Minerals Extraction and Processing: New Developments

Examples of new industrial practice illustrate advances in minerals technology.

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Supplies of raw materials can often be extended by improving the ways of extracting and processing ores. Thus, ores once considered uneconomical may become accessible. Changing economic and legal conditions may require extensions of existing technology or altogether new techniques. Innovation in industrial extraction and processing of metals has in fact been accelerated in the last few years by new environmental constraints and by disruptions in energy supply and costs.

Interest in continuous copper smelting has been largely motivated by the need to reduce sulfur dioxide emissions without incurring excessive costs or facing the closing of plants. The replacement of mercury in gold recovery by a recently improved activated carbon process was similarly motivated by the necessity for pollution control. New recovery processes for nonmagnetic iron ore (of which the United States has huge resources) and for uranium, on the other hand, have opened up hitherto uneconomic deposits and thus extended the resource base. These four examples of newly adopted processes indicate how the technology base is being broadened, although they do not necessarily reflect industry trends.

Continuous Copper Smelting

The control of pollutants in gaseous emission from reverberatory furnaces that smelt copper concentrate to matte (*1*) has long been a troublesome area in smelter operations. This is because the burning of a large amount of fuel with air inside the furnace yields a vast volume of combustion gas lightly flavored with SO_2, from a few tenths to 1 percent. Because costs of cleaning up the gas are generally proportional to the gas volume treated, reverberatory gas-cleanup costs are disproportionately high relative to its SO_2 burden. Combustion with oxygen or air-oxygen mixtures, and prior heating of the combustion air with or without oxygen enrichment, are ways in which the gas volume can be sharply reduced.

A reduction of tenfold or more in the offgas volume is offered by the flash smelting processes introduced about 25 years ago. The International Nickel Co. (INCO), at Sudbury, Canada, injects dried copper concentrate entrained in oxygen (95 percent grade) through lances into opposite ends of a rectangular furnace (*2*). Reaction heat from partial oxidation of sulfides is sufficient to sustain the smelting operation. Gas at a temperature of 1260°C (2300°F) containing 70 to 80 percent SO_2 leaves the furnace through a center uptake. The gas is cooled, cleaned, and processed for daily recovery of 300 tons (1 short ton = 0.9 metric ton) of liquid SO_2, which is marketed. Slag containing 0.6 percent copper is discarded, and matte containing 45 percent copper is blown to blister copper (*3*) in conventional converters.

Outokumpu at Harjavalta, Finland, initially used air heated to 500°C (930°F) for injecting dried concentrate and fuel oil into a vertical cylindrical chamber at one end of a rectangular furnace with the gas uptake at the other end (*4*). The offgas contained 12 percent SO_2. Subsequently, the air was enriched to contain 35 percent O_2 and the preliminary heating was reduced to 200°C (390°F). This permitted substantially autogenous smelting. The capacity was increased about 60 percent, and the offgas grade was increased to 18 percent SO_2. Slag from the furnace contains too much copper to be discarded and must be treated again. Matte contains 40 to 50 percent copper, depending on concentrate analysis and degree of oxygen enrichment. Some 18 Outokumpu-engineered flash furnaces are now operating or are under construction in ten countries. An Outokumpu-type flash furnace built by Phelps Dodge at Hidalgo, New Mexico, started operation at the end of 1975. The SO_2 in the flash-furnace offgas is to be reduced with a hydrocarbon in a high-temperature catalytic system to make 400 tons of elemental sulfur per day (*5*).

Electric resistance heating in lieu of burning fossil fuels is another way in which the gas volume in matte smelting can be drastically decreased. Elkem Spigerverket of Norway pioneered the technology, which uses three, four, or six self-baking carbon electrodes for heating the slag (*6*). Offgas temperature is only 700°C (1300°F), and the SO_2 concentration is about 5 percent. The slag contains about 0.5 percent copper and is discarded. Matte grades range from 40 to 50 percent copper. About six matte-smelting electric furnaces are in operation or are being built. The Tennessee Copper Co. at Ducktown, Tennessee, and the Inspiration Copper Co. at Inspiration, Arizona (*7*), have electric furnaces in operation, with respective capacities of 20,000 and 150,000 tons of copper per year. An electric furnace designed to smelt 120,000 to 150,000 tons of copper per year was started up in December 1975 by Anaconda at Anaconda, Montana.

