Enhanced Ferric Sulphate Leaching of Copper from $CuFeS_2$ and C Particulate Aggregates

by

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Synopsis

Significantly faster leaching kinetics for ferric sulphate are achieved for particulate aggregates of $CuFeS_2$ and C than for $CuFeS_2$ itself. The effect of carbon particles upon the rate of dissolution of chalcopyrite has been increased by a factor of 4 (after 10 hours' leaching), depending upon the carbon type, which varies in electronic conductivity and particle size. Interestingly, when the carbon content is reduced, even to 2 per cent, the enhanced leaching by ferric sulphate is sustained.

The leaching characteristics of aggregates of $CuFeS_2$ and C are described from reaction-rate experiments, conductivity measurements, and scanning-electron-microscope photographs of the elemental-sulphur reaction product. The results provide further evidence for the kinetic significance of the elemental-sulphur reaction-product layer in the leaching of chalcopyrite by ferric sulphate. Rate control by surface reaction is extended in the presence of carbon particles, but eventually the rate appears to become limited by the transport of electrons through the elemental-sulphur reaction-product layer, as was suggested in previous studies.

INTRODUCTION

During the past decades, basic research on hydrometallurgical techniques for the processing of copper sulphide concentrates has received considerable attention. Many varied and unique process strategies have been proposed and investigated. Chalcopyrite is of considerable interest because it is the most abundant of the copper sulphide minerals and, generally, is the most difficult to leach.

The acid ferric sulphate leaching reaction has been studied extensively because of its significance in dump-leaching practice and as a possible leaching reaction for the hydrometallurgical processing of copper sulphide concentrates. One of the most significant features of this reaction is the formation of a tenacious sulphur layer, which is believed by some to limit the reaction rate to unacceptably low levels. Although most authors agree that the ferric sulphate leaching reaction for chalcopyrite follows the equation

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} + 2S^\circ, \quad \ldots\ldots (1)$$

there is less unanimity in the interpretation of the reaction kinetics to explain rate control for this electrochemical reaction.

In this regard, research efforts have been directed to the study of the leaching behaviour of chalcopyrite. Much of this research has involved electrochemical measurements[1-6], which, by design, are limited to initial reaction behaviour and do not necessarily describe rate-control phenomena for a leaching reaction that goes to completion. The intrinsic anodic and cathodic electrochemical behaviour of chalcopyrite has been described in several studies. Warren and Wadsworth[1] studied the passive and transpassive anodic behaviour of chalcopyrite in acid solutions at low temperature. Based on current and mass-balance measurements, two intermediate phases, S_1 and S_2, appeared to form in the sequence $CuFeS_2 \rightarrow S_1 \rightarrow S_2$. In the first step of the reaction, the ferrous ion is released much more rapidly than the cupric ion, forming an intermediate structure according to the reaction

$$\mathrm{CuFeS_2} \rightarrow \mathrm{Cu}_{1-x}\mathrm{Fe}_{1-y}\mathrm{S}_{2-y-x} + x\mathrm{Cu}^{2+} + y\mathrm{Fe}^{2+} + (x+y)\mathrm{S}^{\circ} + 2(x+y)e, \qquad (2)$$

where $y > x$ initially.

An addition of Fe^{2+} drastically increased the current during anodic polarization because of the oxidation of Fe^{2+} to Fe^{3+}. These results confirm the electron-conducting character of the surface during the initial stages of reaction. Sulphur is an electronic insulator, and, if the electrode were passivated by elemental sulphur, it would not be expected to respond to additions of ferrous sulphate. Jones and Peters[7] report similar results for chalcopyrite electrodes.

Parker *et al.*[2,3] studied the electrochemical behaviour of the oxidation leaching of copper from chalcopyrite at elevated temperatures. From electrochemical measurements, they suggested that the initial anodic reaction of chalcopyrite is limited by the transport of ions through an unstable, semiconducting, metal-deficient polysulphide film. This semiconducting passivating film, which seemed to be thermally unstable, was suggested to transport ions slowly to the solution and transfer electrons slowly to oxidants, thus accounting for the kinetic features of the leaching of chalcopyrite. They concluded that the product sulphur layer is of little kinetic consequence in the leaching of chalcopyrite. Most of these studies have considered only initial reaction kinetics. It cannot be assumed that initial rate limitations necessarily prevail during the course of a leaching reaction that goes to completion. In many cases, the behaviour of polished electrode surfaces has been studied. The effect of particle size, an important diagnostic feature in the analysis of heterogeneous reaction kinetics, has not been considered.

A summary of the conclusions drawn from leaching studies reported in the literature is found in the paper by Munoz, Miller, and Wadsworth[8] and the review article by Dutrizac[9]. Lowe[10] and Jones *et al.*[7] attribute rate control to a surface reaction. Linge[4] and researchers at the University of Utah[8,11-13] report that the reaction rate is limited by transport in the chalcopyrite lattice or through the elemental-sulphur reaction-product layer.

Munoz *et al.*[8] presented a model derived from the Wagner theory of oxidation, which is based on the formation of a protective sulphur layer during the reaction, with the rate limited by the transport of electrons through the insulating sulphur. This model was supported by kinetic data in which as much as 60 per cent of the $CuFeS_2$ was reacted over long reaction times. The very slow parabolic reaction kinetics were predicted by Wagner's theory of oxidation, which relates the electrical conductivity of the elemental-sulphur reaction product to the rate of reaction. The diffusion flux ($\mathrm{mol{\cdot}cm^{-2}{\cdot}s^{-1}}$) of a charged species, such as an anion, cation, or electron, is given, for a modest voltage gradient, by

$$J_i = -\frac{t_i \sigma}{z_i^2 e^2}\left(\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx}\right) \qquad (3)$$

where $\frac{d\mu}{dx}$ = chemical potential gradient
$\frac{d\phi}{dx}$ = electric field strength
e = electronic charge
t_i = transport number
σ = electrical conductivity, and
z_i = valence of species i

For electrical neutrality,

$$2J_{\mathrm{Cu}^{2+}} + 2J_{\mathrm{Fe}^{2+}} + 3J_{\mathrm{Fe}^{3+}} = J_{\mathrm{e}}. \qquad (4)$$

If it is assumed that the transport of the hydrated Fe^{3+} toward the inner boundary is negligible and

$J_{\mathrm{Cu}^{2+}} = J_{\mathrm{Fe}^{2+}}$ (coupled mass transfer),

Equation (4) becomes

$$2J_{\mathrm{Cu}^{2+}} + 2J_{\mathrm{Fe}^{2+}} = J_{\mathrm{e}} = 4J_{\mathrm{Fe}^{2+}} \qquad (5)$$

since

$$J_{\mathrm{Fe}^{2+}} = \frac{1}{A}\,\frac{dn}{dt}(\mathrm{CuFeS_2}) \qquad (6)$$

where A is the area of the unreacted core. If electron transport through the sulphur layer is rate controlling ($t_{\mathrm{e}} < t_{\mathrm{Fe}^{3+}}$), the leaching rate would be described by the following equation for spherical coordinates:

$$\frac{dn}{dt}(\mathrm{CuFeS_2}) = -(4\pi r^2)\,\frac{\mathrm{i_e}\sigma}{4e^2}\,\frac{\mathrm{d}\mu_{\mathrm{e}}}{dr} \qquad (7)$$

The predicted reaction rate calculated from the physiochemical properties of the reaction system (conductivity of elemental sulphur, $t_{\mathrm{e}}\sigma$, and the free-energy change for the reaction, ΔG) agrees satisfactorily with experimentally determined rates, thus:

$$\frac{d\alpha}{dt} = 300\,\frac{3t_{\mathrm{e}}\sigma\Delta G}{\rho d_{\mathrm{o}}^2 e^2}\,\frac{(1-\alpha)^{\frac{1}{3}}}{[1-(1-\alpha)^{\frac{1}{3}}]} \qquad (8)$$

where α is the fraction reacted.

Further evidence that supports this analysis includes an experimental activation energy of 20 kcal/mol (84 kJ/mol), which is approximately the same as the apparent activation energy for the transport of electrons through elemental sulphur (23 kcal/mol, or 96 kJ/mol), calculated from measurements of both conductivity and electron mobility. The results from this study suggest that the sulphur layer is of kinetic consequence and the leaching rate is limited by the transport of electrons through the tenacious elemental-sulphur product layer.

Recently, it was shown that, if the leaching reaction is interrupted and the elemental-sulphur reaction-product layer removed, the initial reaction kinetics are restored, as shown in Figure 1[12]. These results clearly establish the kinetic significance of the tenacious sulphur layer.

