Leaching helps to recover metals from complex ores

Hydrometallurgy is getting renewed attention as a means of processing complex mineral sulfides that are unfit for conventional pyrometallurgy. Indeed, a number of leach processes were touted at the International Symposium on Complex Sulfides, recently held (Nov. 10-13) in San Diego, Calif. Sponsored by The Metallurgical Soc. and the Canadian Institute for Mining and Metallurgy, the meeting attracted more than 200 attendees from about 20 countries.

The normal routine with compatible mixed-metal ores is to separate the metals by flotation and send them to separate smelters. Complex sulfides are a problem because the ore may be fine-grained, with intergrown minerals, or may contain toxic elements, such as arsenic, explained Donald Cranstone, a mineral economist with Canada’s Dept. of Energy, Mines and Resources (Ottawa), in his opening address. Nevertheless, the sulfides are attractive because the world has large deposits of high-grade, complex ores that could be profitable with the right process.

Improvements in smelting and flotation have resulted in better recoveries from difficult ores in recent years. (An example of this is an interesting new process, still in the development stage at England’s University of Birmingham [Chem. Eng., Dec. 9/23, 1985, p. 9]. It is a smelting technique that can recover various metals simultaneously from a single smelter.) However, current commercial flotation/smelting routes are not practical for complex sulfides because metal recoveries typically are only about 60-70% of the ore’s content, says Cranstone, compared with 80-95% for simple ores.

Hydrometallurgy, in contrast, offers recoveries that can top 90%, and produces an elemental sulfur byproduct that is easier to store than the sulfuric acid obtained from smelters. Of course, leaching is not generally competitive with pyrometallurgy for conventional ores because it uses too much energy (whereas most modern smelting processes are nearly autogenous). Hydrometallurgy, however, is appealing for complex sulfides that are typically rich in several metals. After all, soft prices for one metal may be offset by high prices for another.

CHLORIDE TECHNIQUES — A process that was judged too expensive for one metal (lead) but that might work for the right metals combination was described by Stephen James, a process engineer with St. Joe Resources Co. (Bartlesville, Okla.).

In St. Joe’s method, lead is selectively leached by a ferric-nickel-chloride solution at atmospheric pressure and 70-90°C. Lead chloride crystals of more than 99.99% purity are obtained by evaporative crystallization at 30°C; then lead metal may be produced by electrowinning. About 85-90% of the available lead can be recovered from complex ores, according to James.

St. Joe’s Missouri lead mines yield high-grade galena (lead ore), he notes, the company is interested in sharing its process with companies that have complex ore deposits.

In St. Joe’s extended flowsheet, copper could be recovered by Duval Corp.’s CLEAR process, which uses a leach solution of ferric and cupric chlorides. Duval’s route was employed commercially in a 100-metric-ton/d copper plant near Tucson, Ariz., for several years until the plant was closed three years ago because of a depressed market for the metal. Archibald Fletcher, acting director of research with Duval, told the complex-sulfides meeting that a modified clear process has been used successfully to produce electrolytic-grade zinc, and said that it has potential for treating more-complex ores.

St. Joe’s process is very similar to one developed some years ago by the U.S. Bureau of Mines’ Reno Research Center, in Nevada (Chem. Eng., Jan. 12, 1981, pp. 53-57). That work was supported by several lead producers, including St. Joe.

Meanwhile, the Canada Centre for Mineral and Energy Technology (CANC MET), of Ottawa, is doing an economic evaluation of its own ferric chloride leach process, and may decide to build a continuous pilot plant early in 1986. “Technically, we have proved it in an 8.4-kg batch leach,” says Bernard Lucas, head of CANMET’s leaching section.

In the process, all metals are dissolved (instead of selectively leached). In tests on a New Brunswick zinc/lead/copper/iron sulfide bulk concentrate, the metals were dissolved at 108°C and atmospheric pressure, then

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lead powder was added at about 90°C to precipitate copper and silver (along with bismuth, arsenic and antimony, if present). Lead chloride was crystallized at about 15°C, then zinc was removed from the solution by solvent extraction. Lucas says that more than 99% of the lead, 98% of the zinc, 97% of the copper and more than 95% of the silver are recoverable from the bulk concentrate.

zinc chloride solution (any existing silver is cemented with copper or other metals). The metals are obtained by electrowinning.

The firm's pilot operation was run at 20-30 L/h, and consumed 1-2 kg/h of complex ore. However, plans for further work have been put on hold because Imetal, Minemét's parent group, last year sold its interest in Portugal's excess of 99% for lead, 98% for zinc, 94-98% for copper, 95-98% for silver.