Copper matte, whether made in reverberatory, flash, or electric furnaces, is blown with air, or sometimes with oxygen-enriched air, to slag off iron and eliminate sulfur as SO_2 (*8*). Converter slags are high in copper and are re-treated by recycling to the matte-smelting furnace or by slow cooling and flotation to make a copper concentrate for recycling to the matte-smelting furnace. Blister copper from the converter is further fire-refined to make a marketable product or is cast into anodes for electrorefining. The converter offgas is another potential source of significant air pollution. Converting is a batch, stagewise process, with wide variations in the SO_2 grade of the offgas. A large smelter in which several converters are used can schedule operations to obtain converter gas containing at least 4 percent SO_2, which is suitable for conversion to sulfuric acid.

Converting matte to blister is an exothermic operation. Smelting concentrate to matte, unless combined with partial converting, is an endothermic operation. To improve fuel efficiency, eliminate or minimize slag recycling, and obtain a uniform flow of rich SO_2 gas, much attention has been given to developing processes for continuous smelting and converting in a single furnace or in contiguous furnaces.

One of the early proponents of continuous smelting was Howard Worner of

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Conzinc Rio Tinto in Australia, the developer of the Worcra process (*9*). Copper concentrate and flux are injected with air through lances into the end of a U-shaped furnace or into the center of a rectangular furnace. Slag flows to one end of the furnace where entrained matte drops out and returns to the melting zone. Slag containing about 0.5 percent copper is discarded. Matte flows to the other end of the furnace where it is continuously converted to blister by top-blowing with air and flux through lances. Slag formed in the converting zone returns to the melting zone. Blister copper containing up to 1 percent sulfur collects in a well for continuous discharge. Furnace offgas contains about 10 percent SO_2. A semicommercial Worcra furnace at Port Kembla, Australia, smelted a nominal 70 tons of concentrate per day—6000 tons of copper per year—in operating campaigns of up to 9-month duration from 1968 to 1970.

Noranda Mines, Ltd., Noranda, Canada, began experimenting with continuous copper smelting in 1964 (*10*). In Noranda's commercial process, operated since 1973, concentrate and flux are formed into pellets and thrown by a slinger belt into one end of a horizontal, cylindrical furnace. A fuel-fired burner extending through the same end melts the feed. Matte that forms is continuously blown to a crude blister, consisting of about 98 percent copper, by air injected through submerged tuyeres. Slag flows the length of the furnace (67 feet) (1 foot = 0.3 meter) before discharging over a weir. A burner firing through the end wall keeps the slag fluid for discharge. The slag, containing about 12 percent copper, is cooled slowly in pits for several days, then crushed, ground, and floated to recover a concentrate—which contains, by analysis, 50 percent copper—for recycling to the Noranda furnace. The flotation tail contains 0.5 percent copper and is discarded. Furnace offgas at a temperature of 1315°C (2400°F) contains about 4 percent SO_2. The furnace at Noranda is rated at 800 tons of concentrate per day—equivalent to 200 tons of copper per day. Because periodic shutdowns are necessary for repairs to the furnace lining, the capacity is about 50,000 tons of copper per year. The remainder of the Noranda smelter capacity of about 200,000 tons of copper per year is provided by conventional reverberatory furnaces and converters.

Owing partly to the interest of Kennecott Copper Co. in using Noranda-type furnaces in its Garfield, Utah, smelter, tests were made at Noranda with oxygen-enriched air. When the burner air was enriched to contain 50 percent O_2 and the tuyere air to contain 35 percent O_2, the furnace capacity doubled and the SO_2 content of the offgas increased to 13 percent. The amount of liquid oxygen used was 422 tons per day. Kennecott has ordered three Noranda-type furnaces. The first is scheduled for operation in 1977. The furnaces in Utah will be operated to produce a matte having 75 to 80 percent copper which will be blown to blister in converters. This is necessary because certain impurities in the Kennecott concentrate, such as bismuth, are best removed by fuming or slagging in a converter.

