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[54] **CHEMICAL MINING OF COPPER PORPHYRY ORES**

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[58] **Field of Search** 299/4, 5; 423/27, 150

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[57] **ABSTRACT**

Copper porphyry ores, especially those too deeply buried for conventional open pit mining, are mined in place by an in situ leaching technique using as a leaching medium a mixture of dilute sulfuric acid, oxygen and an alkali metal or ammonium chloride salt. The chloride ion speeds dissolution of copper minerals, especially chalcopyrite, and the alkali metal or ammonium ion reacts with iron and sulfate in the leaching medium to deposit iron in the form of crystalline jarosites. Precipitation of iron within the ore body as a jarosite maintains the permeability of the ore body to the leaching medium thus increasing both the rate and the total recovery of copper as well as depleting the leach solution of unwanted iron.

8 Claims, No Drawings

CHEMICAL MINING OF COPPER PORPHYRY ORES

BACKGROUND OF THE INVENTION

Many important copper deposits are in the form of low grade porphyry ores. A porphyry copper ore is a disseminated replacement deposit in which the copper minerals occur as the discrete grains and veinlets throughout a large volume of rock which commonly is porphyry. The deposits are typically large tonnage but low grade, having an average copper concentration of less than about 1 percent. Copper minerals found in these deposits usually are sulfides and most commonly are chalcopyrite. When such a deposit is of sufficiently high grade, and either outcrops on the surface or is sufficiently close to the surface, then the ore is mined by open pit methods and the copper minerals are separated from the gangue constituents by techniques such as flotation. Deeply buried or very low grade copper porphyry deposits cannot be economically exploited at this time.

It has been proposed to extract the cooper from deeply buried porphyry deposits by in situ leaching techniques. In situ leaching is a well-known technique which has long been practiced; its origins can be traced as far back as the 15th century. Successful leaching operations at this time are restricted to those copper ore bodies containing copper in the oxide form and having a low percentage of calcareous minerals. Copper oxides such as azurite and malachite are readily soluble in dilute sulfuric acid. If high concentrations of calcareous minerals such as calcite and dolomite are present, then acid usage becomes so high as to make the process uneconomical.

Copper sulfide minerals in general are but very slowly and sparingly dissolved by dilute sulfuric acid. Of the copper sulfide minerals, chalcopyrite is probably the least soluble yet it is the most common copper sulfide. It is known that the use of an over-pressure of oxygen in conjunction with an aqueous sulfuric acid leach medium speeds the dissolution of the copper sulfide minerals. A description of such a technique was reported by Vizolyi et al in an article entitled "Copper and Elemental Sulfur from Chalcopyrite by Pressure Leaching" which was published in the Journal of Metals, volume 19, No. 11 (1967), pages 52–59. Vizolyi found that finely ground chalcopyrite concentrates could be dissolved in an autoclave using an oxygen partial pressure in the range of about 30–500 pounds per square inch at a temperature in the range of about 200° to 300°F. Most of the sulfide sulfur was oxidized to elemental sulfur and most of the iron contained in the chalcopyrite was eventually hydrolyzed during the leaching to ferric hydroxide. Other researchers have investigated the effect of sodium chloride additions to sulfuric acid leach solutions in the extraction of copper from chalcopyrite ores. This work was reported by Dutrizac et al. in article entitled "The Effect of Sodium Chloride on the Dissolution of Chalcopyrite Under Simulated Dump Leaching Conditions" and appearing in Metallurgical Transactions, volume 2, (1971), pages 2310–2312. They found that sodium chloride accelerates the dissolution of chalcopyrite only at temperatures above about 50°C and had a detrimental effect on the rate of chalcopyrite dissolution at lower temperatures. During leaching is a technique used to extract

copper from a low grade waste material produced during the large scale open-pit mining of copper ore deposits. Leach solution is sprayed onto the top of the dump, percolates through the dump, and is collected from a lower level. Temperature of the leaching medium is dependent strongly upon ambient air temperature and seldoms exceeds about 35°C. Hence, the use of sodium chloride as an additive to sulfuric acid leach solutions is of no benfit and is probably detrimental to all operations carried out at ambient temperatures.

One of the most troublesome problems encountered in any copper leaching operation, whether it is a surface leaching process or whether it is an in situ leaching operation is the precipitation of basic iron salts in pipe lines, on the surface of dumps, or within the dump or ore body itself. Iron hydroxide precipitates from solution when the pH of the solution is higher than about 3.0. Iron salt precipitation within dumps or within an ore body is extremely difficult to control since leach solution concentrations and pH are subject to wide local variation. Basic iron salts precipitation results in the formation of impervious gelatinous layers which prevent movement of leach solutions within the dump or ore body. Hence, copper bearing minerals which are coated with precipitated iron hydroxide have no contact with leach solutions and their copper content cannot be recovered no matter how long the leaching is continued.

