect of Temperature on Leaching of HMCC by H_2SO_4 0.5 M·$Fe_2(SO_4)_3$ 0.5 M and H_2SiF_6 0.5 M·$Fe_2(SO_4)_3$ 0.5 M Media (L : S, 22 : 1; conditioning time, 3 h)

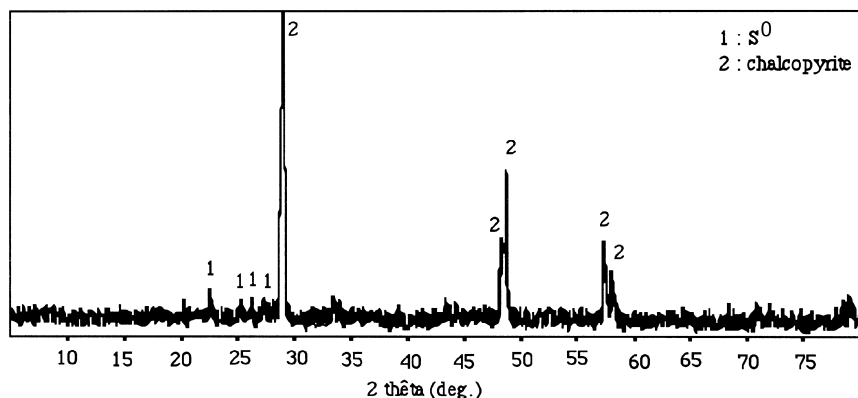| Temperature °C | Dissolution, % | | | | | |
| | H_2SO_4 0.5 M·$Fe_2(SO_4)_3$ 0.5 M | | | H_2SiF_6 0.5 M·$Fe_2(SO_4)_3$ 0.5 M | | |
	Cu	Fe	Zn	Cu	Fe	Zn
22	7	10	58	10	10	57
45	12	13	71	12	15	74
60	12	16	83	14	17	77
85	24	26	97	23	28	96

FIG. 1   X-ray analysis obtained after HMCC leaching by $H_2SO_4 \cdot Fe^2(SO_4)_3$.

Thus, chalcopyrite leaching is inhibited when copper dissolution attains about 25%, although the chalcopyrite reaction stoichiometry of the following equation has been respected

$$CuFeS_2 + 4\,Fe^{3+} = Cu^{2+} + 5\,Fe^{2+} + 2\,S^0$$

This is due to the formation of the passivation coating layer preventing the diffusion of the leaching agents to the surface of the chalcopyrite grain. This diffusion barrier would be formed by the elemental sulphur (9), or by an intermediate sulphide product phase (disulfide and polysulfide) mixed to S^0
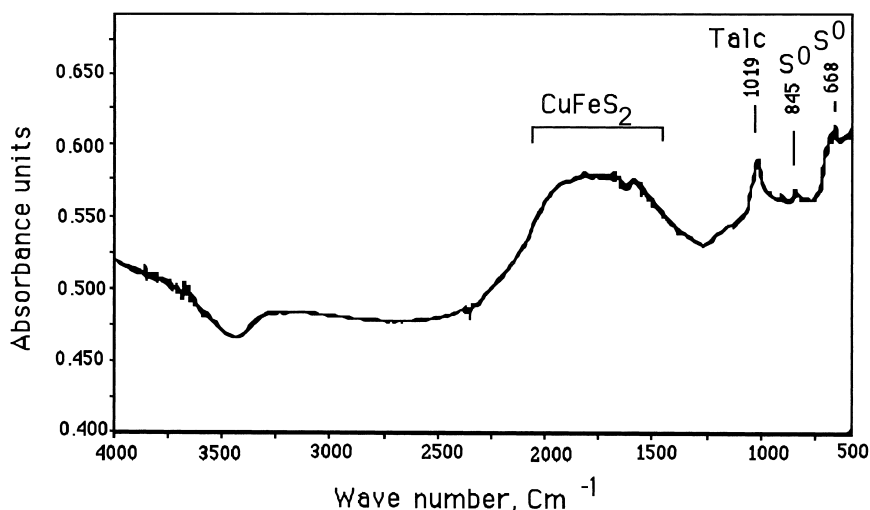

FIG. 2   DRIFTS of the residue obtained after HMCC leaching by $H_2SO_4 \cdot Fe_2(SO_4)_3$.