The second continuous copper smelting system to attain commercial scale is Mitsubishi's, installed at its Naoshima, Japan, smelter in 1974 to produce 50,000 tons of copper per year. A description of the semicommercial operation with a capacity of 18,000 tons of copper per year, which came on-stream in 1971, has been published (*11*). Concentrate and flux were injected through lances with air enriched to 25 percent O_2 into the first of three contiguous stationary hearth furnaces. Both matte and slag flowed from the smelting furnace into an electric furnace settler where pyrite and coke were added to facilitate sedimentation of matte droplets from the slag. From the settler, slag containing 0.5 percent copper was discarded, and matte containing about 50 percent copper flowed to the converting furnace. By top-blowing air and flux through lances, the matte was converted to blister of 98 to 99 percent copper grade, and a slag containing 7 to 15 percent copper was made for recycling to the smelting furnace. Combined offgas from the three furnaces contained 10 percent SO_2. Mitsubishi has a copper-smelting capacity of 150,000 tons per year in conventional reverberatory furnaces and converters in addition to the 50,000-ton annual capacity of the three-furnace system. In April 1975, Texasgulf, Inc., announced it would build a Mitsubishi three-furnace smelter at Timmins, Ontario, Canada, to make 130,000 tons of copper per year (*12*). The Timmins smelter is scheduled to start operation in 1978.

Why has there been commercial adoption of Noranda and Mitsubishi processes and not Worcra, which appears to do the whole smelting job in one furnace and does not require handling slag for recycling outside the furnace? The answer may be that Conzinc Rio Tinto does not operate a copper smelter, whereas both Noranda and Mitsubishi operated large copper smelters and were able to experiment with a part of the capacity.

The demonstration of hydrometallurgical alternatives to smelting of copper concentrate (*13*) was aborted when the Anaconda "Arbiter" process plant at Anaconda, Montana, which is rated at 36,000 tons of copper per year, was placed on standby in June 1975. Both the "Arbiter" plant at Anaconda and the Cyprus Mines "Cymet" demonstration plant at Green Valley, Arizona, started up in the fall of 1974. In announcing the closing of the Arbiter plant, Anaconda said that the plant performed satisfactorily, but that the capacity was in excess of its needs. The Arbiter process leaches copper concentrate in ammoniacal solution at 70°C under about one-third of an atmosphere (several pounds per square inch) of oxygen pressure. Copper is recovered from solution by solvent extraction and electrolysis (*14*). The Cymet plant, designed to produce 1500 to 3000 tons of copper per year, is believed to be in pilot-plant status to work out process modifications because of operating problems in the demonstration unit. Duval's "Clear" process plant at Esperanza, Arizona, slated to produce 32,500 tons of copper per year, is still under construction. Both Cymet and Clear use chloride-leach systems and recover copper powder by reduction of cuprous chloride with a reducing gas or by electrolysis of cuprous chloride solution.

The Hecla–El Paso combination hydromet-pyromet plant at Lakeshore, Arizona, started up in October 1975, and is expected to produce 65,000 tons of copper per year by interlocked flowsheets that separately process oxide and sulfide ores (*15*). About 30,000 tons of copper per year are to be made by electrowinning after the sulfide concentrate has been roasted and leached, and 35,000 tons of copper are to be precipitated from the oxide circuit leach liquor by cementation on iron. The iron for cementation, plus accessory precious metals, is to be recovered by reduction of the silicious iron residue that remains after the sulfide concentrate is roasted and leached. Cement copper containing about 64 percent copper is to be further treated by smelting, or by leaching and electrowinning.

