

## INVITED FEATURE

# Medium-temperature pressure leaching of copper concentrates — Part I: Chemistry and initial process development

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### Abstract

*Over the past eight years, Phelps Dodge (a subsidiary of Freeport-McMoRan Copper & Gold, Inc.) devoted a significant amount of effort to the development of a suite of processes for the effective hydrometallurgical treatment of copper sulfide concentrates. This effort resulted in the development of high-temperature (>200°C) and medium-temperature (150° to 165°C) pressure leaching processes. Specific configurations of both processes have been commercially demonstrated at Phelps Dodge's facility in Bagdad, Arizona. This paper reviews in detail the chemistry of medium-temperature pressure leaching of copper concentrates and reports on the process development work conducted by Phelps Dodge and others for this technology. This paper is Part I of a four-part series on this technology. Part II covers the development of medium-temperature pressure leaching and direct electrowinning technology; Part III considers the large-scale demonstration of the MT-DEW-SX process at Bagdad, Arizona; and Part IV addresses the development and design of a full-scale commercial application at Morenci, Arizona.*

**Key words:** Copper, Pressure leaching

### Introduction and background

In 1998, Phelps Dodge, now a subsidiary of Freeport-McMoRan Copper & Gold, Inc. (effective March 19, 2007), commenced development of sulfate-based pressure-leaching technology for the treatment of copper sulfide concentrates as an alternative to conventional smelting and refining technology. The main drivers for this activity were the relatively high and variable cost of external smelting and refining capacity (i.e., treatment charges and refining charges or TCRCs), the limited availability of smelting and refining capacity in some cases, the high capital cost of installing new smelting capacity (largely driven by increasingly stringent environmental regulations) and the need to cost-effectively generate sulfuric acid at mine sites for use in heap and stockpile leaching operations.

In looking for a suitable alternative to smelting and refining technology for the treatment of chalcopyrite concentrates, Phelps Dodge investigated a number of options, including the following:

- high-temperature (>200°C), sulfate-based pressure leaching;

- medium-temperature (140° to 180°C), sulfate-based pressure leaching;
- low-temperature (100° to 140°C), sulfate-based pressure leaching;
- low-temperature (<100°C), sulfate-based atmospheric leaching;
- simultaneous attrition grinding and atmospheric leaching (sulfate);
- atmospheric biological oxidation and leaching (sulfate);
- silver-catalyzed atmospheric leaching process (sulfate);
- chloride-assisted, medium-temperature sulfate-based pressure leaching;
- coal-assisted, medium-temperature sulfate-based pressure leaching;
- ammonia/ammoniacal (sulfate/carbonate) leaching; and
- chloride/bromide leaching.

In addition, Phelps Dodge has a rich and extensive history in copper concentrate leaching research and devel-

Paper number MMP-07-027. Original manuscript submitted online July 2007 and accepted for publication August 2007. Discussion of this peer-reviewed and approved paper is invited and must be submitted to SME Publications Dept. prior to May 31, 2008. Copyright 2007, Society for Mining, Metallurgy and Exploration Inc.

opment. Extensive research was performed in the 1970s and 1980s, and this work has been reported previously (Marsden et al., 2003, and Marsden and Brewer, 2003).

Preliminary economic evaluation of the most promising options indicated that the candidates most likely to offer successful, long-term alternatives to smelting and refining were the sulfate-based processes. These processes have a number of significant advantages over nonsulfate systems and, in some cases, over systems using other chemical additives (e.g., chloride). These advantages are summarized as follows:

- It is possible to fully integrate concentrate leaching with existing and/or future heap/stockpile/tank-leaching operations.
- Byproduct acid generated by pressure leaching can be utilized for heap/stockpile/tank leaching, providing a credit to the concentrate leaching process.
- Existing solution extraction/electrowinning (SX/EW) capacity can be utilized for copper recovery, where available and applicable.
- Materials of construction are well-proven for sulfate-based solution chemistry (Gillaspie et al., 2005).
- In general, they have comparable or superior overall economics.

As such, Phelps Dodge elected to aggressively pursue sulfate-based hydrometallurgical options for concentrate leaching as an alternative to conventional smelting and refining.

It should be noted that, throughout this paper, the terms "solution extraction" and "SX" are used to refer to the process that is commonly referred to as "solvent extraction" in the industry.

### Process development history

From 1998 through 2001, Phelps Dodge conducted extensive research in the application of sulfate-based leaching systems. The initial potential target for the application of concentrate leaching was the Candelaria mine in Chile, which produced a copper-gold concentrate containing chalcopyrite, pyrite, minor sphalerite and silica gangue. After completion of the acquisition of Cyprus Amax by Phelps Dodge in 2000, the primary sulfide deposits underlying the existing mining operations at Cerro Verde, Peru, and El Abra, Chile, were considered promising candidates for concentrate leaching. The existing operation at Cerro Verde was comprised of crushing and heap leaching of chalcocite-bearing material followed by SX/EW for recovery of copper. Operations at El Abra consisted of crushing and heap leaching of oxidized material followed by SX/EW for recovery of copper. Both operations required sulfuric acid for the ongoing leaching operations, although the secondary sulfide mineralization at Cerro Verde required significantly less acid (per metric ton) for leaching than the El Abra oxide material.

In 2001, a Technology Development Agreement was established with Placer Dome Inc. to advance the further development and commercialization of sulfate-based pressure leaching technology for the treatment of copper and precious-metal-bearing concentrates (King et al., 1993; King and Dreisinger, 1995). In November 2001, Phelps Dodge commenced construction of a commercial demonstration facility at Bagdad, Arizona. The plant was designed to process between 52,500 and 57,300 t/yr chalcopyrite concentrate, depending on the concentrate grade (28.5% to 30.5% copper) and was designed to produce an average of about 16,000 t/yr copper cathode. The facility was commissioned in March 2003 and reached full capacity within three months. Details of the facility design, the reaction chemistry and the plant start-up and performance have been

previously reported in detail (Marsden et al., 2003; Marsden and Brewer, 2003; Brewer, 2004; Wilmot et al., 2004a; Wilmot et al., 2004b).

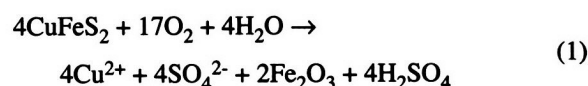
Concurrent with the development and commercialization of high-temperature pressure leaching, Phelps Dodge advanced the development of four other processes:

- Medium-temperature (160° to 170°C) pressure leaching of concentrate following superfine grinding to 80% passing 6 to 7  $\mu\text{m}$  (and 98% passing 12 to 15  $\mu\text{m}$ ) and incorporating SX/EW for copper recovery as cathode.
- Medium-temperature pressure leaching followed by direct EW (stand-alone).
- Medium-temperature pressure leaching followed by direct EW from a high-grade leach solution and SX/EW from a low-grade solution.
- Pressure leaching (both high- and medium-temperature) of concentrate following superfine grinding (see above) with direct EW and reaction of lean electrolyte with concentrate to precipitate copper and produce an acid-rich, copper-lean solution stream for use in heap and stockpile leaching.

The chemistry of the first of these processes (medium-temperature pressure leaching with SX/EW) is reviewed below, together with the process development work required to take this technology to readiness for full commercial application.

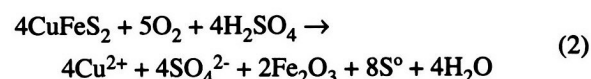
### Process chemistry

At high temperatures (i.e., >200°C), pressure leaching of chalcopyrite in acidic sulfate media and in the presence of sufficient dissolved oxygen proceeds according to

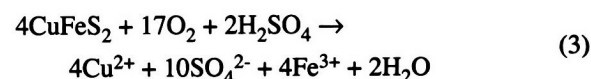


More details on the chemistry of chalcopyrite oxidation at temperatures above 200°C were provided previously (Marsden et al., 2003; Marsden and Brewer, 2003) and are not reviewed further here.

At temperatures above 119°C and below approximately 200°C and in the presence of free acid, a portion of the sulfide sulfur is converted to (molten) elemental sulfur according to



But, under these conditions, oxidation can also occur according to



Importantly, Eq. (2) consumes approximately 70% less oxygen per mole of chalcopyrite oxidized than Eqs. (3) and (1). However, unlike Eq. (1), both Eqs. (2) and (3) require acid to proceed. Equation (2) requires 1.0 mole of sulfuric acid for every mole of chalcopyrite in the feed, whereas Eq. (3) requires 0.5 moles of acid for every mole of chalcopyrite. The theoretical stoichiometric requirements of sulfuric acid for the two reactions, respectively, are 0.53 and 0.27 tons of acid per ton of chalcopyrite.