(18). The presence of elemental sulphur was identified by XRD (Fig. 1) and DRIFTS analyses of solid residues of the two leachant media (Fig. 2). XPS spectra (Fig. 3) show the disappearance of easily leachable sulphate species, the appearance of elemental sulphur formed by chalcopyrite oxidation, and the presence of a polysulphide phase ($Cu_{1-x}Fe_{1-y}S_{2-z}$). These results tend to confirm those obtained in previous studies (18).

Leaching by Hexafluorosilicic Media

The disadvantage of the formation of the passivation layer could be overcome by the use of a more acidic and oxidizing leachant medium, consisting of a $H_2SiF_6 \cdot HNO_3$ mixture. However, if hexafluorosilicic acid and nitric acid are used separately at a concentration of 1 M and at 80°C, the dissolution of copper does not exceed 14% and 44% respectively. Note that in
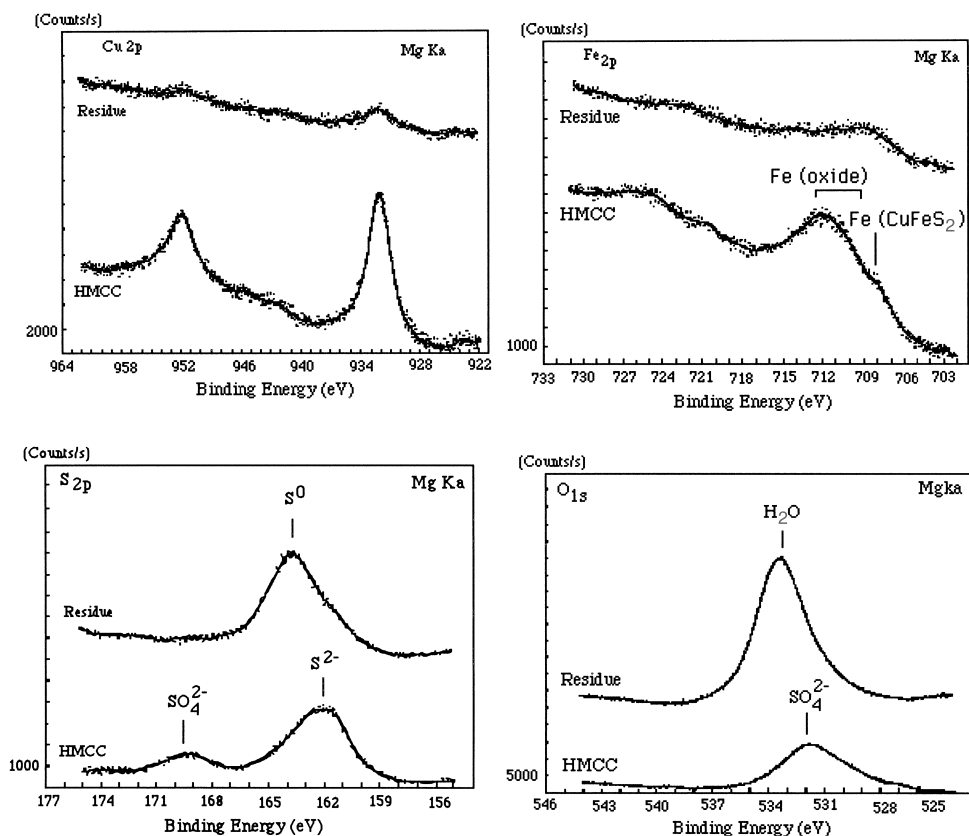