Improved Activated Carbon Systems for Gold

Many of the troublesome and expensive liquid-solid separations in processing minerals have been greatly ameliorated by the development of polymeric flocculants (*16*). Such effective aids for thickening and filtration were unknown in the 1930's when T. G. Chapman at the University of Arizona developed his carbon-in-pulp system for gold cyanidation (*17*). In Chapman's original system, the dissolved gold was adsorbed by finely ground activated charcoal; the charcoal subsequently was separated from the pulp by flotation. Gold was recovered from the carbon concentrate by burning or smelting. In an alternative system, Chapman and his co-workers used particles of activated carbon coarser than the ground ore as the gold adsorbent. The carbon was enclosed in a cylindrical screen that rotated in the leach pulp. A concentrated gold solution was obtained by stripping the gold-loaded carbon with hot cyanide solution (*18*). John Zadra and coworkers of the U.S. Bureau of Mines further modified the system by adding an electrolytic cell for continuous removal of gold from the hot strip liquor (*19*). A commercial carbon-in-pulp plant was operated by the Golden Cycle Corp. at Cripple Creek, Colorado, from 1954 to 1960. Coarse carbon was loaded with gold by mixing and screening in a countercurrent system, and the carbon, loaded to about 40 ounces (1 troy ounce = 31.1 grams) of gold per ton, was stripped and recycled by the Zadra method (*20*).

In December 1970, the Homestake Mining Co. was enjoined by federal decree from using mercury in its milling plant at Lead, South Dakota, because of downstream pollution. When mercury was used to collect gold in the grinding circuit, about 60 percent of the gold was recovered by amalgamation, and an additional 35 percent was recovered by separately leaching the sand and slime fractions in cyanide solution. The slimes-treatment plant contained 30 huge filter presses in which the slimes were sequentially leached and washed. Upon removing mercury from the plant circuit, gold recovery, especially from the slime circuit, dropped precipitously. Homestake's difficulties provided an opportunity for the Bureau of Mines to test its own new concepts for improved gold extraction, gold loading, and carbon handling in a cyanide carbon-in-pulp system (*21*). The new system optimized the separate leaching, loading, stripping, and carbon regeneration operations. Its performance was demonstrated at Homestake in a miniplant that handled 2 tons of slimes per day. By extrapolation of the design from the miniplant, Homestake was able to start up its commercial carbon-in-pulp plant, treating 2000 tons of slimes per day in April 1973 (*22*). Full-scale operation with predicted gold recovery and operating costs was attained in August 1973. The carbon leaving the Homestake four-stage countercurrent mix-and-screen circuit contains between 300 and 400 ounces of gold per ton. Stripped and regenerated carbon for recycling contains 5 ounces of gold per ton.

In another application of Bureau of Mines technology for gold recovery, Cortez Gold Mines at Cortez, Nevada, is heap-leaching low-grade ore with cyanide solution, then loading the gold on activated carbon in a countercurrent expanded-bed system (*23*). The loaded carbon is rapidly stripped with a dilute solution of sodium hydroxide at 3 atmospheres (75 pounds per square inch) and 121°C (250°F), and the strip liquor is electrolyzed for gold recovery. Procedures generally analogous to those used at Cortez are planned for the Smokey Valley Mining Co. operation now being built near Tonopah, Nevada, for heap-leaching about 8000 tons of low-grade gold ore per day.

Flocculation-Flotation of Iron Ore

The Lake Superior iron ore district contains 20 billion long tons or more (1 long ton = 1.016 metric tons) of nonmagnetic iron ore that requires beneficiation to make a marketable concentrate. Only a trickle of concentrate has been made from the nonmagnetic ores compared with production from magnetic ores that now yield about 40 million long tons of iron oxide pellets per year (*24*). The nonmagnetic ores contain hematite and goethite as the main iron minerals and, like the magnetite-bearing taconites, require extremely fine grinding for liberation of iron minerals from the associated gangue. Problems inherent in beneficiating the nonmagnetic ores owing to the intimate and complex association of various and varying iron and gangue minerals were identified by the Bureau of Mines (*25*). Potentially feasible beneficiation methods appeared limited to reductive roasting-magnetic separation and flotation (*26*). The magnetic-roasting route appeared to be more capital- and energy-intensive and more expensive than flotation.