Other Leach Types — In Spain, Técnicas Reunidas S.A. (Madrid) is developing a pressure-leaching method called Comprex, with the purpose of using it on the rich complex sulfides of the Spanish pyrite region, in the southwest. So far, the company has piloted it for about 30 days at a multipurpose facility in its Madrid research center. After handling about 1 ton/d for the length of the run, the company processed 3 m.t. of residue in the lead/silver pilot plant.

Técnicas Reunidas first separates most of the zinc by flotation. An aqueous slurry of the bulk concentrate that contains the rest of the nonferrous met-
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als is then leached by subjecting it to temperatures of 200–240°C and 3,500 kPa, using oxygen as the oxidizing agent.

Sulfides are converted into sulfates, and ferrous sulfate is further oxidized to ferric sulfate, which is unstable in an aqueous medium above 180°C, and undergoes hydrolysis. This results in the production of excess sulfuric acid that dissolves copper and the remaining zinc. Lead and silver sulfates remain insoluble in the residue, along with ferric oxide from the hydrolysis reaction.

The liquid and solids are separated. Lead and silver are leached from the solids by a strong sodium chloride solution at 80–90°C. Then silver is precipitated by adding zinc dust; lead is obtained via the addition of scrap zinc. Both copper and zinc are recovered by solvent extraction and electrowinning.

Eduardo Nogueira, director of research, says that pilot-plant recoveries from concentrate are: 97% for copper, 99% for lead, 98% for silver and 94.5% for zinc.

AUSTRALIA AND U.S. — In Australia, MIM Holdings Ltd. (Brisbane) has been doing laboratory tests of a process for complex zinc/lead minerals. First, there are two flotation steps (for zinc, then lead), followed by selective chloride leaching at 90–100°C and 1 pH to extract lead, leaving a zinc-rich residue (of 50% zinc grade), suitable for conventional processing. About 70% of the available lead has been recovered in laboratory work, and the goal is 80%, says David Royston, formerly manager of research with MIM's hydrometallurgical research laboratory, and now manager of R&D with Coal Corp. of Victoria. Flotation alone, he notes, has produced combined lead/zinc grades of more than 40% “only with serious sacrifices in metal recovery.”

The U.S.'s BuMines Reno Research Center recently completed laboratory-scale tests of a calcium-chloride/oxygen leach process to obtain cobalt and copper from a sulfide ore from the Blackbird Mine, near Cobalt, Idaho. Noranda Inc. (Toronto) has owned the mine since 1977, but has not operated it because the high cost of mining and processing makes it uneconomical at current cobalt prices. Noranda has been seeking an economical hydrometallurgical route because the ore has a high arsenic content, so smelting is out.

BuMines has processed bulk concentrate containing 4% cobalt, 10% copper, 6% arsenic and 15–20% iron, plus a little gold and silver. Concentrate is leached in a calcium chloride solution at about 50 psi and 110°C in an oxygen environment (oxygen is bubbled into the solution). “Everything is dissolved, then we add some calcium carbonate so that there is virtually no free acid,” says Thomas Carnahan, a research supervisor.

Arsenic and iron precipitate as iron arsenate and other compounds; copper that further investigation is needed.

CSS Management Corp. (Baring, Wash.) is using a variation of the BuMines process on arsenopyrite sulfide ore from its gold mine. The plant handles 1 ton/h of concentrate (the mine is small), and has operated successfully since September, says Joseph Cashman, general manager.

Arsenic control is the main objective. CSS used to send its concentrate to Asarco's Tacoma, Wash., smelter until that plant was closed last June because of emissions problems.

“We use a plain calcium carbonate or calcium oxide solution,” says Cashman. Calcium reacts with the arsenic and iron to form an insoluble compound, he explains, while the gold is freed so that it may be leached by thiourea. Elemental sulfur is recovered from the tailings (for more information on gold processing, see Chem. Eng., June 10, 1985, pp. 19-25).

Calcium chloride is blended in for the pressure leach when necessary to extract copper, lead and zinc, which occur intermittently in the ore. In this case, says Cashman, all the minerals are dissolved (except the arsenic and pyrite, which stay with the solids). After gold and silver are recovered, copper oxide chloride is precipitated at 4.5 pH. (Copper oxide chloride is used in the manufacture of insecticides and fungicides.)
Lead and zinc are precipitated at 7.5 pH, leaving a calcium chloride solution for recycle.

**ZINC IN CANADA** — Zinc roasting plants normally require a zinc concentrate of at least 50% zinc, but a 10-ton/d pilot plant that can accept complex sulfide ores containing as little as 6% zinc is being operated by The Research and Productivity Council (Fredericton, Canada) — an agency of the province of New Brunswick. Roy Boorman, executive director, says the plant had some mechanical problems following startup last August, but these have been solved. The plant will operate 24 hours a day for 3-to-8-week runs up to next May. Previously, the process was tested in a 1-m.t./d plant.