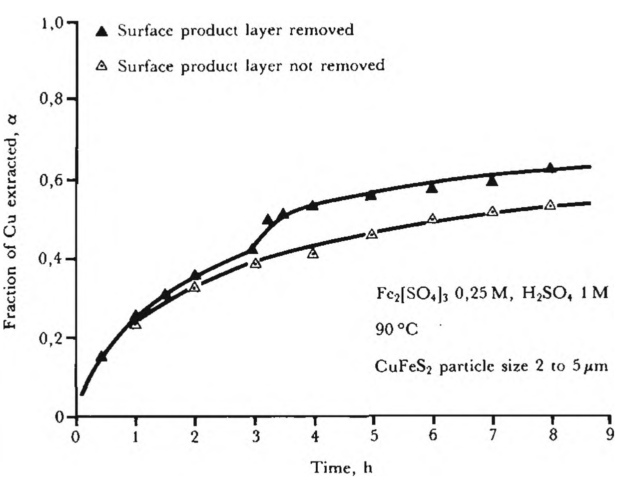


Figure 1. The fraction of Cu extracted from chalcopyrite particles as the leaching reaction is interrupted and the elemental-sulphur product layer is removed by distillation under N_2 atmosphere after 3 hours of leaching

In another investigation, Miller and Portillo[14,15] studied the leaching of chalcopyrite by silver-activated ferric sulphate and found that small additions of silver to the system resulted in a phenomenal increase in the leaching rate. Evidence from this study indicates that the activation involves a metathetic reaction, with the chalcopyrite lattice forming a distinct Ag_2S phase, and that the leaching reaction is limited by the intermediate electrochemical reaction

$$Ag_2S + 2Fe^{3+} \rightarrow 2Ag^+ + 2Fe^{2+} + 2S^\circ \ldots\ldots\ldots (9)$$

The leaching rate was found to be dependent on the concentrations of both ferric and ferrous sulphate, with an activation energy of 15 kcal/mol (65 kJ/mol). In addition, the rate was no longer inversely dependent on the initial particle size squared but was rather insensitive to the chalcopyrite size. The surface sulphur created in the silver-activated reaction is no longer protective but forms a relatively porous reaction-product layer compared with the smooth tenacious layer of elemental sulphur formed in the unactivated reaction.

If the reaction kinetics for the leaching of chalcopyrite by ferric sulphate is limited by electron transport in the elemental-sulphur reaction-product layer, any modification of this reaction-product layer to increase its conductivity should increase the rate of leaching. To increase the electronic conductivity of elemental sulphur, the principles of solid-state chemistry as applied to the conductivity of insulators and semiconductors can be considered. Wagner[16] indicated that the electronic conductivity of an insulator phase can be increased by the addition of dispersed conductor particles imbedded in the matrix, the insulator phase. Under some circumstances, the conductivity increase may be due to the emission of the electrons from the dispersed conductors, with the creation of a space charge surrounding these particles and compensated for by the surface charge acquired. With respect to the conductivity of elemental sulphur, it is known that the addition of carbon particles to sulphur increases the electrical conductivity of sulphur by as much as 10 orders of magnitude[17-19]. Thus, the rate of leaching of chalcopyrite by ferric sulphate can be expected to increase if carbon particles could be imbedded in the elemental-sulphur reaction-product layer.

This current research effort is designed to test the aforementioned hypothesis regarding rate control in the leaching of chalcopyrite by ferric sulphate and to determine whether enhanced rates of leaching by ferric sulphate can be achieved by the addition of conductive carbon particles to the system. The experimental results from the leaching of aggregates of $CuFeS_2$ and C will be used to discuss the mechanistic details of the ferric sulphate leaching reaction in view of the findings of previous investigators.

EXPERIMENTAL DETAILS

To study the leaching of chalcopyrite by ferric sulphate with additions of particulate carbon, an experimental technique to obtain contact between particles of chalcopyrite and of carbon was developed. This technique involved the intimate mixing of the particles and compression of the mixture to form a pellet that contained aggregates of $CuFeS_2$ and C. Leaching experiments were carried out under atmospheric pressure. The significance of the carbon properties was examined in terms of the reaction-rate data.

Materials

The chalcopyrite used in this research was obtained from a Pima flotation concentrate. Chemical and mineralogical analyses are shown in Table 1, provided by the Metallurgical Research Center of the US Bureau of Mines in Salt Lake City.

TABLE 1

Analysis of Pima concentrate as received

Chemical		Mineralogical	
Element	%	Mineral	%
Cu	27,2	$CuFeS_2$	80
Fe	29,2	FeS_2	5
S	20,8	SiO_2	5
Sb	0,60	Al_2O_3	1
Zn	0,50	CaO	1
Mo	0,14	Talc and chlorites	8
Pb	0,07		
As	0,02		

Samples of monosize chalcopyrite were prepared from the concentrate by wet screening and sizing with a Warman Cyclosizer. The gangue minerals were separated from the samples of monosize chalcopyrite in a Carpco laboratory-model magnetic separator. The samples thus prepared have an exceptionally high purity. Also, a monosize sample 5 by 2 μm was prepared from the concentrate by the Donaldson Company with an Accucut Model B air classifier. The particle-size distribution for each sample was determined with a Micromeritics Sedigraph Size Analyzer, as shown in Figure 2.

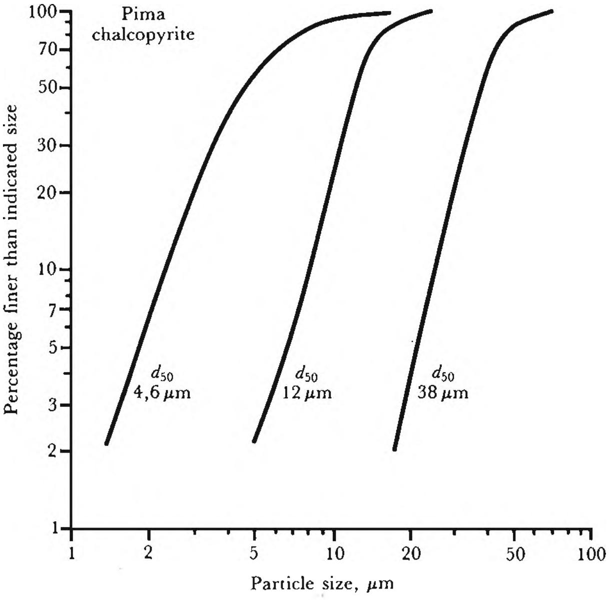


Figure 2. Size distributions of chalcopyrite samples as determined by Micromeritics Sedigraph Size Analyzer

The results of the chemical analysis of each monosize sample (characterized by the median size of their narrow size distribution) are shown in Table 2.

TABLE 2

Chemical analysis for prepared monosize samples of chalcopyrite

d_{50} size μm	Surface area* m²/g	Chemical analysis	
		Cu, %	Fe, %
4,6	0,480	29,95	26,27
12	0,195	30,49	26,85
28	0,090	30,75	27,25
38	0,030	31,58	27,73

* Determined by the Permaran Specific Surface Area meter

The high-purity samples used in this project were examined by semiquantitative spectrographic analysis and found to contain only trace levels of most other elements. Silicon (1 per cent), aluminium (1 per cent), zinc (0,5 to 1,0 per cent), and lead (0,2 per cent) were present at higher levels, as indicated.

Various carbons of high purity were obtained from the Cabot Carbon Corp., Fisher Scientific Company, Cerac Corp., Lonza Inc., and AESAR Inc. Samples of carbon for conductivity measurements were first cleaned by heat treatment at 1100 °C in flowing helium, at an oxygen potential of less than 10^{-40} atmosphere. The particle size of the carbon was determined by Coulter Counter Analysis. The surface areas were measured with the B.E.T. technique—Quantasorb made by Quantachrome Corporation. The effect of carbon type on the conductivity of sulphur composites was evaluated at the Pennsylvania State University with a three-point electrode system[17,18].

Distilled water and reagent-grade chemicals were used in preparing the desired leaching solutions.

Apparatus and procedure

Particles of chalcopyrite and carbon were mixed thoroughly, pressed into pellets of appropriate size, and used for leaching experiments. The pellets were 13 mm in diameter. The thickness of the pellet depends upon the amount of sample used, but most samples were 2,4 mm thick. The pellets were prepared at 20 000 lbf pressure. The compression and porosity of the pellet depend on the particle size and the proportion of chalcopyrite to carbon. The preparation of aggregates of $CuFeS_2$ and C from 38 μm particles of chalcopyrite results in a significant breakage of these particles, particularly if the additions of carbon are small. Generally, aggregates of $CuFeS_2$ and C prepared from fine chalcopyrite particles are more compact and exhibit greater structural integrity.