FIG. 3   Cu (2p), Fe (2p), S (2p) and O (1s) XPS spectra obtained from the surface of HMCC leaching by $H_2SO_4 \cdot Fe_2(SO_4)_3$.
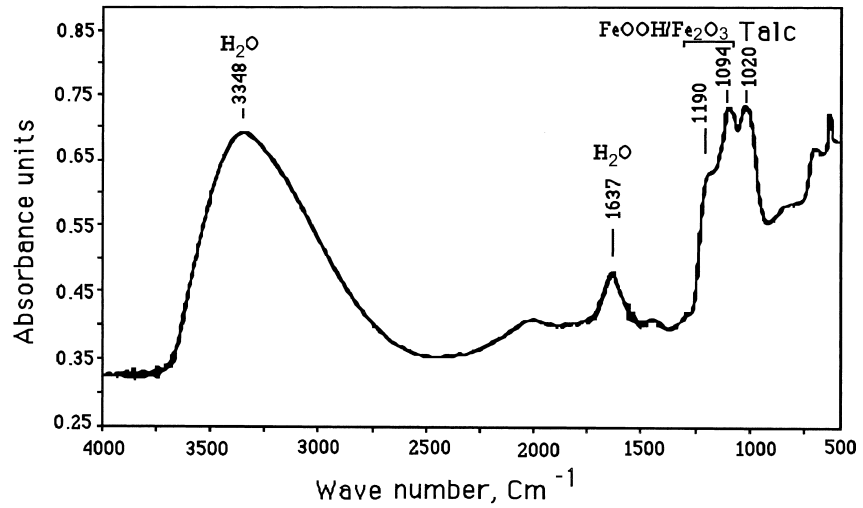
FIG. 4   DRIFTS of the residue obtained after HMCC leaching by HNO_3.

HNO_3 iron dissolution is lower than copper dissolution (13%), because of the formation of an amorphous iron oxide (red powder) not specified through x-ray diffraction. Infrared analysis shows that it should be FeOOH or Fe_2O_3 (Fig. 4).

The parameters investigated in the leaching study in $H_2SiF_6 \cdot HNO_3$ media were: leaching temperature, leaching time, liquid-to-solid ratio, and acid proportions in leaching solutions.

Effect of Acid Proportions

Results are given in Tables 5 and 6. Whatever the concentrations of H_2SiF_6 and HNO_3 in the mixture, in the range 0–2 M, the dissolution remain low, even

TABLE 5
Effect of the Mixture Composition in H_2SiF_6 and HNO_3 on Leaching of HMCC by
H_2SiF_6 0.5 M. (L : S, 11 : 1; conditioning time, 3 h; T, ambient and 40°C)

	Dissolution, %					
	Ambient temperature			Temperature 40°C		
HNO_3, M	Cu	Fe	Zn	Cu	Fe	Zn
0	9	12	0	3	0	3
1	14	8	17	12	13	19
1.5	11	10	12	16	19	49
2	14	13	13	15	17	60

TABLE 6
Effect of the Mixture Composition in H_2SiF_6 and HNO_3 on Leaching of HMCC by
HNO_3 0.5 M. (L : S, 11 : 1; conditioning time, 3 h; T, ambient and 40°C)

	Dissolution, %					
	Ambient temperature			Temperature 40°C		
H_2SiF_6, M	Cu	Fe	Zn	Cu	Fe	Zn
0	11	13	3	12	12	11
1	14	14	16	12	11	14
1.5	13	15	14	16	16	44
2	12	12	15	21	21	57

at 40°C, not exceeding 21% for Cu and Fe, 60% for Zn, but in comparison to ferric sulphate media at 40°C, they are enhanced by a factor of about 2.

In the following tests, two concentrations of acids in the leaching solutions were studied, 0.5 M and 1 M.

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

Experiments were performed at 60°C for 3 h liquid-to-solid ratios of 11 : 1, 8 : 1, 6 : 1, and 5 : 1. From the results of Table 7, it can be seen that the dissolution of copper, iron, and zinc are slightly affected when the liquid-to-solid ratio remains below 8 : 1, whatever the leaching mixture used. Maximum levels of copper, iron, and zinc dissolution are obtained at L : S of 11 : 1.