SUMMARY OF THE INVENTION

We have found that chalcopyrite can be readily leached from copper porphyry ores while avoiding the detrimental effects of ferric hydroxide precipitation by using as a leaching medium a dilute sulfuric acid solution to which is added chloride ion and cation chosen from the group consisting of sodium, potassium and ammonium. The leaching step must be carried out at temperatures above about 50°C and oxygen must be present. Our process is especially well suited to the situ leaching of deeply buried porphyry copper deposits which have been shattered by either conventional or atomic explosives. Essentially all of the co-dissolved ferric iron is precipitated in situ as crystalline jarosites which do not impede flow of the leach solutions. Pregnant leach solutions recovered in our process display very low iron concentration. In addition, most of the sulfur remains deposited within the ore body in the elemental form. A paper describing our invention and entitled "Simulated In Situ Leaching of Copper from A Porphyry Ore" was published as Bureau of Mines Technical Progress Report 69, dated May, 1973.

Hence, it is an object of our invention to extract copper from porphyry ores.

A specific object of our invention is to provide an in situ leaching process to dissolve chalcopyrite and to deposit iron dissolved by the leach solution as a crystalline jarosite within the ore body.

DETAILED DESCRIPTION OF THE INVENTION

We have discovered that the addition of particular chloride salts to a dilute sulfuric acid leach solution in combination with gaseous oxygen speeds the dissolution of copper-iron sulfides such as chalcopyrite and precipitates the iron from the leach solution as a crystalline jarosite. Chloride salts suitable for use in our process include sodium chloride, potassium chloride, and ammonium chloride. Of these salts, sodium chlo-

ride is preferred on the basis of its price and availability. In order to achieve a full benefit from our leaching process, certain conditions must be met. Oxygen must be present with the leach solution. Leaching temperature must be above about 60°C and preferably in the range of 60° to 180°C. Presence of chloride ion in association with sulfuric acid approximately doubles the rate of dissolution of copper-iron sulfides such as chalcopyrite provided that the temperature of the leach solution is above about 50°C; there is little if any enhancement of dissolution rate attributable to the chloride ion at ambient temperature.

Another condition that must be met in order to successfully practice our invention is to allow or cause the pH to rise to 0.5 or greater during the leaching process. Formation of jarosites is both pH and temperature dependent, ocurring only at a pH of about 0.5 to 3.0 and at a temperature of about 60° to 70°C or greater. At a pH higher than about 3.0, iron precipitates as the hydroxide rather than as a jarosite.

Jarosites are crystalline compounds having the general formula $MFe_3(SO_4)_2(OH)_6$ where M designates a cation chosen from the group consisting of sodium, potassium and ammonium ions. All three of these compounds occur in nature. They typically occur as sand-like crystals having a yellow or yellow-brown color. The crystals will spontaneously form in aqueous solutions containing ferric, sulfate and alkali metal or ammonium ions provided that the solution is acidic but has a pH of 0.5 to 3.0 and provided that the temperature is above about 60° to 70°C. Experimental work indicates that essentially complete removal of iron from leach solutions can be accomplished at a temperature of 120° to 150°C by precipitation as sodium jarosite. Iron removal is somewhat less complete at lower temperatures.

Several important advantages accrue to our process by precipitation of iron as a jarosite. Because the jarosites are crystalline and sand-like, their precipitation within the ore does not adversely affect the porosity or permeability of the ore to leach solutions. Thus, the leach solution may permeate through the precipitated jarosite grains to contact sulfide mineralization in the ore allowing improved recovery of copper and pregnant solution. In contrast, when iron precipitates as the basic sulfate or as a hydrated oxide, it deposits as a gelatinous-type material forming layers through which leach solutions cannot pass. Another advantage lies in the removal of unwanted iron from solution. Iron, particularly ferric iron, increases the complexity and expense of recovering copper from the pregnant leach solution.

The important variables in our process are solution composition, temperature and oxygen pressure. Solution composition has a pronounced effect on the copper extraction as well as on the precipitation of codissolved ferric iron as crystalline jarosites. Sulfuric acid concentration in the leach solution must be sufficient to maintain the pH below about 3 in order to dissolve the copper sulfide minerals. Much higher acid concentrations are preferred, and the pH of the entering, or lean, leach solution may be 1 or below. Acid may be added directly to the leach solution, or if pyrite is present in the deposit, sulfuric acid will be generated by oxidation of the pyrite during the leach cycle. Concentration of sodium, potassium, or ammonium ion in the leach solution must at least be sufficient to provide stoichiometric amounts of those ions for the precipitation of the co-dissolved ferric iron as a jarosite. It is preferred that the chloride salts be present in excess over that theoretically required as this excess accelerates both the dissolution of the copper-iron sulfides and formation of jarosites.