All the leaching experiments were carried out in one-litre cylindrical reactors immersed in thermostatically controlled water-baths. The baffled glass reactors had a clamp-held lid containing four fitted openings. A stirrer, fritted solution sampler, condenser, and thermometer were placed into the reactors through these openings. The impeller was inserted through the centre port by means of a Chesapeake stirrer connection. Generally, the experiments were made at 0,2 per cent solids and 90 °C. For most of the tests, pellets were prepared from $CuFeS_2$ particles 325 by 400 mesh (d_{50} = 38 μm). Unless otherwise stated, the whole pellet was placed unbroken in the reactor. During the course of the reaction, the pellets break up to a certain extent depending on the carbon content and particle size of the chalcopyrite. As shown from experimental results, the size of the pellet or aggregate does not influence the leaching rate of 38 μm particles but does have a significant effect on the leaching of 4,8 μm particles. Solution samples, about 5 ml, were withdrawn through the fritted-glass sampling device at selected time intervals and analysed for their copper content with a Perkin–Elmer atomic-absorption spectrophotometer, Model 305.

The surface morphology of the various products obtained before and after the leaching reaction was examined and analysed with a scanning electron microscope (S.E.M.) or the scanning transmission electron microscope, and elemental analysis by EDAX (energy-dispersive X-ray analysis).

Reaction rates were determined from the data by fitting the experimental data to a polynomial regression equation. Similarly, the reaction parameters were deduced by a best-fit statistical analysis of the rate data.

EXPERIMENTAL RESULTS

The following stoichiometry was found for acid leaching of chalcopyrite by ferric sulphate:

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} + 2S^{\circ} \ldots\ldots (10)$$

The anodic dissolution of chalcopyrite occurs according to the above reaction, forming elemental sulphur. It is thought that the formation of a dense and tenacious sulphur layer passivates the reaction and slows the leaching rate to unacceptably low levels. The addition of carbon particles prevents the passivation to a certain extent and increases the leaching rate significantly.

These studies are concerned primarily with the kinetics of the leaching reaction in which the elemental sulpur has formed. It is believed that the results provide further evidence that the sulphur layer has kinetic significance. The kinetics of leaching of aggregates of $CuFeS_2$ and C by ferric sulphate has been studied as a function of carbon type, chalcopyrite particle size, temperature, and ferric-ion concentration. As can be seen in Figure 3, the aggregates of $CuFeS_2$ and C react significantly faster at low speed than suspended $CuFeS_2$ particles do in the absence of carbon particles at high speed. The formation of the elemental-sulphur product layer in the aggregates differs significantly from the sulphur structure that forms in the absence of carbon.

Carbon type

Nine different types of carbon have been evaluated for the leaching of 38 μm aggregates of $CuFeS_2$ and carbon at 1 M H_2SO_4, 0,25 M $Fe_2(SO_4)_3$, 0,2 per cent solids, and 90 to 100 r/min. The carbon content of the aggregates of $CuFeS_2$ and C has been varied from 2 to 50 per cent by mass. The carbon types studied were 'Pearl 2000', 'Monarch 800', 'Monarch 1100', 'Fisher 38', 'Lonza KS–2.5', 'Spheron–6', 'Cerac Pure Carbon', 'AESAR Graphite Fiber', and 'Activated Carbon'. Of these carbons, 'Pearl 2000', which has the smallest particle size and the highest electronic conductivity for composites of C and S (see Table 3), increases the leaching kinetics to the largest extent at 9 per cent carbon, as shown in Figure 4. Interestingly, when the carbon content is reduced, even to 2 per cent by mass, the leaching rate does not change substantially. The photographs in Figure 5, taken with a scanning electron microscope, show a chalcopyrite particle in the aggregate before reaction with a small number of attached carbon particles.

The attached carbon particles accelerate the leaching rate of chalcopyrite, which can be explained in part by the improved transport of electrons through the sulphur-reaction product layer. The dissolution rate for copper increases with an increase in the electrical conductivity of the product layer, as indicated by the conduction measure-

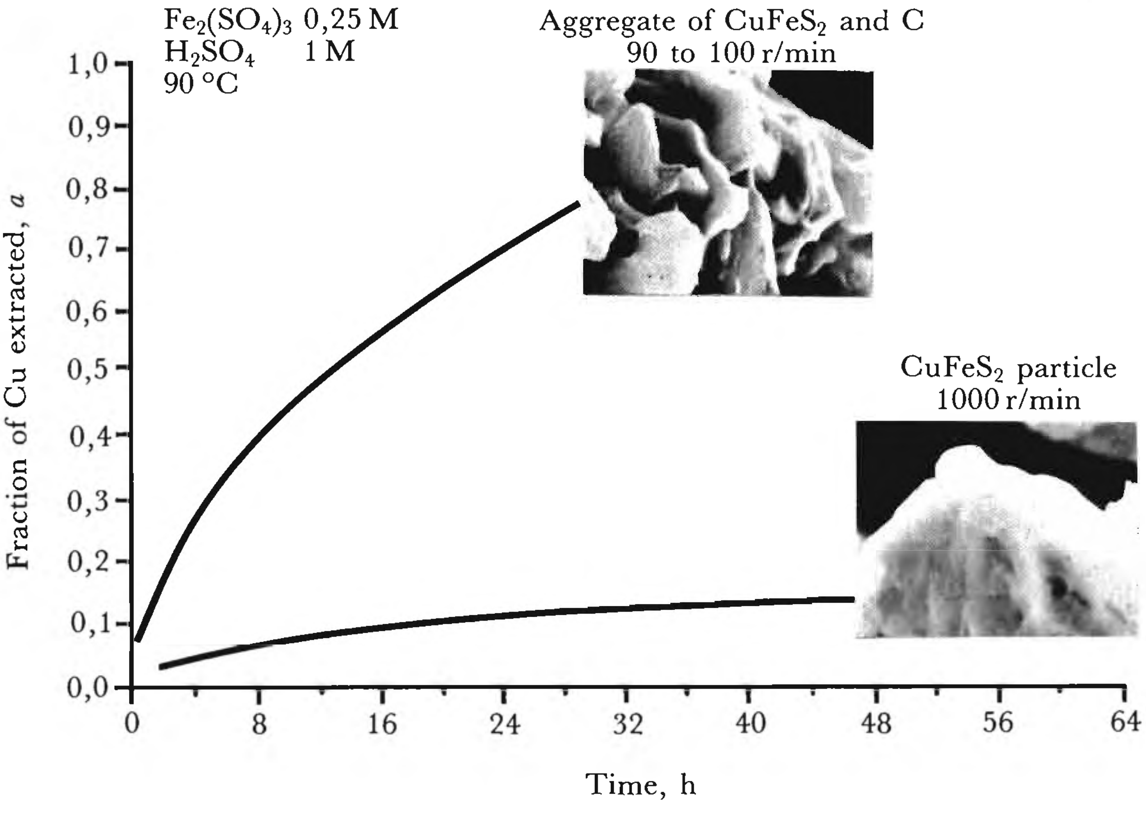


Figure 3. Comparison of the reaction rate of aggregates of $CuFeS_2$ and C to the rate of suspended $CuFeS_2$ particles. $d_0 = 38\,\mu m$