Effect of Leaching Time

Leaching time ranged from 30 min to 5 h. Table 8 shows that at 60°C the dissolution of Cu, Fe, and Zn increase with conditioning time and with concentrations of H_2SiF_6 and HNO_3 in the mixture.

TABLE 7
Effect of Liquid-to-Solid Ratio (L : S) on Leaching of HMCC by $H_2SiF_6 \cdot HNO_3$ Mixture.
(T, 60°C; conditioning time, 3 h)

	Dissolution, %					
	H_2SiF_6 0.5 M·HNO_3 0.5 M			H_2SiF_6 1 M·HNO_3 1 M		
L : S	Cu	Fe	Zn	Cu	Fe	Zn
11	27	32	79	49	50	85
8	17	17	20	45	46	81
6	14	15	20	41	42	81
5	16	16	21	41	43	79

TABLE 8
Effect of Conditioning Time on Leaching of HMCC by $H_2SiF_6 \cdot HNO_3$ Mixture.
(T, 60°C; L : S, 11 : 1)

Leaching time, h	Dissolution, %					
	H_2SiF_6 0.5 M·HNO_3 0.5 M			H_2SiF_6 1 M·HNO_3 1 M		
	Cu	Fe	Zn	Cu	Fe	Zn
0.5	16	15	20	21	23	37
1	23	22	44	28	32	51
1.66	23	24	58	38	40	64
3	27	32	79	49	50	85
5	41	41	91	65	64	94

Leaching data of chalcopyrite and sphalerite obtained from 30 min to 5 h, and H_2SiF_6 1 M · HNO_3 1 M, are compared with the shrinking-unreacted core models, which are

- Spencer-Toply's relation (19), for the chemical control model, Eq. 1,
- Valensis' relation (20), for the diffusional control model, Eq. 2,
- Wadsworth's relation (21), for the mixed control model, Eq. 3.

$$1 - (1 - \alpha)^{1/3} = k_1 t \tag{1}$$

$$1 - (2/3)\, \alpha - (1 - \alpha)^{2/3} = k_2 t \tag{2}$$

$$1 - (2/3)\, \alpha - (1 - \alpha)^{2/3} + 0{,}45\, [1 - (1 - \alpha)^{1/3}] = k_3 t \tag{3}$$

where $\alpha = [1 - (r/r_0)^3]$ is the fraction of chalcopyrite reacted at time t (r_0 and r are the radius of particles before and after the reaction); k_1, k_2 and k_3 are the rate constants.

As presented in Figs. 5 and 6, the data are straight whichever the equation model is used. One can deduce that the mixed kinetic model seems to be consistent with the data of the oxidation reactions of chalcopyrite and sphalerite, although not with enough certainty to propose the model, because of various uncertainties related by Prosser (22). The dissolution constant rate of sphalerite is about 2.5 times greater than that of chalcopyrite.