The RPC process, as it is called, uses a modified zinc roast, followed by a two-stage leach. The roast is done at 685°C to produce zinc sulfate, most of which is then dissolved in dilute sulfuric acid at room temperature. The solution is purified by the standard procedure of adding zinc dust to precipitate cobalt, nickel and copper (if present), then zinc is electrowon from the solution.

New Brunswick has complex sulfides whose principal metals are zinc and lead, with some copper and silver. Solids from the first leach, containing more inert zinc ferrite, plus other minerals and impurities, are further leached by a strong sulfuric acid solution at 95°C (most complex ores are pyritic). This solution is mixed with the feed to the roaster, where zinc is converted to the appropriate sulfate form for the first, dilute leach.

Lead and silver, which are insoluble, stay with the solids (a lead/silver/hematite residue), which are processed by RPC's patented plumbate process (plumbate is a calcium/lead oxide). Lead and silver are dissolved in a sodium chloride solution, then lead plumbate and silver are precipitated by adding lime. Boorman notes that the production of lead oxide (other processes produce lead chloride) is a key feature, as chloride tends to react with refractories in blast furnaces.

In conventional zinc processing, concentrate is "dead roasted" at about 930°C to drive off sulfur and produce zinc oxide, which is then leached to dissolve zinc for electrowinning. Boorman points out that the feed must be concentrated to at least 50% zinc to provide a high zinc/iron ratio, because a relatively high iron content raises the cost of the entire process.

Essentially all the iron goes into solution in the hot acid leach of the conventional process, and is then precipitated as jarosite by adding an ammonia or sodium compound (jarosite is a very fine sulfate of iron with ammonia or sodium). Boorman notes that jarosite is an environmental hazard because it is very fine and is easily blown around, whereas the hematite waste from the RPC process is coarser and heavier and can be stockpiled.

*Gerald Parkinson*

**China trade talk is heard in Midwest**

At times, trade between the U.S. and China has been marked by tension and uncertainty. But a recent trade-promotion conference in the Midwest indicates that the Chinese are now more disposed to improve economic relations with the U.S. Invitations to do more business with China were extended to about 500 corporate representatives at the meeting, which was held in Chicago in late November.

Cosponsored by the U.S. Deps. of State and Commerce, and by the new Chinese consulate in Chicago, the session attracted corporate managers from several industries with plants in Illinois, Wisconsin, Minnesota, Indiana and other Midwestern states. A key attraction was a speech by Guo Shangqiang, China's deputy consul-general in the Midwest.

**NEW LAWS** — Guo summarized what he says are China's ongoing efforts to make it easier for U.S. corporations to develop joint ventures and sell products. "Great attention has been paid to improving our economic legal system," he said. "We have enacted more than 40 laws and regulations concerning our economic ties with foreign countries, and a few others are still in the making. You'll be pretty secure in China."

Recent provisions approved by the Chinese government include a law on trademarks, regulations on compensation for technology transfers, a patent law, and a statute regulating foreign sales contracts. Guo insisted that U.S. executives should not worry about the future political stability of China. "You must have read that we have just convened a national [Communist] Party congress at which a large number of the 'Old Guards' stepped down," he said. "Many new reform-minded younger leaders [have entered] the central political scene. Isn't that enough of a guarantee for the continuity of our present policy?"

U.S. and Illinois representatives at the conference lobbied for greater interest in China trade by explaining the assistance programs they sponsor. Each spokesman said China-trade experts in government work closely with interested companies, and continue to provide guidance even after the initial contacts between two companies have been arranged.

Illinois has had extensive dealings with the Chinese through its Dept. of Commerce and Community Affairs, which maintains a "China list" of firms interested in market opportunities in the Asian nation.

Conference speakers were unable to estimate the value of chemical-industry business in China, but they emphasized that total U.S.-China trade increased from less than $1 billion in 1978 to more than $6 billion in 1984. They calculate that this will go up to $7 billion in 1985 even though economic relations are not as strong as they could be. Firms trying to sell to China, they said, can still be affected by problems that plague their particular industries, and by broader economic and political policy disputes.

Chemical companies must accept that the Chinese are still learning how to buy supplies based on actual market need. "Their purchasing is not always predictable," said Michael O'Laughlin, the Beijing representative of McDer- mott, Will & Emery, a Chicago law firm. "Sometimes, even though they don't need chemical supplies, they keep buying." That can lead to government directives to suddenly discontinue purchases in order to compensate for the surplus. O'Laughlin noted that the Chinese are now making a valiant effort to normalize their chemical acquisition procedures.