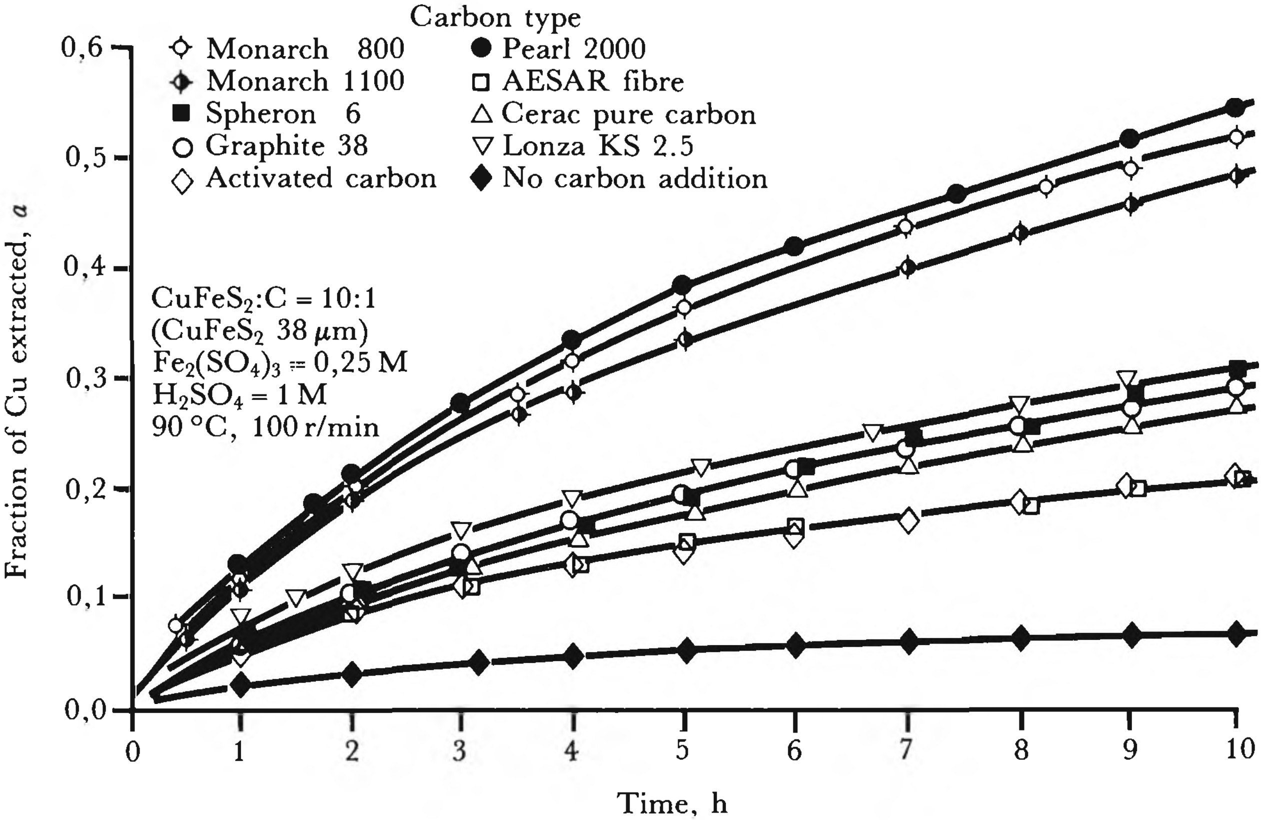


Figure 4. Fraction of Cu extracted from aggregates of $CuFeS_2$ and C prepared with different carbon types

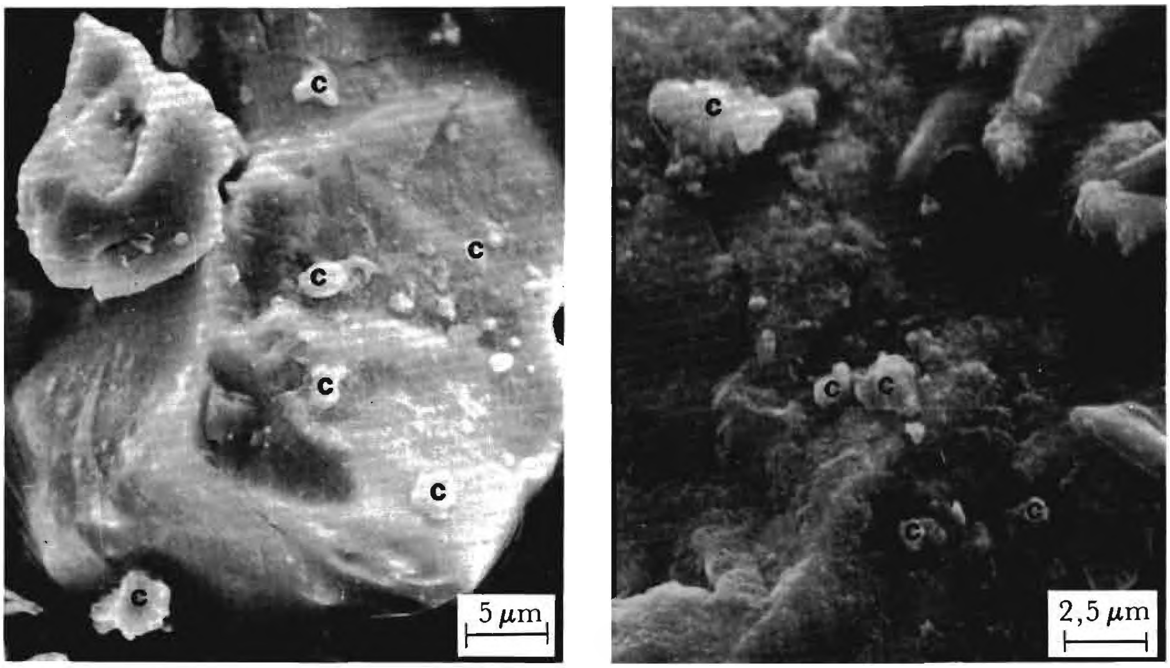


Figure 5. S.E.M. photomicrographs of aggregates of $CuFeS_2$ and C

TABLE 3

The influence of carbon properties on the conductivity of composites of C and S and the leaching response of aggregates of $CuFeS_2$ and C

Carbon type	Particle size, μm		Surface area m²/g	σ_1* 5% C/S composite $(\Omega \cdot cm)^{-1}$	σ_2* 15,9% C/S composite $(\Omega \cdot cm)^{-1}$	Fraction of Cu reacted from aggregates of $CuFeS_2$ and C after 10 h
	Size reported by manufacturer	Coulter counter d_{50}				
Pearl 2000	15 nm	–	1348	$2,6 \times 10^{-2}$	$2,2 \times 10^{-1}$	0,560
Monarch 800	17 nm	2,1 μm	237,9	$1,05 \times 10^{-3}$	–	0,524
Monarch 1100	14 nm	2,25 μm	258,8	$9,0 \times 10^{-4}$	–	0,488
Lonza KS-2,5	< 5 nm	4,3 μm	24,6	$5,4 \times 10^{-4}$	$1,6 \times 10^{-1}$	0,322
Spheron 6	25 nm	7,9 μm	11,9	$2,2 \times 10^{-4}$	–	0,314
Fisher 38		10 μm	20,4	–	$6,2 \times 10^{-2}$	0,316
Cerac Pure	–	13 μm	3,5	–	$9,1 \times 10^{-2}$	0,281
Calgon Activated carbon	–	4,3 μm		–	$2,4 \times 10^{-3}$	0,209
AESAR Graphite Fibre	Diam. 8 μm Length 6,4 mm			–	–	0,210
			Conductivity $(\Omega \cdot cm)^{-1}$			
Chalcopyrite (no carbon)			$\approx 10^{+1}$			0,067
Pure sulphur			$\approx 10^{-13}$			

*σ_1 and σ_2 are measured at 5 vol. % and 15,92 vol. % carbon, respectively, in pure sulphur at 90 °C

ments of composites of C and S presented in Table 3. A generally higher conductivity is achieved for carbons of smaller particle size. The smaller the particle size, the higher the conductivity and the higher the rate of leaching. Particle sizes are reported in Table 3, based on Coulter Counter measurements in our laboratory and on electromicrographs as provided by the manufacturer. It seems that the former size is a measure of carbon agglomerates, which can become dispersed, depending on the environment. It has been found, from measurements of contact angles, that sulphur completely wets a carbon surface, and in this regard it is not surprising that the composites of C and S exhibit good dispersion characteristics. The extent of dispersion of carbon in liquid sulphur is so great that individual particles of carbon are difficult to identify even with the S.E.M.

It is important to note that the increased leaching rate is achieved at lower agitation speeds, which presumably is an indication that aggregate integrity must be preserved. Details of the effect of the properties of carbon on the ferric sulphate leaching reaction have been reported[20].

Effect of particle size of chalcopyrite

The effect of the particle size of $CuFeS_2$ on the leaching of particles of chalcopyrite and aggregates of these particles prepared with additions of carbon can be compared in Figures 6 and 7 in terms of fraction of copper extracted vs time. For particles of chalcopyrite without carbon, the rapid decrease in the leaching rate with time is similar to that observed by other investigators; the tenacious sulphur layer on the chalcopyrite surface passivates the reaction. The beneficial effect of additions of carbon seems to be more pronounced for coarse particles of chalcopyrite, probably owing to the breakage of these $CuFeS_2$ particles during the compaction of the aggregate pellet. The particle-size distributions of the chalcopyrite before and after the compaction of the aggregate were determined with a Micromeritics Sedigraph Size Analyzer. The significance of the breakage of coarse particles of chalcopyrite during the compaction of the aggregate is shown in Figure 6. Such breakage is not significant for the smaller particles of chalcopyrite as shown in Figure 7. However, the enhanced leaching rate is achieved at lower agitation speeds, which indicated the importance of compaction between particles of carbon and chalcopyrite. Figures 6 and 7 also indicate the enhanced leaching rate of the mixed agglomerates of chalcopyrite and carbon particles (without pressing), which certainly is not as high as the compressed pellets of $CuFeS_2$ and C especially for the coarse chalcopyrite particles.