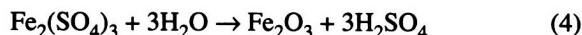
Pressure leaching of sulfide minerals at temperatures above the melting point of sulfur (119°C) but below 200°C is complicated by the relationship between sulfur viscosity and

temperature, as shown in Fig. 1. At temperatures above the melting point of sulfur, the sulfur tends to wet sulfide mineral surfaces and, under certain conditions, agglomerates to form "prills." This can interfere with mineral oxidation by coating and occluding reactive mineral particles. In addition, prill formation can interfere with the physical transfer of material within the pressure leach vessel and can adversely affect discharge from the vessel. Elemental sulfur can also form a nucleus for scale formation in the vessel under certain conditions. It is well known that the addition of a suitable sulfur dispersant, such as calcium lignosulfonate (CLS), sodium lignosulfonate or coal, can help reduce sulfur wetting and coalescence of sulfur into agglomerates/prills.

It can be seen from Fig. 1 that sulfur viscosity increases dramatically with increasing temperature above approximately 160°C, reaching a maximum value at 185° to 188°C. As viscosity increases, the tendency for elemental sulfur to interfere with oxidation by coating and occluding unreacted sulfide mineral particles increases, and the material becomes increasingly difficult to handle. These practical constraints limit the application of pressure leaching of chalcopyrite to the temperature range in which elemental sulfur is formed, i.e., between 140° and 170°C.

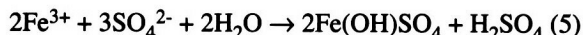
At temperatures below 119°C (the melting point of sulfur), oxidation of chalcopyrite proceeds according to Eqs. (2) and (3); however, the reaction occurs in the absence of sulfur-wetting of mineral surfaces.

In addition to the simultaneous oxidation and dissolution of chalcopyrite, iron hydrolysis also occurs. Between 150° and 165°C and at low acid concentrations, hematite is formed as follows



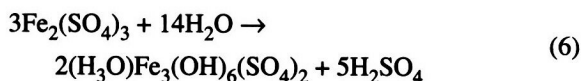
It should be noted that this is also the primary iron precipitation reaction under high-temperature pressure leaching conditions (i.e., >200°C). The extent to which this hydrolysis reaction occurs must be taken into account when determining the stoichiometric acid requirements for Eqs. (2) and (3). For example, if complete hydrolysis were to occur, Eq. (3) becomes Eq. (1), and 1.0 mole of sulfuric acid would be generated for each mole of chalcopyrite oxidized.

At high acid concentrations (i.e., >50 g/L in the discharge), and at high temperature (>220°C), basic iron sulfate can form as follows:



There is significant evidence in the literature that basic iron sulfate formation occurs at lower temperature (although this depends on acid concentration), but this was not specifically observed during this work.

At medium temperature (about 160°C) and with 500 kg/t acid addition (i.e., 20 to 25 g/L acid in the discharge), some jarosite forms as follows



The preferred iron species in both high- and medium-temperature pressure leaching is hematite; however, some iron sulfate species are generally present in final residues from copper pressure leaching processes.

After leaving the pressure-leaching vessel and on cooling of the slurry, some of the hematite dissolves according to the reverse of Eq. (4), as follows:

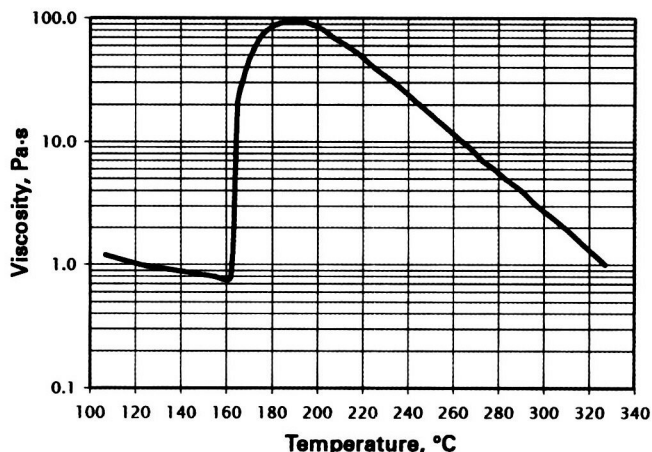


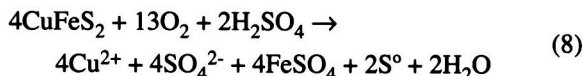
Figure 1 — Viscosity of molten sulfur as a function of temperature (adapted from Bacon and Fanelli, 1943).



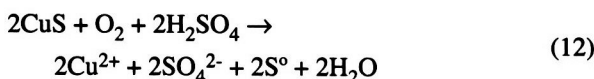
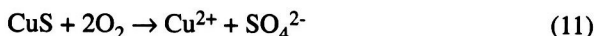
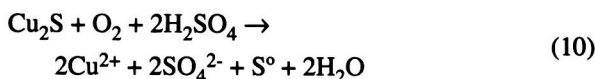
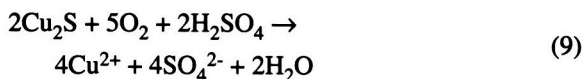
The extent to which this reaction occurs is dependent on time, temperature and acid concentration, and the dissolution of iron can continue for as long as the solution remains in contact with the solid leach residue. The minimization of iron in solution requires that the solid residue be separated from the solution as quickly as possible. In some situations it may be desirable to maximize the amount of iron in solution, and this can be done by optimizing the conditions for redissolution to occur.

Any ferric present in the pressure leach solution, either produced by the oxidation and dissolution of iron-bearing sulfides or introduced in recycle streams returned to the pressure-leaching vessel, is available to assist with oxidation of sulfide minerals. On the other hand, the presence of significant ferric in solution can adversely affect current efficiency, especially in the case of direct EW without the use of an intermediate SX step for concentration and purification of the solution. This is an important factor that is explored in more detail in Parts II, III and IV in this series of papers.

When insufficient oxygen is available for the oxidation reactions, undesirable products may form, including iron (ferrous) sulfate, shown for the example of chalcopyrite as follows



Other copper sulfide minerals such as chalcocite ( $\text{Cu}_2\text{S}$ ) and covellite ( $\text{CuS}$ ) react as follows



**Table 1** — Chemical analyses of concentrates used in batch and continuous work.

Constituent	Candelaria concentrate, Batch work	Bagdad concentrate, Continuous pilot plant	Candelaria concentrate, Continuous pilot plant
Ag, g/t	116	79	84
As, %	0.0043	0.0500	0.0086
Au, g/t	6.3	0.29	5.4
Ba, %	0.008	<0.005	0.007
C <sub>T</sub> , %	0.06	0.04	0.06
Ca, %	0.46	0.25	0.41
Cl <sup>-</sup> (water soluble), %	<0.001	0.003	0.006
F, %	<0.01	0.01	<0.01
CO <sub>2</sub> (reported as C), %	<0.01	<0.01	<0.01
Cu, %	29.3	31.0	29.3
Fe, %	29.2	29.3	28.6
Mo, %	0.008	0.05	0.009
Ni, %	0.007	<0.001	0.003
Pb, %	0.016	0.017	0.044
S <sub>T</sub> , %	33.6	34.0	31.6
S <sup>-2</sup> , %	33.5	33.4	30.6
Sb, %	0.005	0.045	<0.005
Zn, %	0.18	0.13	0.32

Chalcocite primarily forms sulfate (Eq. (9)) regardless of acid addition at medium-temperature conditions. Covellite also primarily forms sulfate (Eq. (11)), but the proportion of sulfide sulfur converted to elemental sulfur (Eq. (12)) increases with acid addition, reaching about 40% at 400 kg/t.

Pyrite, which is often a constituent in copper concentrates, particularly chalcopyrite-dominant concentrates, does not form elemental sulfur under most medium-temperature pressure leaching conditions but reacts as follows



However, some elemental sulfur can be formed at very high acid concentrations (i.e., 900 kg/t). Under such conditions, approximately 5% elemental sulfur can be formed. It should be noted that, in the presence of moderate chloride concentrations in solution (i.e., 10 to 15 g/L), significant elemental sulfur can form, depending on the exact conditions applied.

### Batch pressure leaching at medium temperature

Between 1999 and 2001, Phelps Dodge conducted a series of batch experiments to investigate low- to medium-temperature pressure leaching of copper sulfide concentrate. The testing was performed at Hazen Research Inc. (Golden, Colorado), at Dawson Metallurgical Laboratories Inc. (Salt Lake City, Utah) and at Lakefield Research Ltd. (Lakefield, Ontario). The batch experiments were conducted on flotation concentrate from the Phelps Dodge Candelaria mine in Chile, which contained approximately 90% chalcopyrite, 3% pyrite, 5% gangue, <1% magnetite and minor to trace amounts of other minerals. The chemical analyses of the concentrates used in the batch and continuous work are shown in Table 1. The Bagdad concentrate referred to in Table 1 had a typical mineralogical composition of 83% to 85% chalcopyrite, 5% to 8% pyrite and 7% to 12% gangue.

The batch runs were designed primarily to investigate the

effects of temperature, acid addition, particle size, retention time and sulfur dispersant addition on copper extraction, degree of elemental sulfur formation, precious metal and minor element deportment, and the characteristics of the residue material. In addition, for comparative purposes, the addition of silver (as a catalyst) and coal were also tested. Initially, a temperature range of 100° to 200°C was considered for this work. The results of work conducted at higher temperatures (>200°C) were reported previously (Marsden and Brewer, 2003).