As has been previously stated, the temperature of our leaching process must be above about 60°C in order to speed dissolution of the copperiron sulfides and to allow precipitation of jarosites. Temperature also has an effect upon the conversion of sulfide sulfur to elemental sulfur. It is generally advantageous to seek the maximum conversion of sulfide sulfur to elemental sulfur as that alleviates a problem of waste disposal and treatment. Elemental sulfur formed remains to a large extent within the interstices of the leached ore. Maximum conversion of sulfide sulfur to elemental sulfur in our process occurs at temperature of about 100°C. At this temperature, some 80% of the sulfide sulfur is converted to the elemental form. Higher or lower temperatures tend to decrease the formation of elemental sulfur.

Free oxygen in association with our leach solution performs the function of oxidizing sulfide sulfur to the elemental form and in some cases to the sulfate form. One of the chemical reactions taking place during leaching is the oxidation of pyrite to produce sulfuric acid and ferrous sulfate which in turn is further oxidized to ferric sulfate. The ferric sulfate-sulfuric acid solution, in association with oxygen, then dissolves chalcopyrite and other copper sulfide minerals present in the porphyry ore. Oxygen over pressure has a definite effect on the rate of oxidation and dissolution of chalcopyrite when using the sulfuric acid-chloride salt leach solutions of our process. As a general rule, the higher the pressure the faster the chalcopyrite dissolution. The increase in dissolution rate of chalcopyrite caused by an increased oxygen over pressure is more pronounced at lower temperatures than at high temperatures. Enough oxygen must be provided to oxidize sulfide sulfur contained in the ore to stable forms which may be elemental sulfur or sulfate. We prefer to operate our porcess with oxygen over pressures of at least 25 psi. Little increase in dissolution rate of chalcopyrite was observed at oxygen over pressures greater than about 200 psi. However, such higher pressures may be used. Oxygen may be supplied as air, oxygen enriched air, or pure oxygen.

Because of the limitations of temperature and oxygen over pressure, our process is not feasible for use in conventional surface heap leaching. While our process can be practiced in an autoclave-type reactor, such use would seldom be economically practical because of the low value of copper porphyry ores. Our process is, however, admirably suited for use in the in situ leaching of copper porphyry deposits; particularly deeply buried porphyry deposits which cannot be economically worked by conventional methods.

Porphyry ore deposits seldom if ever have sufficient natural permeability to either liquids or gases to allow a successful leaching operation to proceed. Hence, an extensive fracture system must be created within the ore body before leaching. Fracturing has been accomplished by the use of conventional chemical explosives as well as by hydraulic means. It has also been proposed to fracture deep ore bodies by means of nuclear blasting. This technique has been shown to be practicable

in the test known as the Piledriver event which was conducted in granite. Such a nuclear blast creates a vertically oriented, cigar-shaped, fractured chimney caused by overlying rocks collapsing into the spherical shaped blast zone of the nuclear explosive. A substantial proportion of the rock sizes within the fracture chimney would have sizes of minus 12 inches in diameter and would display many more micro fractures than rocks shattered by conventional blasting because of the intense shock waves created by the nuclear blast.

Initial temperatures within the shattered ore zone are dependent upon the depth of the ore body, the local geothermal gradient and the method of blasting. Typical initial temperatures within the fractured ore body would be in the neighborhood of 60°C. Oxidation of the pyrite and chalcopyrite minerals with its attendant release of heat would further raise temperatures within the ore body to an expected level of about 150 to 200°C. Hydrostatic pressures within the fractured ore body are a function of depth of the fractured zone and are on the order of 1,000 psig at 2,000 foot depth. Leaching of the fractured ore body is accomplished by introducing oxygen and barren leach solution through wells from the surface to the base of the fractured zone. Other wells communicating between the surface and the top of the fractured zone recover pregnant leach solution and vent gas accumulating at the top of the zone. The pregnant leach solution is then processed at the surface to remove its dissolved copper and is recycled back to the leaching zone. Recovery of copper from the pregnant leach solution may be accomplished by such conventional techniques as cementation, precipitation, and electrowinning. Of these approaches, electrowinning is preferred because the pregnant leach solution, being low in iron, is a desirable feed for that operation. Electrowinning also has the advantage of regenerating sulfuric acid for recycle to the leaching zone.