Effect of Leaching Temperature

The leaching temperature varied from ambient to 95°C, for a leaching time of 3 h and L : S of 11 : 1. As shown in Table 9, increasing the temperature greatly enhances the dissolution of Cu, Fe, and Zn, reaching 90%, 88%, and 99% respectively at 95°C, in a H_2SiF_6 1 M · HNO_3 1 M mixture. Furthermore, in H_2SiF_6 1 M · HNO_3 1 M no red ferrous solid phases appear during the dissolution of chalcopyrite when the temperature is greater than 60°C, as was ob-
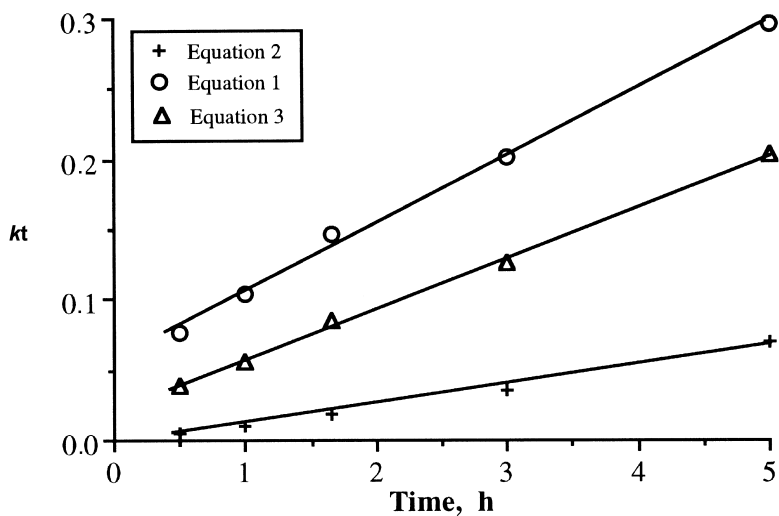
FIG. 5   Dissolution kinetic models of chalcopyrite for temperature of 60°C (H_2SiF_6 1 M · HNO_3 1 M), k = constant rate (k_1, k_2 or k_3).
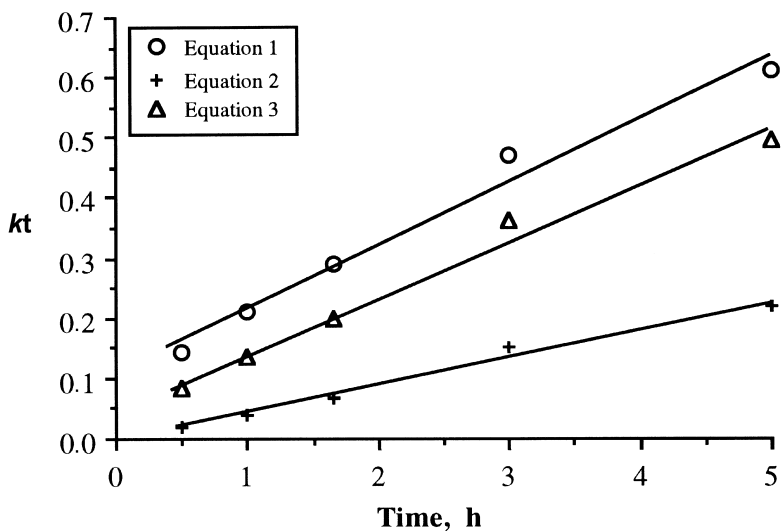

FIG. 6   Dissolution kinetic models of sphalerite for temperature of 60°C (H_2SiF_6 1 M · HNO_3 1 M), k = constant rate (k_1, k_2 or k_3).

TABLE 9
Effect of Temperature on Leaching of HMCC by $H_2SiF_6 \cdot HNO_3$ Mixture.
(L : S, 11 : 1; conditioning time, 3 h)

Temperature, °C	Dissolution, %					
	H_2SiF_6 0.5 M$\cdot HNO_3$ 0.5 M			H_2SiF_6 1 M$\cdot HNO_3$ 1 M		
	Cu	Fe	Zn	Cu	Fe	Zn
22	23	21	11	16	15	20
40	12	15	44	23	22	44
60	27	32	79	49	50	85
80	55	55	78	82	81	95
95	67	65	86	90	88	99

served when HNO_3 1 M was used alone. Thus, these phases are not stable in this strong acidic and oxidizing medium. Thus dissolution of chalcopyrite is not inhibited.