For many of the leach experiments, superfine grinding of the concentrate was required prior to pressure leaching. In such cases, the material was ground using one of the following two methods:

- a conventional 127- to 152-mm (5- by 6-in.) steel ball mill, with a 6.35- to 2.54-mm- (1/4- to 1/10-in.-) diameter charge of steel balls, to achieve product sizes down to a P<sub>80</sub> of about 8 µm or
- a Szegvari Attritor System (Union Process Mill) using a charge of equal weights of 6.35- and 9.52-mm- (1/4- and 3/8-in.-) diameter alumina balls to achieve product sizes down to a P<sub>80</sub> of 5.4 µm.

The particle size of the product was measured using both a Malvern Mastersizer (Malvern Instruments Inc., Malvern, Worcestershire, UK) and a Quantachrome Microscan sedimentation particle size analyzer (Quantachrome Instruments, Boynton Beach, Florida). The Malvern results were used in this paper. The particle size distribution and its measurement is a critical factor for medium-temperature pressure leaching, and additional information is to be reported in the fourth paper in this series.

The pressure-leaching experiments were performed in batches using a standard 2-L Parr autoclave fitted with a 316 stainless steel head and titanium internals and shell. Two pitched-blade impellers were used with a baffle. A relatively rapid stirring rate of 900 rpm was used in most cases. For each batch test, the autoclave shell was loaded with ground concentrate, reagents and water (or synthetic raffinate). For most of the experiments, slurry containing 20% solids by weight was used, but this was varied down to 10% in certain cases. A small oxygen overpressure was applied to minimize reducing conditions during heat-up. After heating to the operating temperature, the full oxygen overpressure was established with a small (vent) bleed. Most of the runs were conducted with an oxygen overpressure of 690 kPa (100 psi). Oxygen flow was measured using mass flow meters to provide a rough estimate of oxygen consumption over time. At the end, the autoclave was rapidly cooled to <100°C, the remaining pressure was released, and the contents of the autoclave were diluted with water to prevent crystallization. The slurry was filtered as quickly as possible. During experiments in which beads (prills) or "clinker" were formed, the residue was screened and each fraction was separated for analysis. The residue solids were dried at low temperature (50°C).

A synthetic raffinate solution was used as the aqueous phase in most experiments. This introduced minor amounts of elements that might be present in recycled solution streams. The synthetic raffinate was prepared by dissolving appropriate quantities of reagent-grade sulfate salt in water.

**Results of medium-temperature batch pressure leaching.** The batch results over a range of temperatures between 130° and 180°C are summarized in the following sections:

**Effect of particle size:** Concentrate particle size was the dominant factor in determining copper extraction. Copper extractions from as-received concentrate ( $P_{80}$  of  $\sim 50 \mu\text{m}$ ) were typically in the range of 40% to 45%. Copper extractions from material ground to a  $P_{80}$  of  $8 \mu\text{m}$  increased to the mid- to high-90s, depending on temperature, acid addition and dispersant addition.

Optical examinations of residues from runs yielding poor extractions indicated the presence of sulfur prills and fragments carrying abundant coarse chalcopyrite particles. This coarse chalcopyrite was generally concentrated in the peripheral regions of the sulfur particles but was also disseminated throughout the sulfur matrix. An example of this occurrence is shown in Fig. 2. The optical evidence, along with chemical analyses of size fractions, clearly showed sulfur preferentially entrapping coarser ( $>10$  to  $15 \mu\text{m}$ ) chalcopyrite.

Following an economic evaluation of concentrate grind size versus copper extraction, it was determined that, in addition to the typical  $P_{80}$  specification, a  $P_{98}$  specification was required to adequately define the feed particle size distribution. A  $P_{98}$  of  $15 \mu\text{m}$  or smaller consistently generated copper extractions greater than 98% (depending on other conditions), while size distributions that contained more than 2% of the plus  $15\text{-}\mu\text{m}$  particles showed extraction losses to coarse chalcopyrite. This relation was borne out in subsequent continuous pressure leaching work.

When a relatively high acid addition was applied (i.e.,  $>600 \text{ kg/t}$ ) to as-received, unground concentrate ( $P_{80}$  of  $\sim 50 \mu\text{m}$ ), the reaction proceeded initially, but then stopped as indicated by the oxygen flow rate. This resulted in low copper extraction and, on opening the pressure leach vessel, a significant amount of bead and clinker material was discovered (see Fig. 3). The beads and clinker consisted of unreacted chalcopyrite particles cemented together by elemental sulfur.

**Effect of temperature and acid addition:** Copper extractions between 97% and 99% were achieved over a range of temperatures ranging from  $140^\circ$  to  $180^\circ\text{C}$ , with acid additions of 400 to  $800 \text{ kg/t}$  concentrate and using concentrate finely ground to approximately 80% passing  $8 \mu\text{m}$ . The relationship between copper extraction and temperature is shown in Fig. 4. The maximum copper extraction was achieved at  $160^\circ\text{C}$  and at acid additions of 500 to  $600 \text{ kg/t}$ . Copper extraction was found to decrease significantly below about  $140^\circ\text{C}$ . Sulfur prill formation and the formation of agglomerates severely impacted copper extraction between about  $180^\circ$  and  $200^\circ\text{C}$ . At temperatures above  $200^\circ\text{C}$ , essentially all of the sulfide sulfur was converted to sulfate.

As stated above, at  $160^\circ\text{C}$  acid additions between approximately 500 and  $600 \text{ kg/t}$  yielded maximum copper extractions. Above and below this range, extractions decreased, as shown in Fig. 5.

The amount of iron in solution in the oxidized slurry depended on the amount of acid addition and on the acid concentration in the pressure leach discharge, as shown in Fig. 6. Lower free acid concentrations favored iron hydrolysis and precipitation, and the iron concentration decreased to less than  $1 \text{ g/L}$  as the free acid concentration was reduced below  $15 \text{ g/L}$ .

**Effect of retention time:** Most of the batch experiments lasted 180 minutes. Little or no benefit was obtained by extending the leaching period, and there was little if any detrimental effect observed from reducing retention times to 120 minutes. This was to be studied in more detail during continuous leaching.

**Sulfur deportment:** The extent of sulfide sulfur conversion to elemental sulfur depended on the temperature and the amount of acid addition. These effects are illustrated in Fig. 7. Under

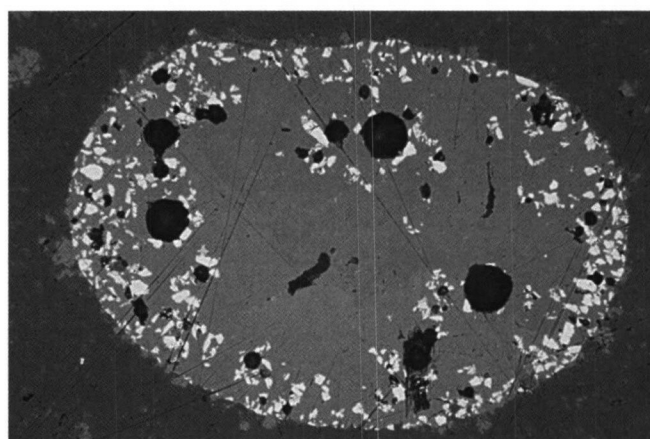


Figure 2 — Photomicrograph showing coarse sulfur prill ( $\sim 300 \mu\text{m}$ ) with abundant relatively coarse ( $10$  to  $25 \mu\text{m}$ ) chalcopyrite concentrated in the peripheral region of the prill.

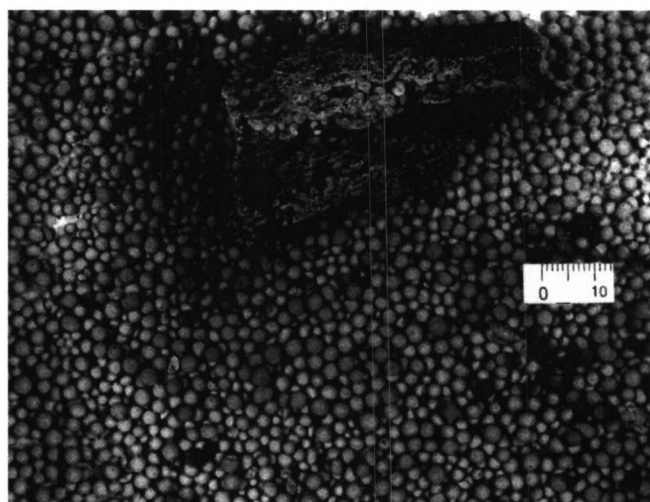


Figure 3 — Photo showing beads and clinker material formation (from batch testing).