Generally, aggregate diffusion does not affect the rate of reaction for the coarse chalcopyrite par-

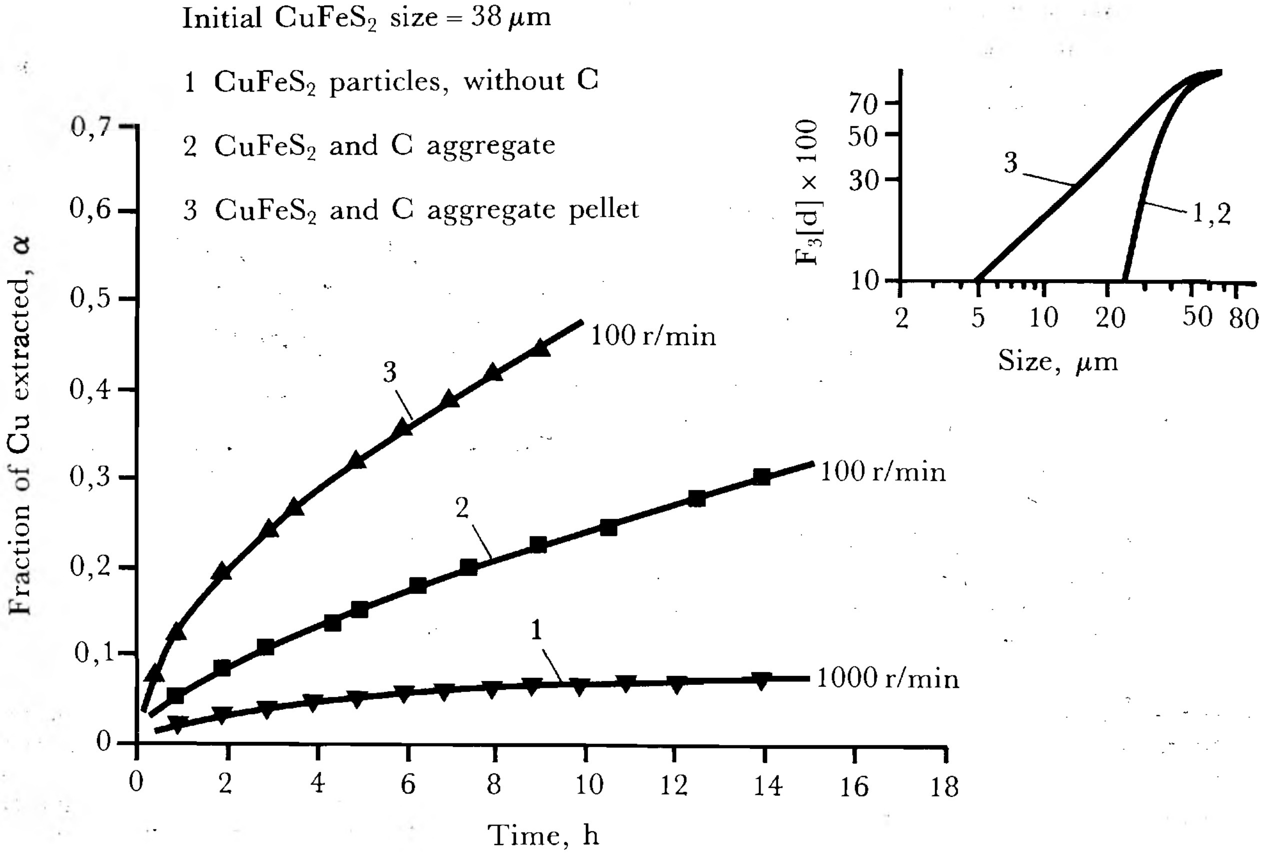


Figure 6. Fraction of Cu extracted from chalcopyrite in an acid ferric sulphate solution as dispersed CuFeS$_2$ particles and as aggregates of CuFeS$_2$ and C, 1,0 M H$_2$SO$_4$, 0,25 M Fe$_2$(SO$_4$)$_3$, 90 °C, CuFeS$_2$:Monarch 800 carbon = 10:1. Initial CuFeS$_2$ size = 38 μm

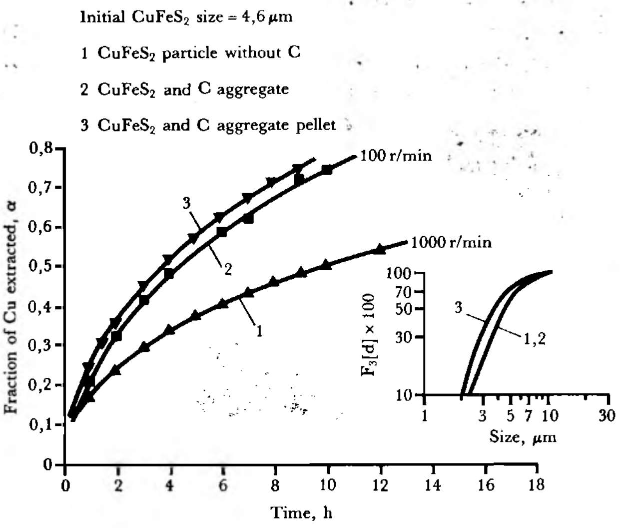


Figure 7. Fraction of Cu extracted from chalcopyrite as dispersed CuFeS$_2$ particles and as aggregates of CuFeS$_2$ and C, 1,0 M H$_2$SO$_4$, 0,25 M Fe$_2$(SO$_4$)$_3$, 90 °C, CuFeS$_2$:Monarch 800 carbon = 25:1. Initial CuFeS$_2$ size = 4,6 μm

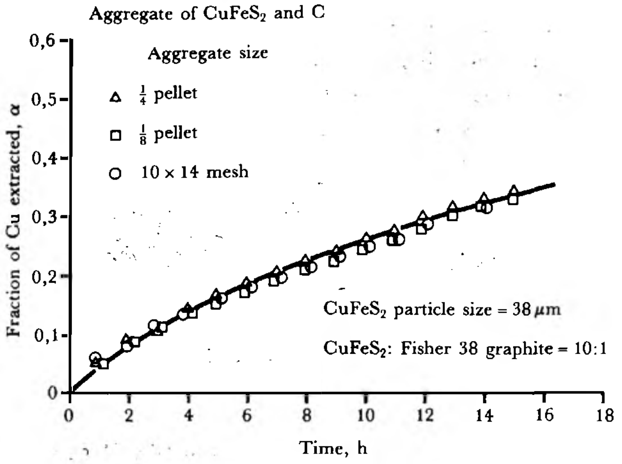


Figure 8. Aggregate size effect for leaching of 38 μm chalcopyrite from aggregates of CuFeS$_2$ and C, 0,25 M Fe$_2$(SO$_4$)$_3$, 1 M H$_2$SO$_4$, 90 °C, 90 to 100 r/min

ticles. Figure 8 shows the effect of aggregate size for the aggregates of CuFeS$_2$ and C prepared from 38 μm particles of chalcopyrite. The pellet prepared from the coarse chalcopyrite is porous, and transport through the aggregate does not limit the rate of reaction. On the other hand, such is not the case for 4,6 μm particles of chalcopyrite. As shown in Figure 9, the leaching rate increased as the aggregate size decreased. In this case, transport through the aggregate does have a significant influence on the leaching rate.