Among the iron ore flotation methods described by Clemmer in the 1940's were anionic (fatty acid) flotation of iron oxide, depression of iron oxides and anionic flotation of activated silicious gangue, and depression of iron oxides and cationic (amine) flotation of silicious gangue (*27*). All three methods usually required thorough desliming of the ground ore at about 20 micrometers to assure subsequent selectivity in flotation and to avoid excessive reagent consumption. The slime fraction was discarded. For ores containing iron oxides of earthy texture, desliming often resulted in excessive loss of iron oxides. Commercial flotation of nonmagnetic ores was initiated at the Humbolt mill of the Cleveland Cliffs Iron Co. on the Marquette Range in Michigan in 1955. This was followed by a second Cleveland Cliffs operation, the Republic Mill, in 1956, and by Hanna Mining Co.'s mill at Groveland, Michigan, in 1959. The last two mills are still operating. All three mills floated hematite with a fatty acid reagent from a deslimed pulp (*24, 28*). Other Lake Superior iron ores responded less favorably to the hematite flotation procedure.

In searching for a flotation technique that would be widely applicable to diverse iron ore types, Frommer and co-workers of the U.S. Bureau of Mines observed and capitalized on the selective flocculation of iron oxides that occurred when starch was added to a dispersed ore pulp (*29*). When the iron minerals were properly flocculated, silicious fines could be discarded by desliming with minimum loss of iron oxides. Nonslime silicious particles then could be selectively floated with either anionic or cationic reagents and discarded. The product of the flotation operation was high-grade iron oxide concentrate. The technique was refined in cooperative studies by the Bureau of Mines and the Cleveland Cliffs Iron Co. starting in 1961, and then developed for commercial production from Cleveland Cliffs' Tilden, Michigan, ore body (*24, 30*).

The Tilden plant began operation in October 1974 and attained its design production rate of 4 million long tons of pellets annually from 10.5 million long tons of 36 percent iron ore at the end of 1975. Cost of mine development and mill construction exceeded $200 million. As an aid to blending the ore for uniform mill feed, relatively small (75-ton capacity) trucks are used for hauling the ore from the open-pit mine. A gyratory crusher breaks the ore to 10-inch (1 inch = 2.54 centimeters) size.

Primary grinding is done in six autogenous mills, 27 feet in diameter by 14.5 feet long, each driven by two motors capable of a combined output of 5720 horsepower. Caustic soda and sodium silicate are fed to the primary mills for thorough dispersion of the ore slurry. Secondary grinding is done in 12 pebble mills, 15.5 feet in diameter by 30 feet long, in closed circuit with cyclone sizers. Pebbles for fine grinding are minus 3-inch, plus 5/8-inch ore that are screened from the primary mill circulating load. Solids in the cyclone overflow are 75 to 80 percent minus 500 mesh (33 micrometers). The ground ore slurry has a *p*H of about 11 and a density of about 11 percent solids.

To flocculate the iron oxides, a 2.5 percent solution of corn starch is added to the slurry of finely ground ore, which then flows to 12 thickeners 55 feet in diameter for desliming. Slimes in the thickener overflow (at about 2 percent solids) contain 10 to 13 percent iron and are discarded; water is reclaimed for further use. Thickener underflow (50 percent solids) is conditioned with more starch to ensure iron flocculation and depression, and then floated in six banks of cells. Each bank contains 25 cells; individual cells have a capacity of 500 cubic feet. Silica is floated by the addition of an amine reagent to the flotation cells and discarded. Cationic flotation was selected over the anionic method because of better stability as the hardness of the process water changed. The amine used is a primary amine containing 16 to 18 carbon atoms and is prepared from tallow fatty acids. It is 30 percent neutralized with acetic acid, and fed as a 5 percent dispersion in water. The concentrate, containing about 65 percent iron, is thickened and then filtered while hot to obtain a filter cake containing 10.5 percent moisture for balling; bentonite is added as binder. The green balls are first heated on a grate, then indurated in a rotary kiln 25 feet in diameter by 160 feet long. About 11,000 tons of finished pellets containing 66 percent iron are produced daily by milling 30,000 tons of 36 percent ore per day. Distribution of iron in the feed is 7 percent in the slime thickener overflow, 23 percent in the floated silica, and 70 percent in the pellets. Two expansion stages of the Tilden operation are contemplated, with timing dependent on economic conditions. Each expansion would add 4 million tons of pellet capacity annually.