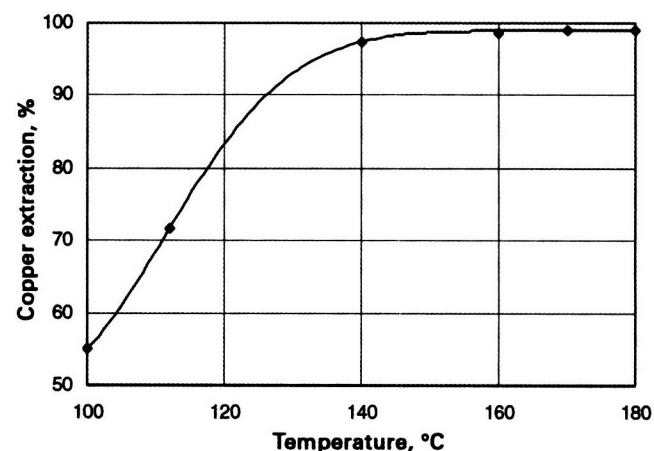
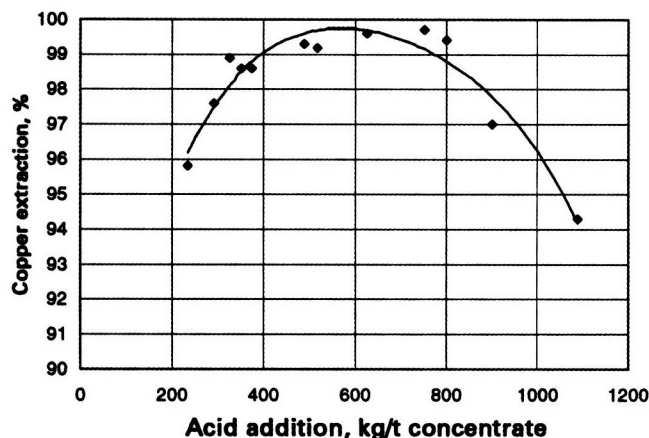
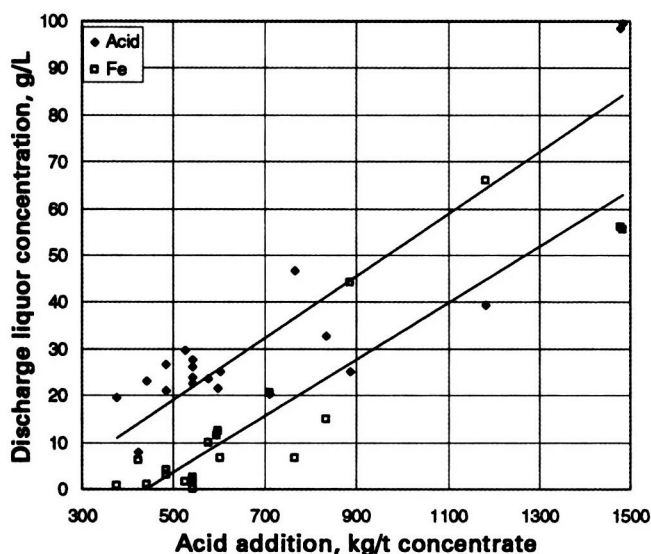


Figure 4 — General relationship between average copper extraction and temperature at various acid addition rates (batch testing).





**Figure 5** — Relationship between copper extraction and acid addition (batch tests at 160°C).

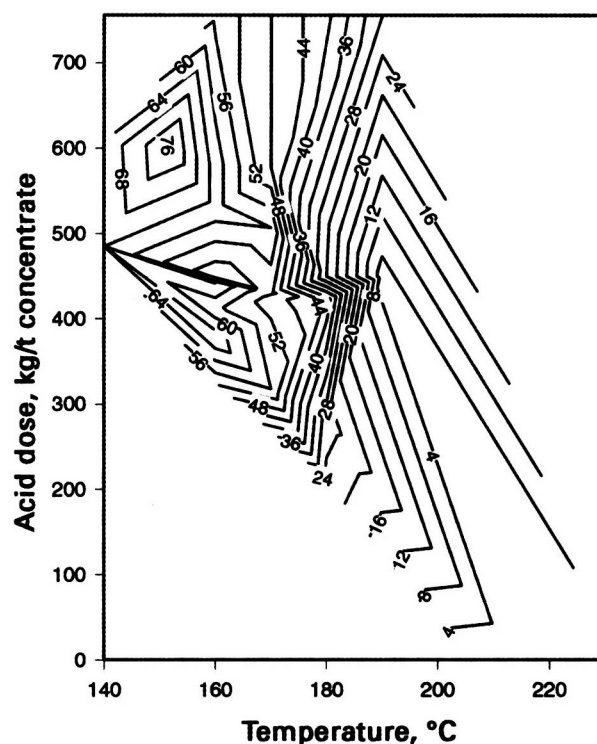


**Figure 6** — Relationship between acid addition and acid and iron concentrations in pressure-leach-vessel discharge (batch).

conditions in which copper extraction was maximized, or close to maximized, approximately 65% of the sulfide sulfur was converted to elemental sulfur. However, higher conversion rates, in excess of 75%, could be achieved at the expense of copper extraction.

The acid addition amount, and consequently the acid concentration during leaching and in the pressure leach discharge, was determined to be a compromise between maximizing copper extraction, maximizing sulfide sulfur conversion to elemental sulfur and optimizing iron concentration for the overall process flowsheet. It should be noted that the maximum conversion of sulfide sulfur to elemental sulfur in this case coincided with the maximum extraction of copper as well when compared to Figs. 4 and 5, i.e., an acid dosing of approximately 600 kg/t concentrate and a temperature of 160°C.

**Effect of sulfur dispersants:** The addition of a suitable dispersant was critical to maximize copper extraction under a particular set of conditions (i.e., particle size, acid addition and

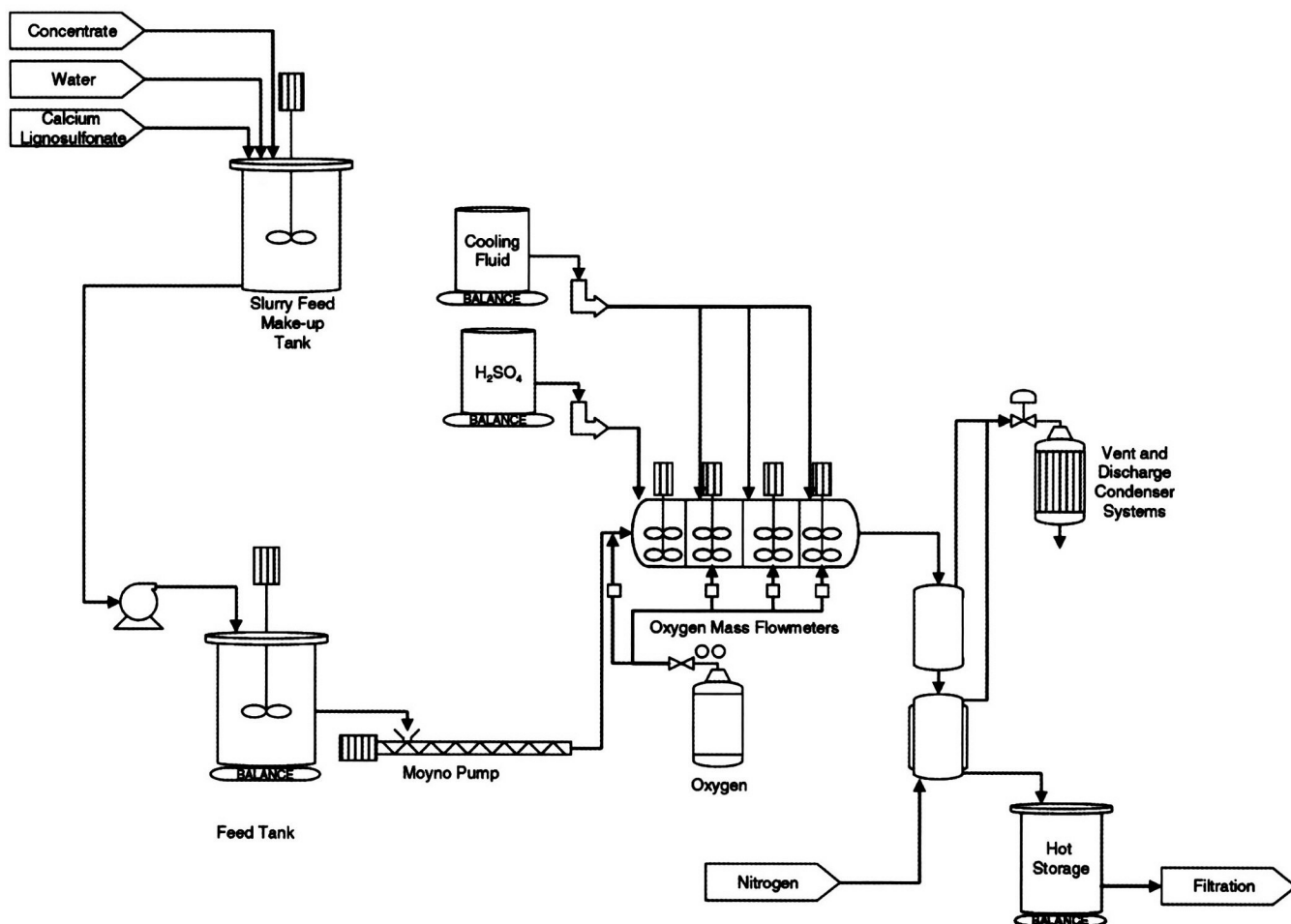


**Figure 7** — Effect of temperature and acid addition on extent of conversion of sulfide sulfur to elemental sulfur using batch test results — the contour lines represent the percentage conversion of sulfide sulfur in concentrate to elemental sulfur.

temperature). The following dispersants were examined during batch leaching: calcium lignosulfonate (5 to 20 kg/t), Ultrathinz (10 kg/t) and coal (40 kg/t). Ultrathinz is a sodium-based lignosulfonate product (Georgia-Pacific) that was claimed to be stable at high temperatures. Calcium lignosulfonate (CLS) additions of 5 to 10 kg/t were found to provide adequate sulfur dispersion and achieve good copper extraction. Ultrathinz reagent proved to be less effective than CLS at the dose used.