The Arrhenius plots of chalcopyrite and sphalerite oxydations, in H_2SiF_6 1 M $\cdot HNO_3$ 1 M, presented in Figs. 7 and 8, are straight and permit calculation of the apparent activation energies, which are about 22 ± 1.9 kJ/mole for chalcopyrite, and which change from about 29 ± 1.5 kJ/mole below 60°C, to 6 ± 0.3 kJ/mole for temperatures higher than 60°C.
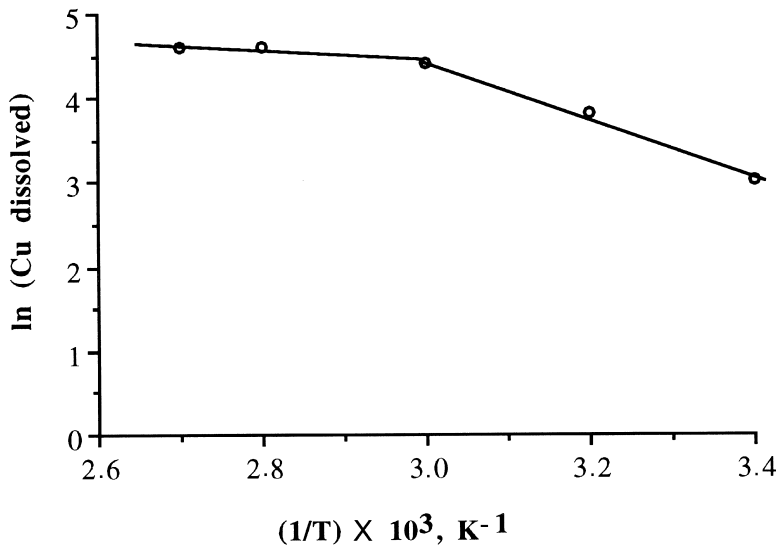

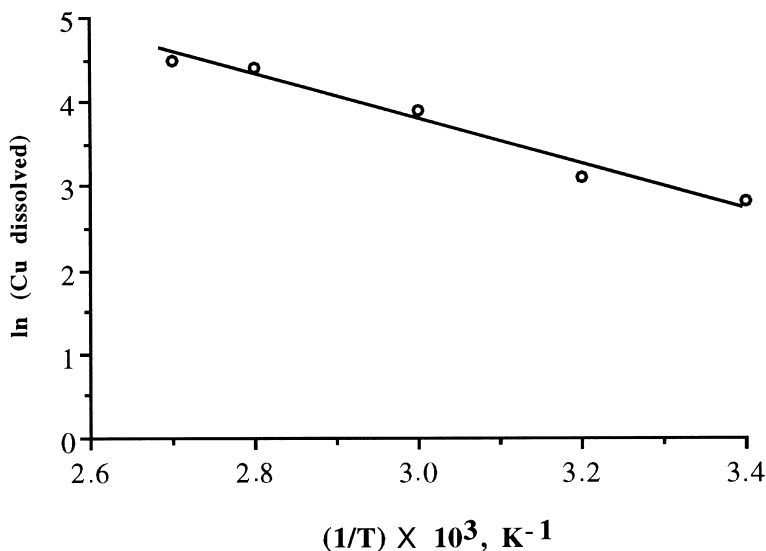FIG. 7   Arrhenius plot for sphalerite dissolution (H_2SiF_6 1 M $\cdot HNO_3$ 1 M, 3 hours).

FIG. 8   Arrhenius plot for chalcopyrite dissolution (H_2SiF_6 1 M $\cdot$ HNO_3 1 M, 3 hours).

Optimal Conditions of Leaching in H_2SiF_6–HNO_3

It appears from the results of comparative studies that the media composed of hexafluorosilicic and nitric acids enable more effective dissolution of copper than those using ferric sulfphate and sulphuric acid, although there is no selectivity. The leaching of HMCC is very dependent on the composition of the leaching solution, the conditioning time, the temperature, and the liquid-to-solid ratio.

Nevertheless, in the oxidizing solution of H_2SiF_6 1 M $\cdot$ HNO_3 1 M, at L : S = 11 : 1, the best results of copper dissolution (92% Cu) were obtained at 80°C and 5 h of residential time. At these operating conditions, the dissolution of the other elements reach 89% Fe and 98% Zn. However, conditioning time can be reduced from 5 to 3 h, as shown in Table 10, if the leaching temperature is 95°C. Thus, the leaching solution contains 25.8 g/L Cu, 23.4 g/L Fe,