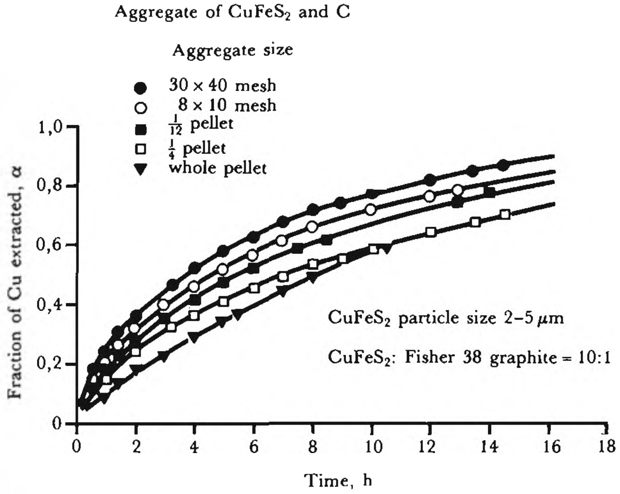


Figure 9. Aggregate size effect for leaching of 4,6 μm chalcopyrite from aggregates of $CuFeS_2$ and C, 0,25 M $Fe_2(SO_4)_3$, 1 M H_2SO_4, 90 °C, 90 to 100 r/min

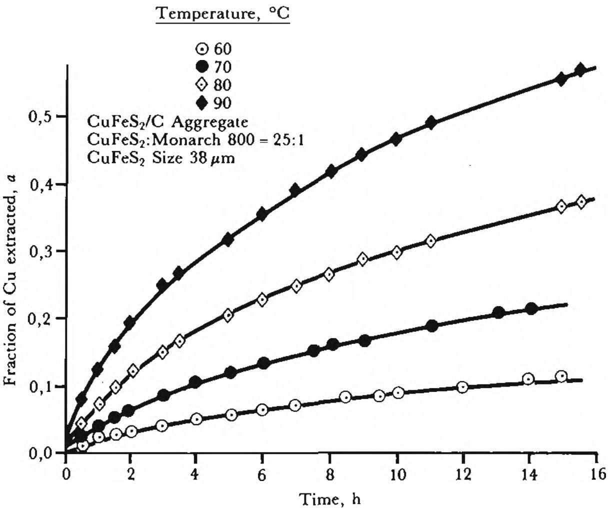


Figure 10. Temperature effect for the leaching of aggregates of $CuFeS_2$ and C by ferric sulphate $CuFeS_2$:Monarch 800 = 25:1, 1,0 M H_2SO_4, 0,25 M $Fe_2(SO_4)_3$, 90 to 100 r/min

Effect of concentration of ferric sulphate and temperature

In general, as the concentration of the reactant is increased, an increase in the reaction rate would be expected, especially if reactant transport were the rate-limiting step. This effect was not observed in the acid leaching of chalcopyrite particles by ferric sulphate[8]. A similar response was observed for the aggregates of $CuFeS_2$ and C; the reaction kinetics were, for the most part, independent of the concentration of ferric sulphate. Only at low concentrations and during the initial stages of reaction was a dependence on the concentration of ferric sulphate found.

The temperature dependence of the leaching of aggregates of $CuFeS_2$ and C (Figure 10) was determined so that the apparent activation energy for aggregate leaching could be compared with the activation energy for the leaching of particles of $CuFeS_2$ in the absence of carbon. At long reaction times, an apparent activation energy of approximately 27 kcal/mol (113 kJ/mol) was estimated for the leaching of aggregates of $CuFeS_2$ and C by ferric sulphate compared with 20 kcal/mol (83,78 kJ/mol) without additions of carbon.

Product characterization

Photographs of a partially leached aggregate of $CuFeS_2$ and C taken with an S.E.M. are shown in Figure 11. The element-sulphur reaction product

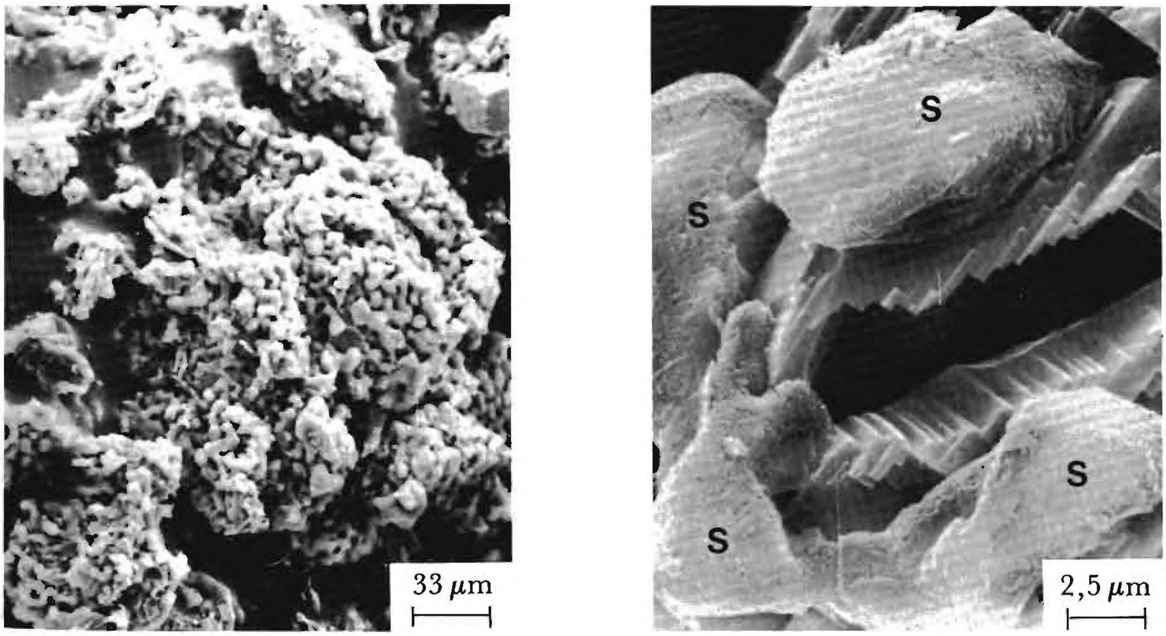


Figure 11. S.E.M. photomicrograph of aggregate of chalcopyrite and carbon partially leached by ferric sulphate solution; $d_0 = 38\mu m$, $\alpha = 0,70$

appears to be clustered and non-protective, with areas that appear to be an exposed chalcopyrite surface. This morphology differs significantly from that of the dense, tenacious sulphur layer that forms in the absence of carbon, as displayed in Figure 12.

Not only does the preparation of pellets for aggregates of $CuFeS_2$ and C change the chalcopyrite particle size (most pronounced for 38 μm particles), but also the deformation stresses may excite the crystal lattice for sulphur nucleation. X-ray-diffraction analysis of the pressed pellets indicated that strain energy is stored in the $CuFeS_2$ lattice[12]. The significance of this effect on the leaching kinetics seems to be of secondary importance. Recently, Murr and Hiskey[21] studied the kinetic effects of particle size and crystal dislocation density on the leaching of chalcopyrite by dichromate. An unambiguous effect of dislocations was observed for the largest size fractions, 48 by 65 mesh, at 50 °C (the reaction rate was increased about 190 per cent). However, dislocation effects at all other particle sizes and at higher temperatures did not appear to be significant.

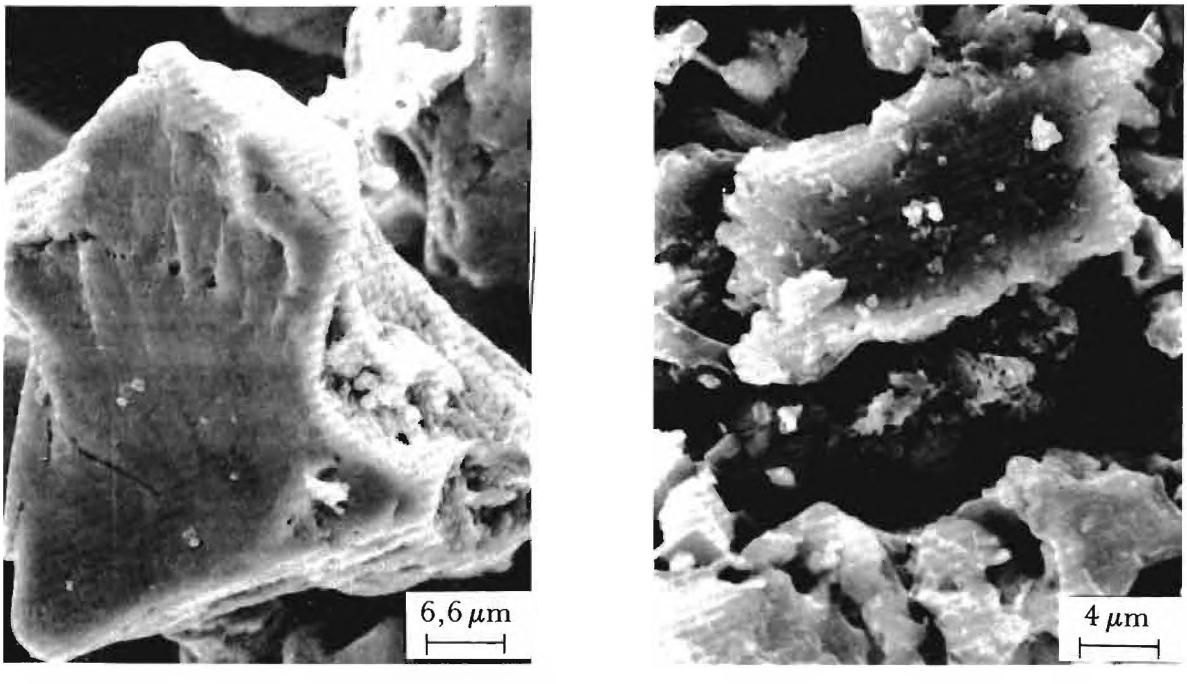
In this study, it has been found that chalcopyrite compacted with non-conductive particles, such as talc, silica, or alumina, to form aggregates did not improve the rate to the same extent as carbon did.[20] The small extent of the increase in leaching by these non-conductive particles can be accounted for by the breakage of the chalcopyrite particles or the deformation of the crystal lattice, or both. This supports the proposition that the conductive carbon particles change the conductivity of the reaction-product layer and enhance the leaching rate.