In the case of coal, a sample containing 22% moisture, 4.4% ash and 0.41% sulfur with a higher heating value of 22.7 MJ/kg (9,760 Btu/lb) was used for the batch test runs. The coal was found to be an effective dispersant at the dose tested under certain conditions, but was judged to be less cost effective overall than CLS (a balance between reagent cost and copper extraction).

**Effect of silver catalyst addition:** The beneficial effect of silver ions on the dissolution of chalcopyrite is well known and well documented (Hackl et al., 1995). The silver interferes with the formation of a polysulfide layer on the surface of the copper sulfide mineral(s), thereby reducing the passivating effect. A number of experiments were run for comparative purposes to examine the effect of silver on pressure leaching of chalcopyrite. In these runs, between 1.37 and 1.47 kg/t silver sulfate were added to the leach slurry in some cases in conjunction with one of the dispersants described above. In the best case, copper extractions of 75% to 80% were achieved. This poor performance may be attributable to the formation of argentojarosite and/or precipitation of silver sulfide under medium-temperature pressure leaching conditions. Notwithstanding the poor results, the addition of silver in the amounts used is not economically viable, unless the silver is already



**Figure 8** — Continuous pilot plant flowsheet configuration.

present in the concentrate (or other) source material.

**Solid residue characteristics:** The solid residue product from most of the leach tests consisted of intimate mixtures of elemental sulfur, unreactive gangue and iron hydrolysis products. As noted above, the iron content of the solid residue generally increased with decreasing acid addition to the pressure leach vessel. At the highest acid addition (~1,100 kg/t), the residue contained 8% iron, whereas at a lower acid addition (~500 kg/t), the residue contained 35% iron. X-ray diffraction analysis indicated that hydronium jarosite was the main iron product at higher acid additions, but some hematite was also present. At lower acid additions, the residue consisted mainly of hematite with only a minor amount of jarosite present.

### Continuous pilot plant pressure leaching

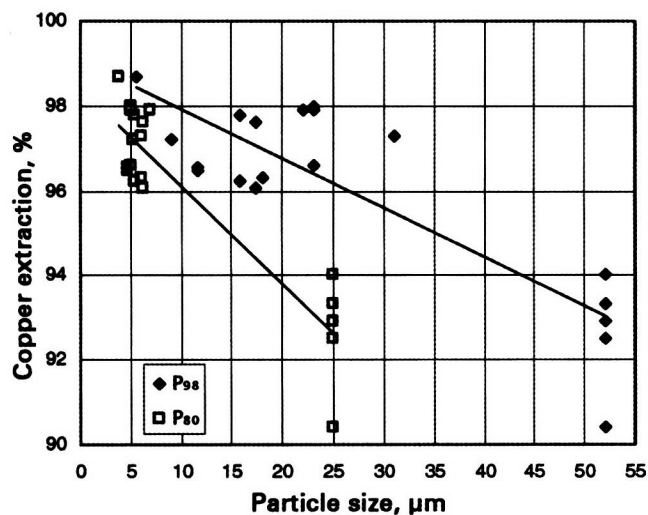
Based on the batch results from Hazen Research, Dawson Metallurgical Laboratories and Lakefield Research and following preliminary process development and flowsheet design, a series of continuous pilot plant runs was conducted at Hazen Research. The main objectives of the pilot plant campaigns were to:

- determine the operating conditions necessary for continuous medium-temperature pressure leaching of chalcopyrite concentrates;
- demonstrate continuous operation of the Phelps Dodge medium-temperature concentrate leaching process for an extended period of time (25 hr);

- characterize discharge solution and solid residue;
- produce sufficient quantities of pressure leach vessel discharge to allow the operation of a continuous SX pilot circuit;
- produce sufficient quantities of pressure leach vessel discharge slurry for thickening, filtration, and neutralization tests;
- collect samples for environmental analysis to assist permitting of a demonstration plant;
- determine the need for addition of CLS to the concentrate feed for effective pressure leaching operation; and
- determine whether stockpile leach raffinate solution from the Bagdad (Arizona) operation could be used as quench water for temperature control in the pressure leach vessel.

In all, 26 runs were completed using medium-temperature pressure-leaching conditions to meet the above objectives, ranging in duration from about 8 to 25 hours each. Twenty-one of these runs were conducted on flotation concentrate from the Candelaria mine in Chile and five were conducted on flotation concentrate from the Bagdad operation in Arizona. The chemical analyses for these concentrates are listed in Table 1.

The flowsheet for the pressure-leaching section of the pilot plant is shown in Fig. 8. The pilot plant consisted of a slurry make-up tank, a day storage tank and a feed tank, all of which were equipped with balances to record the weights of material fed to the leaching circuit. Slurry was delivered to the pres-



**Figure 9** — Effect of particle size on copper extraction (continuous pilot plant at 160°C).

sure-leach vessel using one of two variable-speed, 12-stage progressive cavity (Moyno) pumps. The feed line to the pressure leach vessel was fitted with a steam jacket to preheat the slurry. Electrical heat tape and insulation were installed on all slurry transfer lines, the letdown system and the pressure leach exhaust lines to help mitigate potential plugging problems that were anticipated under medium-temperature conditions (due to elemental sulfur formation). The feed slurry was fed into the vessel below the slurry level in the first compartment. The target feed density was 34.5% solids for all runs, but the feed slurry was diluted with water or raffinate to the required level to satisfy the heat balance for reactions in the first compartment reactions, typically 10% to 17% solids.

The pressure-leach vessel was a horizontal cylinder divided into four compartments and was fabricated out of Grade 12 titanium. Each compartment was equipped with a mechanical agitator that was fitted with two 100-mm-diameter, pitched-blade impellers. The agitators were operated at 600 rpm during all the runs.

The partitions dividing the four compartments were bolted to circumferential rings that were welded to the vessel shell. Each partition covered the entire cross-section of the vessel, except for an 18 by 100 mm opening at the top, which provided a continuous vapor space over the top of all four compartments. A rectangular hole located at the slurry-vapor interface was provided in each partition, and this allowed slurry to overflow into the next compartment. An enclosed baffle was welded to the downstream side of the partition to direct the overflowing slurry downward and into the bottom section of the next compartment. The slurry level decreased by 12 mm in each subsequent compartment. Individual compartment samples were withdrawn from the vessel as required and were captured in water-cooled "bombs" using short lengths of tubing inserted into well-mixed zones in each compartment.

The cooling fluid required for the first compartment was delivered to the discharge of the Moyno feed pump rather than directly into the vessel. The oxygen supply to the first compartment was injected into the slurry feed line immediately prior to entering the vessel. Oxygen was metered into each of the last three compartments and was injected into the slurry phase through 6-mm-diameter tubing. Cooling fluid (water or

raffinate) was pumped into each of the last three cells from a (weighed) storage tank. The cooling fluid was injected through the same tubing used to deliver oxygen, thereby humidifying the oxygen prior to entering the pressure leach vessel.

Slurry was discharged from the vessel through a two-vessel pressure letdown system. The two-stage letdown system permitted the slurry to continuously overflow without losing the liquid seal created by the slurry. This allowed for continuous monitoring of the exhaust gas composition using an oxygen analyzer.

After cooling and letdown of the pressure-leach discharge slurry, the material was weighed, sampled and then transferred to solid-liquid separation. Flocculant was added, and the product was held for two hours to allow the solids to settle. The product also cooled during this two-hour period, which was intended to simulate the cooling that would occur in a large-scale thickening operation. The bulk of the liquor was then decanted from the settled solids. The remaining settled slurry was vacuum filtered.

**Results of continuous pilot plant pressure leaching.** The 26 pilot plant runs were conducted in three campaigns. Between each campaign, the pilot plant was shut down, and the data for the prior campaign were compiled and analyzed. In addition, adjustments were made to one or more parameters between runs.