TABLE 10
Leaching of HMCC by H_2SiF_6 1 M·HNO_3 1 M Mixture

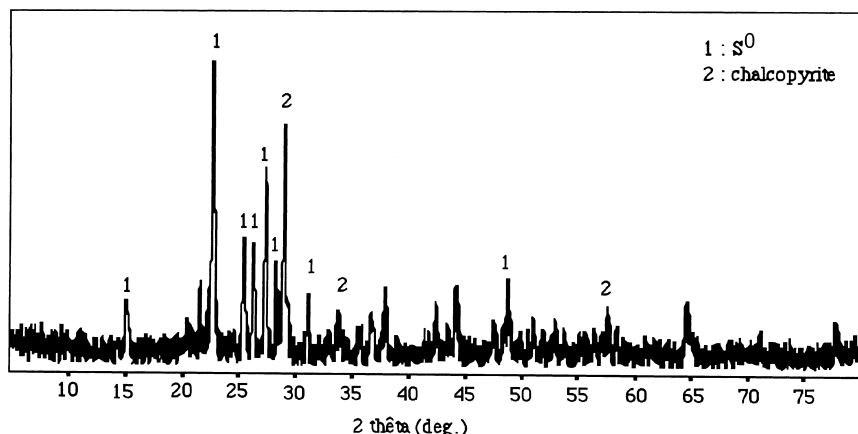| Temperature, °C	L : S	Leaching time, H	Dissolution, %		
			Cu	Fe	Zn
80	11	5	92	89	98
95	11	3	90	88	99

FIG. 9   X ray analysis obtained after HMCC leaching by $H_2SiF_6 \cdot HNO_3$.

5.7 g/L Zn, and the solid leachate residue, which represents 40% by weight of the initial sample, assays 5.9% Cu, 7.3% Fe and 0.2% Zn, and 56.4% S_{total}.

X-ray diffraction analysis (Fig. 9) and SEM analyses of the solid residue obtained by H_2SiF_6 1 M $\cdot$ HNO$_3$ 1 M media show the presence of CuFeS$_2$, in smaller proportions than in the original sample, talc, quartz and the appearance of elemental sulphur. By DRIFTS (Fig. 10) and XPS (Fig. 11) analyses, the presence of S^0 is confirmed; note the disappearance of the superficial ox-
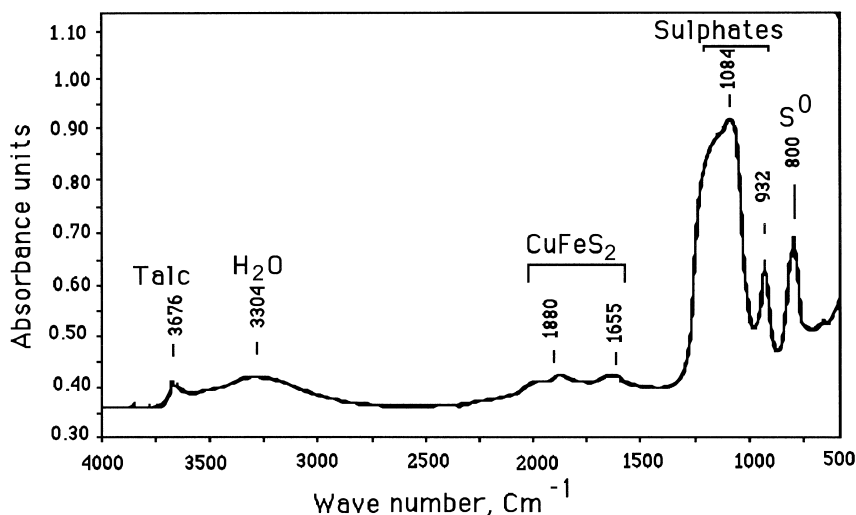