The following examples serve to more fully illustrate the effect of process variables on the practice of our invention.

EXAMPLE 1

Samples of porphyry copper ore were obtained from a Nevada copper mine. The principle copper mineral was chalcopyrite with some bornite. Little if any pyrite was present. About one-third of the iron values were combined with copper as chalcopyrite and about two-thirds of the iron was present as complex silicates. The principle ferruginous gangue material was epidote with smaller amounts of chlorite and biotite. Only trace amounts of calcite were present. Copper, iron, and sulfur contents of the ores were 1.1, 3.4, and 1.0 percent respectively. A series of pressure leaching tests were conducted on samples of the porphyry copper ore crushed to three-eights of an inch diameter using sulfuric acid solution with and without additions of sodium chloride. The leaching was conducted under 200 psi of oxygen over pressure for 64 hours. Temperatures in successive tests were varied from 100° to 300°C. Results obtained are shown in Table 1.

Table 1

Leach solution composition	Temperature, °C	Extractions, %Cu	%Fe
10 M H_2SO_4	100	20	18
10 M H_2SO_4	200	50	24
10 M H_2SO_4	300	70	18
1 M H_2SO_4	100	27	24
1 M H_2SO_4 + 3.3 M NaCl	100	83	4
1 M H_2SO_4 + 3.3 M NaCl	200	74	1
1 M H_2SO_4 + 3.3 M NaCl	300	52	3

As may be seen from the table, the effect of sodium chloride additions to sulfuric acid are most pronounced at the lower temperatures. The percentages of copper and iron extracted represent the amount of the original metal content of the ore which was recovered in the leach solution. Iron extractions in the last three tests are very low because of the precipitation of extracted iron as sodium jarosite within the ore particles.

EXAMPLE 2

Additional tests were carried out to delineate the effect of leach solution composition upon the dissolution of chalcopyrite contained in the porphyry ore used in Example 1. Crushed ore charges were digested at 80°C under an oxygen atmosphere for 336 hours at varying concentrations of sulfuric acid and sodium chloride. Results obtained are set out in table 2.

Table 2

Composition of leach solution	Extractions %Cu	%Fe
1 M H_2SO_4 + 0.16 M NaCl	18	21
1 M H_2SO_4 + 0.8 M NaCl	43	14
1 M H_2SO_4 + 3.3 M NaCl	81	2
4 M H_2SO_4 + 0.16 M NaCl	60	58
4 M H_2SO_4 + 0.8 M NaCl	80	69
4 M H_2SO_4 + 3.3 M NaCl	91	69

The leach solutions made up with 0.16 M sodium chloride theoretically contained just enough sodium ions to react with 80% of the total iron to form the jarosite. The data shown that increasing the sodium chloride concentration increases the rate of chalcopyrite dissolution at both acid concentrations used in the tests. Iron extraction was much greater in the 4 M acid solutions than in the 1 M acid solutions. This result is attributed to the fact that the pH was too low for jarosite formation in the stronger acid solutions. Results of the test using 1 M acid solutions show a definite trend of decreasing iron in solution as copper extraction increased. This trend is to be expected since the pH of the leach solution rises as copper extraction increases thus favoring the formation of jarosites.

EXAMPLE 3

A series of pressure leaching tests were conducted to compare the effect of sodium chloride with that of sodium sulfate as additives to a sulfuric acid leach solution. A copper porphyry ore having a composition of that used in Example 1 was crushed to a inch particle size and was leached at 100°C under 200 psi of oxygen for 64 hours. Sodium compounds were added in such amount as to provide an equal concentration of sodium ion in the leach solution. Results obtained are set out in the following table.

Table 3

Leach solution composition	Extractions	
	% Cu	%Fe
1 M H_2SO_4	27	24
1 M H_2SO_4 + 3.3 M NaCl	83	4
1 M H_2SO_4 + 1.7 M Na_2SO_4	25	19

Addition of sodium sulfate to sulfuric acid had little if any effect on the extraction of copper and iron from the porphyry ore as compared to sulfuric acid used alone. Theoretically, sodium sulfate furnished sodium ions for the in situ precipitation of co-dissolved iron as jarosites. No such result was observed in these tests but that is attributed to the acidity of the leach solution rather than to the lack of sodium ions.

EXAMPLE 4

Tests were made to determine the effect of oxygen over pressure on the dissolution of chalcopyrite from the copper porphyry ore of Example 1. Several charges of ore were treated with a 1 to 1 weight ratio of a 1.0 M H_2SO_4 + 1.6 M NaCl solution at varying temperatures and oxygen pressures for 48 hours. Results are shown in the following table.