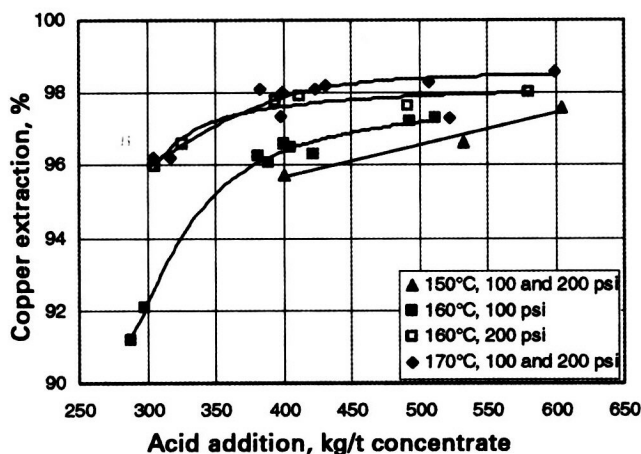
The results indicated that copper extractions of about 98% could be achieved from concentrate ground to 80% passing 6 µm (and 98% passing 12 µm). The conditions required to achieve such copper extractions were:

- a temperature of 160° to 170°C,
- an oxygen overpressure of 620 to 760 kPa (90 to 110 psi),
- a sulfuric acid addition of 400 to 600 kg/t,
- a retention time of 90 to 120 minutes,
- a calcium lignosulfonate addition of 10 kg/t and
- a quench liquid consisting of water or process raffinate.

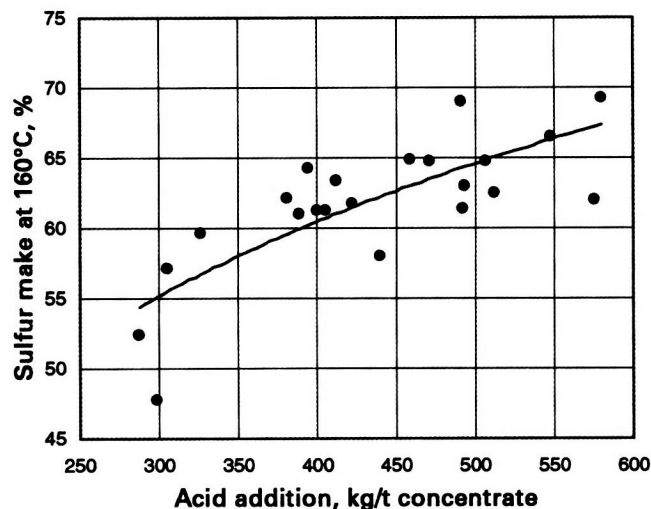
An extended pilot plant run at 170°C, 400 kg/t acid addition, 90 minutes retention time and 10 kg/t CLS addition yielded a copper extraction of 98.2%. The undissolved copper consisted of unreacted chalcopyrite encapsulated in elemental sulfur and copper intimately associated with hematite. Under the conditions applied, approximately 50% of the sulfide sulfur in the feed was converted to elemental sulfur, with the remainder forming sulfate.

**Effect of particle size:** The batch results indicated that superfine grinding of the concentrate to tight P<sub>88</sub> and P<sub>80</sub> specifications was necessary to achieve optimal copper extractions. To confirm the batch results, the continuous pilot plant runs investigated a range of grind sizes for the concentrate with P<sub>80</sub> sizes ranging from 25 to 4 µm (with 98% passing 52 to 6 µm). The results are summarized in Fig. 9. It should be noted that conditions other than grind size were varied somewhat for the points used in this figure, but this illustrates the general trend of the relationship between copper extraction and grind size. Inspection of the data indicated that the optimal particle size was 80% passing 6 µm (98% passing 12 µm). However, most importantly, the shape of the full-size distribution was found to be critical to achieving the optimal copper extraction. The cost to superfine grind as-received concentrate (80% passing 45 µm) down to a P<sub>80</sub> of 6 to 7 µm and a P<sub>88</sub> of 12 to 15 µm was estimated to be approximately \$0.01/lb copper, based





**Figure 10** — Effect of temperature and acid addition on copper extraction in the continuous pilot plant (Note: 100 psi = 690 kPa, 200 psi = 1,380 kPa).



**Figure 11** — Effect of acid addition on elemental sulfur formation (continuous pilot plant at 160°C).

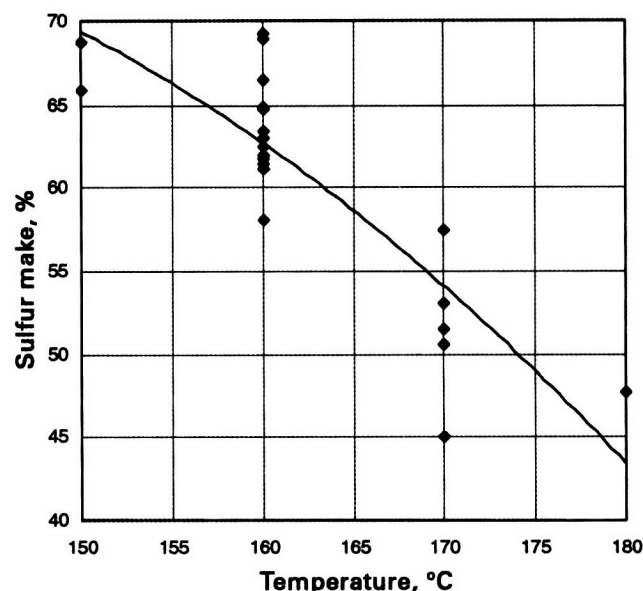
on 2001 economic conditions (which has subsequently been determined to be reasonably accurate). Economic evaluation of the value of incremental copper extraction and the cost of superfine grinding indicated an economic "optimum" grind at a  $P_{80}$  of 6 to 7  $\mu\text{m}$  and a  $P_{98}$  of 12 to 15  $\mu\text{m}$ , although the exact target size depends on metal price(s), unit power cost, concentrate hardness and grindability, grinding equipment and configuration employed, and other factors.

Mineralogical investigations of pilot plant samples from both the first compartment and the final residue material indicated that coarse chalcopyrite particles (i.e., >10  $\mu\text{m}$ ) had become encapsulated in elemental sulfur formed during leaching, and oxidation of this encapsulated material was greatly hindered. To produce a minimum amount of coarse particles, controlled superfine grinding was required. This could be achieved either by classifying the product during the grinding step (i.e., by cycloning) or by using specialized fine-grinding equipment, for example, horizontally or vertically stirred mills.

**Effect of temperature and acid addition:** The continuous pilot plant runs examined a range of temperatures from 150° to 180°C. The results are summarized in Figs. 10, 11 and 12, which show the effects of temperature and acid addition on copper extraction and elemental sulfur formation. Excellent copper extractions (i.e., >98%) were achieved at 160° to 170°C at the optimal superfine grind size.

Both the batch work and the continuous pilot plant operation demonstrated that the amount of acid added to the pressure leach vessel was important. The acid concentration in pressure leaching affects copper dissolution, sulfur morphology, the amount of elemental sulfur formed and the iron concentration in solution. If there is insufficient acid in the feed, the stoichiometric requirement for the reaction to proceed to completion is not met. Too much acid causes the elemental sulfur formed during the reaction to agglomerate and may encapsulate unreacted chalcopyrite, thereby hindering copper extraction. At temperatures between 160° and 170°C, an acid addition of 400 kg/t was found to be sufficient to achieve copper extractions of about 98% in 90 minutes.

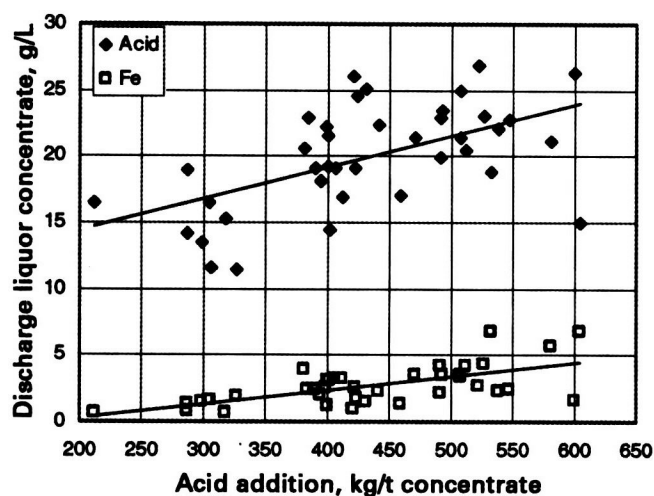
Operation at temperatures at the higher end of the range (i.e., 170°C and above) was initially considered to be desirable because more acid was generated under these conditions, at the expense of slightly higher oxygen usage, and less acid had to



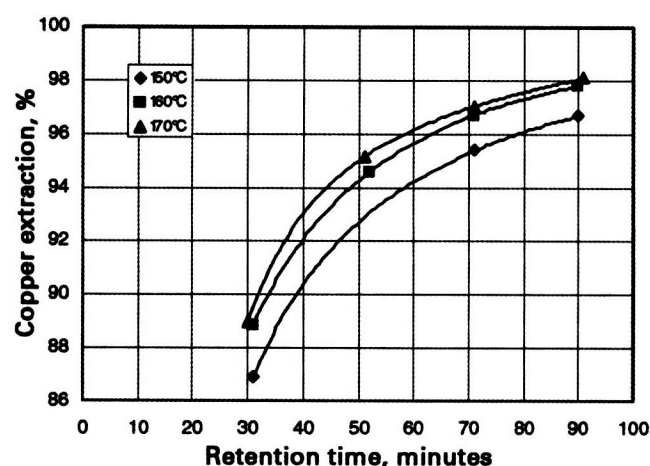
**Figure 12** — Effect of temperature on elemental sulfur formation (continuous pilot plant).

be added to achieve equivalent copper extraction. On the other hand, continuous operation above 170°C proved to be highly problematic due to difficulties in handling the sulfur-bearing product as a result of excessive prill and clinker formation. This problem could not be overcome by increasing the CLS dosage. A compromise in operating conditions would therefore be required to optimize the overall process.