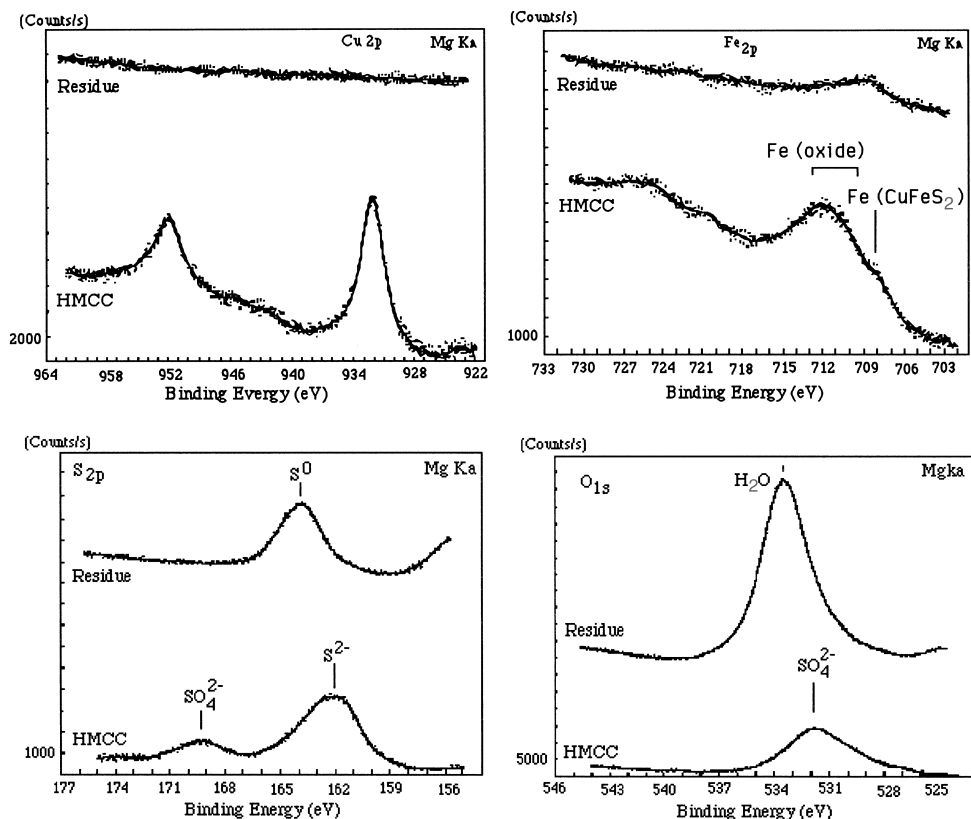FIG. 10   DRIFTS of the residue obtained after HMCC leaching by $H_2SiF_6 \cdot HNO_3$.

FIG. 11   Cu (2p), Fe (2p), S (2p) and O (1s) XPS spectra obtained from the surface of HMCC leaching by $H_2SiF_6 \cdot HNO_3$.

ides existing at the surface of the crude HMCC. Cu : Fe ratio at the grain surface is different than the initial sample because of the formation of an intermediate product ($Cu_{1-x}Fe_{1-y}S_{2-z}$). In this media, the coating layer, formed by elemental sulphur and this intermediate product, does not affect the "normal" leaching kinetic of the chalcopyrite, whereas in sulphate media it stops the reaction.

CONCLUSION

Tests performed with hexafluorosilicic-nitric mixtures show that the leaching of chalcopyrite concentrate is more efficient than that of sulphate media. Recovery of copper by sulphate media is not selective and did not exceed 28–30%, as a result of the coating layer formed by $Cu_{1-x}Fe_{1-y}S_{2-z}$ and elemental sulphur. This passivation layer had no effect on copper leaching by hex-

afluorosilicic-nitric media, where its dissolution is not selective. Dissolution of elements can reach 92% Cu, 89% Fe, and 98% Zn. Solid residue represents 40% of the initial sample, and the concentration of total sulphur is greater in the residue than in the initial sample. Part of the sulphur in the solid leachate residue is in elemental form. Leaching solution is rich in Cu, Fe, and Zn.

Taking into account the fact that the principal action of the passivation layer is negligible in $H_2SiF_6 \cdot HNO_3$ media, another approach could investigate the hydrometallurgical treatment of chalcopyrite concentrates. Such concentrates would consist of a combination of ferric sulphate–sulfuric acid, as a lixiviant medium, and a fluorosilicic acid–nitric acid mixture, as a solvent to avoid the passivation layer.

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