Table 4

Temperature, °C	25 psi O_2 extraction		200 psi O_2 extraction	
	%Cu	%Fe	%Cu	%Fe
55	9.5	17	14	15
80	16	23	22	24
100	20	26	43	29
150	63	3*	74	1*

*The codissolved ferric iron was precipitated as a natrojarosite.

EXAMPLE 5

Since it was observed that appreciable amounts of elemental sulfur were produced during the pressure leaching treatment of chalcopyrite with the sulfuric acid-sodium chloride system, a series of tests were conducted to determined the effect of temperature on the conversion of sulfide sulfur to elemental sulfur. Charges of the copper porphyry ore of Example 1 were treated with sulfuric acid-sodium chloride leach solutions under 200 psi oxygen pressure for 48 hours at varying temperatures. Acid strength was 1.9 molar and sodium chloride strength was 3.3 molar. For comparative purposes, test No. 19 was conducted without addition of sodium chloride. Sulfuric acid concentration in test No. 19 was also 1.9 molar. Results obtained are shown in the following table.

Table 5

Test No.	Temperature, °C	Cu extraction, pct.	$S^=$ converted to S^o, pct.
17	80	46	70
18	100	62	84
19	100	17	22
20	120	75	72
21	140	76	64
22	160	79	61

These data show that the optimum conversion of sulfide sulfur to elemental sulfur occurs at a temperature around 100°C. A comparison of test No. 19 with the other tests in this series shows the marked effect of sodium chloride in increasing the conversion of sulfide sulfur to elemental forms.

EXAMPLE 6

A two-inch diameter specimen of the copper porphyry ore of Example 1 was leached with a sulfuric acid-sodium chloride solution for 14 days at 120°C under 200 psi oxygen over pressure. Acid concentration of the leach solution was 1.9 molar and sodium chloride concentration was 3.3 molar. Visual inspection of the leached rock showed that the continuous sulfide veinlets had been dissolved. Finely disseminated sulfides within one-sixths inch from the surface or from a fracture were also leached. Water freely percolated through the leached specimen.

Visual inspection also showed the presence of globules of elemental sulfur. Presence of natrojarosite deposited within the leached specimen was confirmed by X-ray diffraction analyses. Chemical analyses were performed both on the leached specimen and upon the pregnant leach solution. These analyses indicated a 75% conversion of sulfide sulfur to elemental sulfur and a copper extraction of 53%. The leach solution contained 20.0 grams of copper per liter and only 24 ppm of iron. These examples are for the purpose of more fully describing and illustrating our invention. Minor variations and changes will be obvious to those skilled in the art.

We claim:

1. A process for extracting copper from a porphyry ore containing chalcopyrite which comprises:

contacting said ore with a leach solution comprising an aqueous mixture of sulfuric acid and a salt chosen from the group consisting of sodium chloride, potassium chloride and ammonium chloride in the presence of free oxygen at a temperature above about 60°C for a time sufficient to dissolve chalcopyrite contained in said ore and to attain a pH of said leach solution of above about 0.5 but below about 3.0 thereby precipitating iron dissolved by said leach solution within the ore as a granular, crystalline jarosite having the formula $MFe_3(SO_4)_2(OH)_6$ wherein M is chosen from the group consisting of sodium, potassium and ammonium ions;

separating spent, copper-containing leach solution from the ore, and

recovering copper from the leach solution.

2. The process of claim **1** wherein said porphyry ore is a buried ore body and wherein a zone in said ore body is first fractured and the fractured ore is thereafter leached in place.

3. The process of claim **2** wherein leaching of the fracutred ore body is accomplished by introducing barren leach solution and oxygen through wells communicating between the surface and the base of the fractured ore zone and wherein pregnant leach solution and gases are removed through wells communicating between the surface and the top of the fractured ore zone.

4. The process of claim **3** wherein the salt is sodium chloride.

5. The process of claim **4** wherein the concentration of sodium chloride in the leach solution is substantially in excess of that required to furnish sodium ions for the

precipitation of all ferric iron dissolved by the solution as natrojarosite.

6. The process of claim **5** wherein the oxygen over pressure within the leaching zone is in excess of 25 psi.

7. The process of claim **5** wherein copper is recovered from the pregnant leach solution by electrowinning and wherein barren leach solution comprising electrolyte from the electrowinning step is recycled to the fractured ore zone.

8. The process of claim **5** wherein the leaching step is carried out at temperatures of about 100°C thereby maximizing the conversion of sulfide sulfur to elemental sulfur within the fractured ore zone.

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