Higher acid additions also solubilize more hematite, resulting in higher iron concentrations in the pressure leach discharge solution. This increased iron concentration may either be desirable or undesirable in the process flowsheet, depending on the exact configuration and need. The relationship between acid and iron concentration in the pressure-leach discharge solution is shown in Fig. 13. The continuous pilot plant runs demonstrated that iron concentrations of <1 g/L can be



**Figure 13** — Relationship between acid addition, acid concentration, and iron concentrations in the pressure leach vessel discharge (continuous pilot plant).

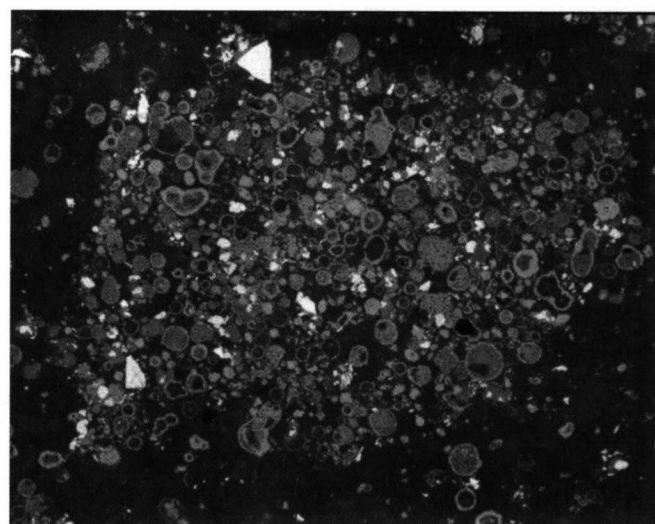


**Figure 14** — Copper extraction as a function of retention time for various temperatures using concentrate ground to 98% <6  $\mu\text{m}$  (continuous pilot plant).

achieved at acid concentrations <15 g/L in the pressure leach discharge, and that this could be accomplished with an acid addition of 400 kg/t at 160° to 170°C. However, the solution must be separated from the solid residue rapidly to prevent redissolution of iron (this is considered further in Parts II, III and IV in this paper series).

**Effect of retention time:** Compartment sampling conducted during the continuous pilot plant runs indicated that the majority of sulfide oxidation and copper dissolution occurred within the first two compartments, as shown in Fig. 14. For example, under the best operating conditions, 89% copper dissolution and 84% sulfide oxidation were achieved after 30 minutes; increasing to 96% and 92%, respectively, after 60 minutes; and finally to 98% and 93%, respectively after 90 minutes. An extended pilot plant run at the optimal conditions indicated that 90 minutes was adequate to achieve optimal copper extraction.

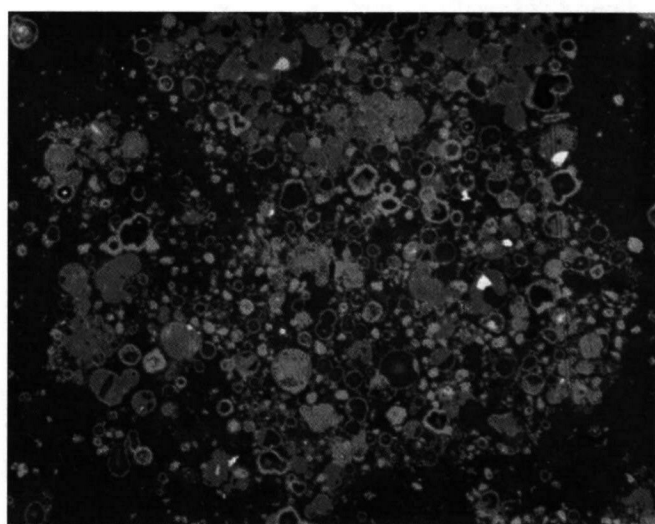
It should be noted that optimal copper extraction did not require that sulfide oxidation be maximized. Sulfide oxidation typically varied from 90% to 98%; however, optimal copper



— = 50  $\mu\text{m}$

500 x

**Figure 15** — Photomicrograph of first compartment discharge solids illustrating the agglomeration of micro-spheres of elemental sulfur (medium-gray color) frequently enveloped by hematite (rings on sulfur prills). Residual chalcopyrite (light-gray color) is abundant, occurring as liberated particles but also frequently enclosed by sulfur. Pyrite particles (white) are also shown.



— = 50  $\mu\text{m}$

500 x

**Figure 16** — Photomicrograph of pressure-leach discharge solids illustrating coalescence of sulfur spheres and the presence of a small amount of residual chalcopyrite (light-gray color).

extractions were often achieved with sulfide oxidations at the lower end of this range.

Figures 15 and 16 display photomicrographs showing the morphology and composition of material sampled from the first compartment and the last compartment discharge of the pressure leach vessel during a "typical" continuous pilot plant run.

**Effect of sulfur dispersants:** Based on the results of the batch tests, most of the continuous pilot plant runs were con-

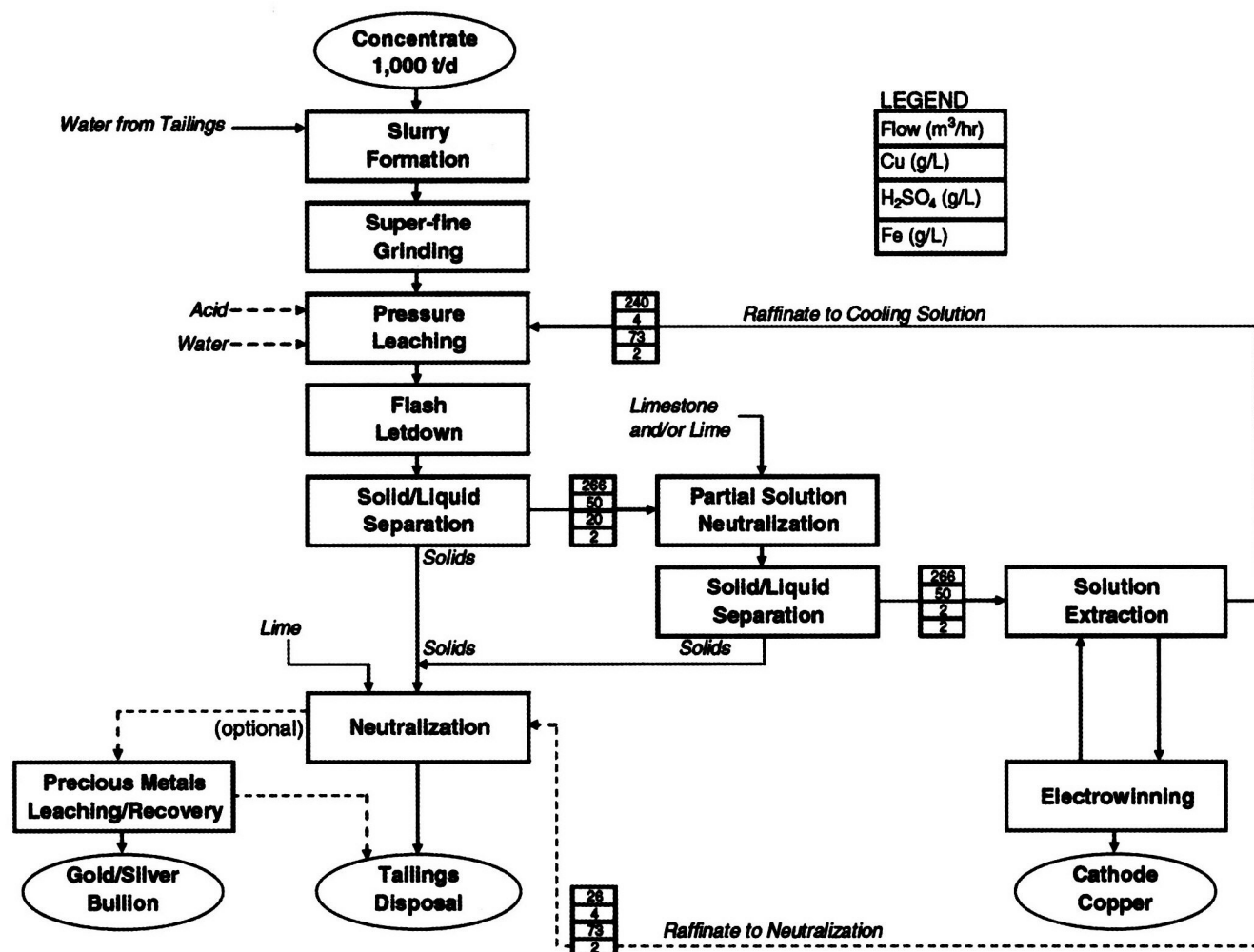


Figure 17 — Simplified medium-temperature pressure-leaching process flowsheet.