In situ Leaching of Uranium

Uranium deposits too deep and too low in grade for economical uranium recovery by surface or underground mining and conventional milling are known in southern Texas. These loosely consolidated, uranium-bearing sandstones, occurring at depths of about 300 to 700 feet, have long been an attractive target for in-place leaching proposals and experiments. The development of a successful technique promised low capital and operating costs, minimum land-surface disruption, and avoidance of disposal or storage of mill tailings.

Among the established alternatives to surface or underground workings for extracting minerals are the solution mining of salt (*31*) and potash (*32*), the mining of sulfur by the Frasch process (*33*), and underground leaching of copper (*34*) and uranium (*35*) from caved ore and wall rock. The underground leaching usually has been performed in conjunction with, or as the terminal phase of, underground mining. There was little in any of these techniques directly transferrable to the in-place leaching of the Texas uranium ores. However, uranium-recovery practice from mine water in the Grants, New Mexico, district does suggest a clue. In the Grants district about 5000 gallons (1 gallon = 3.8 liters) per minute of barely alkaline mine water containing 10 parts per million (ppm) of U_3O_8 is treated by resin ion exchange for recovery of 100 tons per year of U_3O_8. Part of the depleted solution from ion exchange is recycled to worked-out areas of the mines. The clue to in-place leaching of the Texas uranium deposits without excessive reagent use and without plugging the ore formation appears in the use of extremely dilute alkaline leach solution with a low uranium-loading and a high circulation rate.

In April 1975, a commercial in-place leaching operation was started by Atlantic Richfield Co. (Arco) and partners near George West, Texas, for the planned production of 125 tons per year of U_3O_8 (*36*). The leach solution for this project is believed to be a dilute solution of sodium or ammonium carbonate and bicarbonate. It is circulated through the ore strata at a rate of 2000 gallons per minute through an initial pattern of 66 injection wells and 46 extraction wells over an area of 3 acres (1 acre = 0.4 hectare). Maximum distance between an injection and extraction well is about 35 feet. Oxidation is necessary for satisfactory dissolution of the uraninite ore mineral. This probably is effected by sparging oxygen into the strata or by adding hydrogen peroxide to the leach solution. Leach liquor from the extraction wells is clarified by passage through a column of activated carbon. Uranium is recovered from the clarified solution by conventional anion resin exchange in columns, and the depleted solution is recycled to the injection wells. Groundwaters in the leach area were characterized before leaching started, and a ring of monitor wells was established to warn of escaping leach solution. To assure a hydraulic gradient toward the extraction wells, more solution must be pumped than is injected.

Wyoming Minerals Co., a subsidiary of Westinghouse, plans to have its in-place leaching operation in production near Bruni, Texas, early in 1976. The Wyoming Minerals operation, also rated at 125 tons of U_3O_8 annually, is believed to be generally similar to Arco's. Also Union Carbide Corp. has scheduled uranium production by in-place leaching at its Palangana Dome property in Duval County, Texas, starting in 1976. The Mobil Oil Corp. has a uranium in-place leaching test program under way in Webb County, Texas.

To yield the planned production of 125 tons of U_3O_8 per year, Arco's 2000 gallons per minute of leach solution would have to contain about 30 ppm of U_3O_8. This is only 1/20 or less of the uranium content in leach solution processed by conventional mine-mill operations. However, dilute alkaline solutions are notably amenable to ion-exchange processing, compared with highly contaminated acid leach solutions. Compared with the production of 125 tons of U_3O_8 annually by the in-place leaching operations, the 19 U.S. uranium mills in operation, on standby, or under construction have capacities of 200 to 4000 tons of U_3O_8 per year. For meeting the uranium requirements of nuclear power generation, 125 tons of U_3O_8 is roughly equivalent to the annual requirement of a 500-megawatt reactor.

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