DISCUSSION OF REACTION KINETICS

The experimental results show that enhanced reaction kinetics in the leaching of aggregates of $CuFeS_2$ and C by ferric sulphate can be expected under certain circumstances. In addition to the data reported for aggregates of Pima chalcopyrite and carbon, the enhanced reaction rates also have been found for aggregates of Transvaal chalcopyrite and carbon[12].

Sulphur morphology

The kinetic aspects of the leaching of aggregates of $CuFeS_2$ and C by ferric sulphate are complicated. More than one rate process may be involved. The sulphur product has been found to have a more botryoidal and less protective character. The inability to identify carbon particles by microscopic examination of composites of C and S suggests that there is an excellent dispersion of carbon agglomerates in liquid sulphur. The carbon must be present as submicrometre particles of the order of 10 nm. If such phenomena occur at the $CuFeS_2$ interface during leaching at 90 °C, the elemental-sulphur reaction-product layer should be more conductive, thus leading to improved leaching rates. Preliminary experiments of sulphur-wetting behaviour have demonstrated that elemental sulphur wets a carbon surface completely, but not a chalcopyrite surface[20]. The particles of carbon at



(A) (B)

Figure 12. S.E.M. photomicrograph of chalcopyrite particle partially leached by ferric sulphate solution; (A) $d_0 = 38\ \mu m, \alpha = 0{,}17$; *(B)* $d_0 = 12\ \mu m, \alpha = 0{,}20$

the chalcopyrite surface can act as nuclei for sulphur growth and contribute to the non-uniform, less-protective nature of the sulphur.

Rate prediction for control of the surface reaction

Although the sulphur product formed in the leaching reaction of aggregates of $CuFeS_2$ and C is less protective, the leaching is still very slow. The enhanced leaching rate of aggregates of $CuFeS_2$ and C is far from the rate predicted for the control of surface reactions, as revealed in Figure 13. The predicted curves in Figure 13 are calculated on the rate constant obtained from electrochemical measurements and the initial rate constant of leaching experiments. If the initial surface-reaction rate is preserved during the course of leaching, the rate expression for spherical particles will be

$$\frac{d\alpha}{dt} = \frac{6(b/a)M_{CuFeS_2}}{\rho_{CuFeS_2}\, d_0}\, k[Fe^{3+}]^n\,(1-\alpha)^{\frac{2}{3}} \;\ldots\ldots\; (11)$$

where α = fraction reacted at time t
k = reaction rate constant (cm/s for $n=1$)
n = order of the reaction
d_0 = initial particle diameter (cm)
ρ_{CuFeS_2} = density
M_{CuFeS_2} = molecular mass of $CuFeS_2$ (g/mol)
b/a = stoichiometry factor (moles of $CuFeS_2$ per mole of Fe^{3+})
$[Fe^{3+}]$ = concentration of ferric ion (mol/cm^3).

The value for the rate constant k was evaluated from experimental leaching data as $t \rightarrow 0$. The electrochemical estimate of the rate constant was calculated from anodic polarization curves for a chalcopyrite electrode at 90 °C. The current density corresponding to the expected leaching rate was selected at a mixed potential established by the cathodic polarization curve for the Fe^{3+}/Fe^{2+} half-cell reaction at a graphite electrode[12].

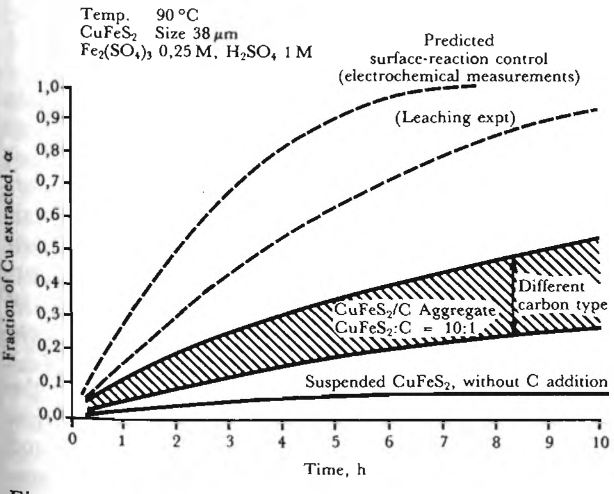


Figure 13. Comparison of the experimental reaction rate of aggregates of $CuFeS_2$ and C and suspended $CuFeS_2$ particles with the predicted rate for control by surface reaction

Reaction mechanisms

Since the sulphur layer is not of uniform thickness in the leaching of aggregates of $CuFeS_2$ and C, short transport paths may allow electrochemical processes to become significant and limit the rate during the early stages of the reaction.

One explanation that accounts for the kinetic response is that the addition of particles of carbon alters the structure of sulphur and facilitates electron transport through the sulphur-product layer. Under these circumstances, rate control during the early stages of reaction may be limited by a surface reaction. In the absence of carbon, the contribution of the surface reaction is insignificant and can be ignored, as suggested in earlier work[8] (see Equation 8). For aggregates of $CuFeS_2$ and C, however, provision for a surface reaction seems necessary, and, in this regard, it has been found that the rate data can be analysed with a mixed-kinetics rate expression involving both the surface reaction and product-layer transport.

$$t = \frac{d_0}{k_s{}'}\,\{1-[1-\alpha^{\frac{1}{3}}]\} + \frac{d_0^2}{k' t_e \sigma}\,\{1-\tfrac{2}{3}\alpha-[1-\alpha]^{\frac{2}{3}}\} \;\ldots\ldots\ldots\ldots\ldots\; (12)$$

or

$$\frac{t}{\{1-[1-\alpha]^{\frac{1}{3}}\}} = \frac{1}{k_s} + \frac{1}{k_p}\{1-\tfrac{2}{3}\,\alpha-[1-\alpha]^{\frac{2}{3}}\}\,\{1-(1-\alpha)^{\frac{1}{3}}\}^{-1} \;\ldots\ldots\ldots\ldots\ldots\; (13)$$

where

α = fraction reaction at time t
d_0 = initial particle size (cm)
k_s = surface reaction constant ($time^{-1}$)
k_p = parabolic rate constant ($time^{-1}$)
$t_e\sigma$ = electrical conductivity of the reaction product layer $(\Omega \cdot cm)^{-1}$.

The parabolic rate constant involves the conductivity of the sulphur layer ($t_e\sigma$), the free energy change for the reaction (ΔG), and the charge on the electron (e).