ducted using 10 kg/t CLS added with the feed into the first compartment of the pressure leach vessel. However, for two of the runs (one at a  $P_{98}$  feed size of 52  $\mu\text{m}$  and the other at  $P_{98}$  of 12  $\mu\text{m}$ ), CLS was added into all four compartments of the vessel to determine whether the reagent was degraded under pressure leaching conditions and to ensure that an adequate amount was available for effective sulfur dispersion. In the first of these runs, CLS additions of 10, 2, 2 and 2 kg/t were made into the four compartments, respectively. In the second run, CLS additions were 12, 3, 3 and 2 kg/t into the four compartments, respectively. For both of these runs, no significant improvement in extraction was observed compared to similar conditions without the staged addition of CLS.

One run was conducted at 160°C with a  $P_{98}$  of 12  $\mu\text{m}$ , 690-kPa (100-psi) oxygen over-pressure and 499-kg/t acid addition, but with no CLS added to the feed. This run was terminated prematurely, as expected, due to the build-up of large amounts of sulfur-bearing prills in all compartments of the pressure leach vessel.

Based on the results of the continuous pilot plant runs, it was concluded that 10 kg/t CLS was adequate for effective sulfur dispersion; however, the exact addition was not optimized, and there was potential to reduce the addition below this level.

### Initial process-development work

Based on the batch and continuous work reported above, a preliminary scoping-level assessment was prepared for the medium-temperature process. A conceptual flowsheet was developed that included superfine grinding of the concentrate (to approximately 80% passing 7  $\mu\text{m}$  and 98% passing 15  $\mu\text{m}$ ), pressure leaching under medium-temperature conditions, single-stage flash letdown, four-stage counter-current decantation for solid-liquid separation and washing of the solids, and SX/EW for recovery of copper from the solution phase (see Fig. 17). For this flowsheet, it was assumed that the pressure-leaching solution would be blended with a larger volume of low-grade stockpile and/or heap-leach solution prior to treatment for metal recovery.

The development of the medium-temperature process followed the development of the high-temperature process (Marsden et al, 2003; Marsden and Brewer, 2003). From an economic point of view, the process would consume significantly less oxygen than high-temperature pressure leaching (approximately 40% to 50% less, depending on the concentrate mineralogy and exact operating conditions, with estimated savings of \$0.03 to 0.04/lb). However, the process would require the addition of concentrated acid with the concentrate feed, which represented a direct cost (to purchase acid) and also an

additional cost for neutralization. The cost of the necessary acid addition varied from about \$0.03/lb copper at 400 kg/t to \$0.05/lb at 700 kg/t, assuming a \$50/t acid price (note that acid prices vary dramatically by location based on acid availability, transport, etc.). This meant that a 100 kg/t increase in acid addition would be valued at about \$0.008/lb and would need to provide approximately 1% additional copper extraction to offset the cost.

## Summary and conclusions

As this paper has outlined, between 1999 and 2001, Phelps Dodge completed the development of a preliminary flowsheet to treat chalcopyrite-dominant copper concentrates using medium-temperature pressure leaching. This process was developed specifically to provide a pressure-leaching approach for the treatment of copper concentrates at locations where the full amount of byproduct acid generated by high-temperature pressure leaching could not be used beneficially at the site for heap, stockpile and/or agitated leaching operations. The key design and operating parameters for the process were identified during extended continuous pilot plant work.

This process had several key advantages compared to high-temperature pressure leaching, including significantly lower oxygen consumption (40% to 50%) and lower temperature and pressure operation (i.e., capital cost benefits and materials of construction benefits). These were largely offset by the need for significant fresh acid addition to the pressure leach feed (\$0.03 to 0.05/lb copper), superfine grinding of the concentrate (<\$0.01/lb), the addition of CLS (<\$0.01/lb) and the need to neutralize any excess acid that could not be used beneficially at the site (\$0.02 to 0.04/lb). The acid requirements and the need to neutralize excess acid were found to be important cost drivers for the process, and attention was directed towards the development of a process that avoided or mitigated these costs. Was there a way to provide the acid necessary for the leaching reactions in the pressure leach vessel while avoiding the cost of purchasing acid and the cost to neutralize excess acid at the back end of the process?

The next paper in this series (Part II) addresses the development of direct EW in conjunction with medium-temperature pressure leaching, whereby lean electrolyte is recycled back to pressure leaching step to meet the acid addition requirements. This development provided an acid-autogenous medium-temperature flowsheet. Part III considers the large-scale demonstration of the MT-DEW-SX process at Bagdad, Arizona; and

Part IV addresses the development and design of a full-scale commercial application at Morenci, Arizona.

## Acknowledgments

The authors thank Freeport-McMoRan Copper & Gold Inc. for permission to publish this paper. Many Freeport-McMoRan and heritage Phelps Dodge staff members have contributed to the concentrate leaching developments described in this paper, and, in particular, the efforts of the late Bob Brewer and Jodi Robertson are recognized. The authors also thank David Baughman, Christel Bemelmans, Dennis Gertenbach, K.C. Oberg and Roland Schmidt of Hazen Research (Golden, Colorado) and Phil Thompson of Dawson Metallurgical Laboratories (Salt Lake City, Utah) for their assistance with metallurgical and process development work.

## References

- Bacon, R.F., and Fanelli, R., 1943, *Journal of the American Chemical Society*, Vol. 65, p. 539.
- Brewer, R.E., 2004, "Copper concentrate pressure leaching - Plant scale-up from continuous lab testing," *Minerals & Metallurgical Processing*, November, Vol. 21, No. 4, pp. 202-208, SME, Littleton, Colorado.
- Gillaspie, J.D., Wilmot, J.C., and Mathern, D.R., 2005, "Corrosion experience at Phelps Dodge's Concentrate Leaching Demonstration Plant in Bagdad, Arizona," *Proceedings of the 2005 Corrosion Solutions Conference*, ATI-Wah Chang Sponsored, September, 2005, Sun River, Oregon.
- Hackl, R.P., Dreisinger, D.E., and King, J.A., 1995, "Effect of sulfur-dispersing surfactants on the oxygen pressure leaching of chalcopyrite," *Proceedings Copper 95/Cobre 95 Int. Conf.*, Vol. 3, W.C. Cooper et al., eds., CIM.
- King, J.A., Dreisinger, D.B., and Knight, D.A., 1993, "The total pressure oxidation of copper concentrates," *The Paul E. Queneau Int. Symp.*, Vol. 1, R.G. Reddy et al., eds., SME.
- King, J.A., and Dreisinger, D.B., 1995, "Autoclaving of copper concentrates," *Proc. Copper 95/Cobre 95 Int. Conf.*, Vol. 3, W. C. Cooper et al., eds., CIM.
- Marsden, J.O., Brewer, R.E., and Hazen, N., 2003, "Copper concentrate leaching developments by Phelps Dodge Corporation," *Hydrometallurgy 2003: Proceedings of the 5th International Symposium in Honor of Professor Ian Ritchie*, Vol. 2: Electrometallurgy and Environmental Hydrometallurgy, C.A. Young, A.M. Alfantazi, C.G. Anderson, D.B. Dreisinger, B. Harris and A. James, eds., The Metallurgical Society of AIME, pp. 1429-1446.
- Marsden, J.O., and Brewer, R.E., 2003, "Hydrometallurgical processing of copper concentrates by Phelps Dodge at the Bagdad Mine in Arizona," *ALTA 2003 Copper-8 Technical Proceedings*, ALTA Metallurgical Services, Castlemaine, VIC, Australia.
- Wilmot, J.C., Smith, R.J., and Brewer, R.E., 2004, "Start up and operation of the Phelps Dodge concentrate leach facility at the Bagdad Mine in Arizona," *Hydro-Sulfides 2004 - International Colloquium on Hydrometallurgical Processing of Copper Concentrates*, April 16-19, 2004, Santiago, Chile.
- Wilmot, J.C., Smith, R.J., and Brewer, R.E., 2004, "Concentrate leach plant startup, operation and optimization at the Phelps Dodge Bagdad Mine in Arizona," *Pressure Hydrometallurgy 2004 - International Conference on the Use of Pressure Vessels for Metals Extraction and Recovery*, M.J. Collins and V.G. Papangelakis, eds., Banff, Alberta, Canada, October, 2004, Canadian Institute of Mining, Metallurgy and Petroleum.