If the reaction fits the mixed-kinetics model, a plot of $t\{1-[1-\alpha]^{\frac{1}{3}}\}^{-1}$ against $\{1-\frac{2}{3}\alpha-[1-\alpha]^{\frac{2}{3}}\}\{1-[1-\alpha]^{\frac{1}{3}}\}^{-1}$ should be linear and have a slope equivalent to the parabolic rate constant and an intercept related to the surface-reaction rate constant. Figure 14 indicates a good fit of the data taken from Figure 3 to the mixed-rate expression for the leaching of aggregates of $CuFeS_2$ and C by ferric sulphate with different carbon types at 9 per cent C by mass. It is interesting to note that the plots in Figure 14 give the same intercept for different types of carbon. Thus, the leaching kinetics for aggregates of $CuFeS_2$ and C with different types of carbon exhibit the same linear rate constant as in Table 4. On the other hand, the parabolic rate constant, which describes the control of product-layer transport, varies significantly with the type of carbon. The parabolic rate constants derived from these experimental results can be compared with the electrical conducti-

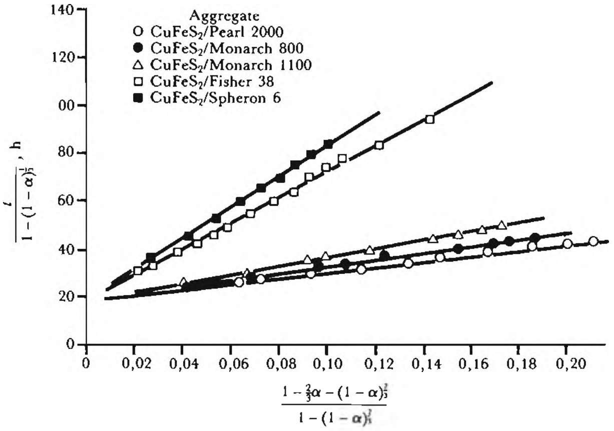


Figure 14. Mixed-kinetics plots for the leaching of aggregates of $CuFeS_2$ *and C prepared with different types of carbon. Data taken from Figure 4*

vities of composites of C and S in Table 4, in which the electrical conductivity σ is measured at 90 °C for 5 per cent carbon (by volume) dispersed in pure sulphur. The fact that the parabolic rate constant of the aggregates of $CuFeS_2$ and C increases with an increase in the electrical conductivity of the corresponding composites of C and S supports the proposed reaction mechanism.

Further support for this reaction mechanism is given by the temperature dependence of the leaching data for $CuFeS_2$ and C. The effect of temperature on the reaction kinetics is shown in Figure 10 for 38 μm particles of chalcopyrite compacted with Monarch 800 carbon. The experimental data are linearized according to Equation (13); the mixed-control model is shown in Figure 15. The surface-reaction rate constants and parabolic rate constants for different temperatures derived from the experimental data were then plotted against the reciprocal temperature (Figure 16) to determine the apparent activation energy. An activation energy, E_a, of 16,2 kcal/mol (67,8 kJ/mol) was calculated by regression analysis for the surface reaction, which is similar to the range of values 10 to 15 kcal/mol, reported in the literature[10,13]. A very high activation energy of 27,5 kcal/mol (115,1 kJ/mol) was obtained for the parabolic rate constant. This observed activation energy is larger than normally would be expected for a transport process but is similar to the temperature coefficient for electron transport in sulphur, 23 kcal/mol (96,3 kJ/mol).

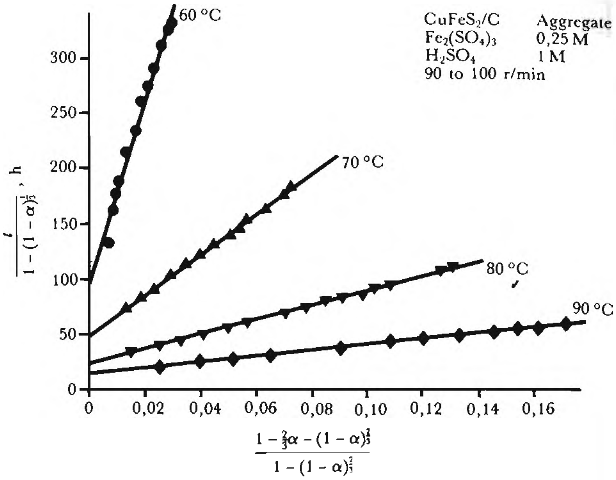


Figure 15. Mixed-kinetics plots for the leaching of aggregates of $CuFeS_2$ *and C at various temperatures. Data taken from Figure 10*

TABLE 4

Comparison of k_s *and* k_p *with electronic conductivity of composites of C and S*

Aggregates* of $CuFeS_2$ and C for different carbon types	Rate constants from mixed-kinetics model		Electronic conductivity of composites of C and S C(5 vol.%)/S
	k_s h^{-1}	k_p h^{-1}	$(\Omega \cdot cm)^{-1}$
Pearl 2000	$5,43 \times 10^{-2}$	$8,52 \times 10^{-3}$	$2,6 \times 10^{-2}$
Monarch 800	$5,40 \times 10^{-2}$	$6,96 \times 10^{-3}$	$1,05 \times 10^{-3}$
Monarch 1100	$6,04 \times 10^{-2}$	$5,26 \times 10^{-3}$	$9,0 \times 10^{-4}$
Lonza KS-2.5	$5,40 \times 10^{-2}$	$1,60 \times 10^{-3}$	$5,4 \times 10^{-4}$
Spheron 6	$6,37 \times 10^{-2}$	$1,46 \times 10^{-3}$	$2,2 \times 10^{-4}$

* CuFeS:C = 10:1 (mass ratio)

It should be noted from Table 4 that the increase in the leaching rate with different carbon types (different conductivities) is not proportional to these variables. For example, the fraction of Cu reacted varies by a factor of S, whereas the conductivity of composites of C and S varies by two orders of magnitude. The explanation for this lack of proportionality is that the extent to which the carbon attaches to the $CuFeS_2$ surface during the formation of pellets is not predictable. Evidence from the S.E.M. shows that only a small fraction of the carbon added actually attaches at the $CuFeS_2$ surface, as shown in Figure 11. Further, the extent of dispersion of the carbon in the product layer may vary with the carbon type. It is thought that these factors account for the lack of proportionality between the leaching rate and the carbon variables.

Other mechanistic interpretations are possible to explain the observed kinetics. For example, the

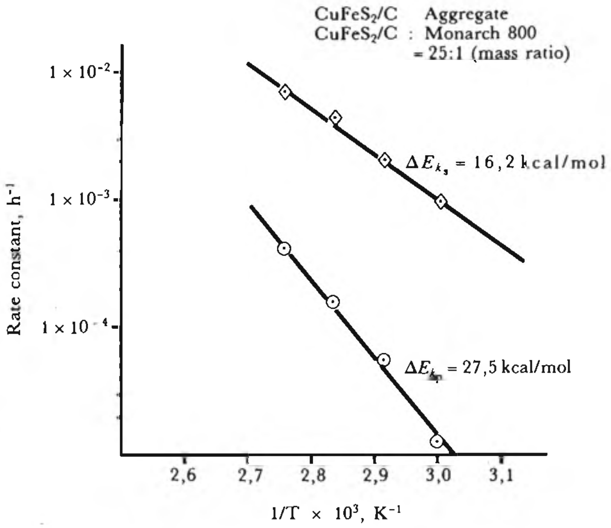


Figure 16. Arrhenius plots of reaction rate constants, k_s and k_p, vs inverse absolute temperature for aggregates of $CuFeS_2$ and C. Data taken from Figure 5

mixed kinetic mechanism presented requires that the reaction should be topochemical with an ever-increasing thickness of the elemental sulphur reaction product layer. Experimental evidence from S.E.M. photographs and particle-size dependence does not support this requirement. Other more appropriate explanations include mixed kinetics with flate-plate geometry and mixed kinetics with constant product-layer thickness. Analysis of the experimental data with these models leads to the same conclusions and may give a better account of the particle-size dependence.

SUMMARY

The experimental results have established conclusively that the rate of copper dissolution from aggregates of $CuFeS_2$ and C by ferric sulphate solution can be enhanced by the presence of conductive carbon particles. The addition of carbon particles (even 2 per cent by mass) has been found to increase the leaching rate of chalcopyrite by a factor of as much as 4, depending upon the electronic conductivity and particle size of carbon used. Non-conductive particles of similar size do not have the same effect on the leaching rate. Consistently, the measurements of the electrical conductivity have indicated that the addition of carbon to solid sulphur increases the conductivity substantially when compared with pure sulphur. Also, the improved electrical conductivity depends upon the particle size, structure, and amount of carbon used.

In addition to an improved conductivity of the elemental-sulphur product, the sulphur has been found to have a more botryoidal, less protective character. It was shown that elemental sulphur, in the liquid state, completely wets carbon but not chalcopyrite. In this view, the carbon particles at the chalcopyrite surface may act as nuclei for sulphur growth during the leaching reaction and contribute to the less-protective nature of the product layer. The kinetic aspects of the leaching of $CuFeS_2$ and C are found to be complicated, and more than one rate process appears to be involved. The experimental data can be explained with a mixed-kinetics model which involves both surface-reaction and product-layer transport processes.

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