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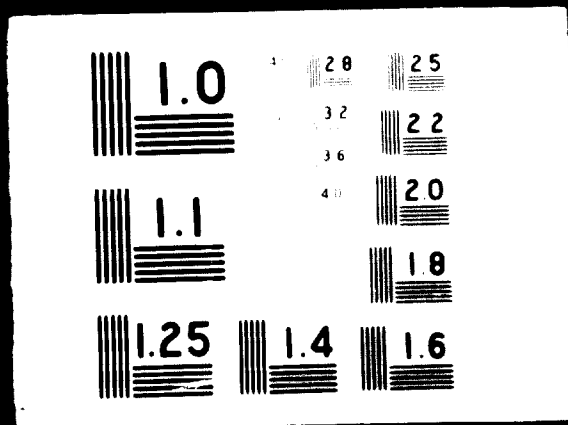
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Seminar on Copper Production and
Group Study Tour of Copper Plants
in the USSR

Tashkent, USSR, 1 - 15 October 1970

SOME HYDROMETALLURGICAL TECHNIQUES FOR PROCESSING COPPER ORE AND CONCENTRATE [1]/
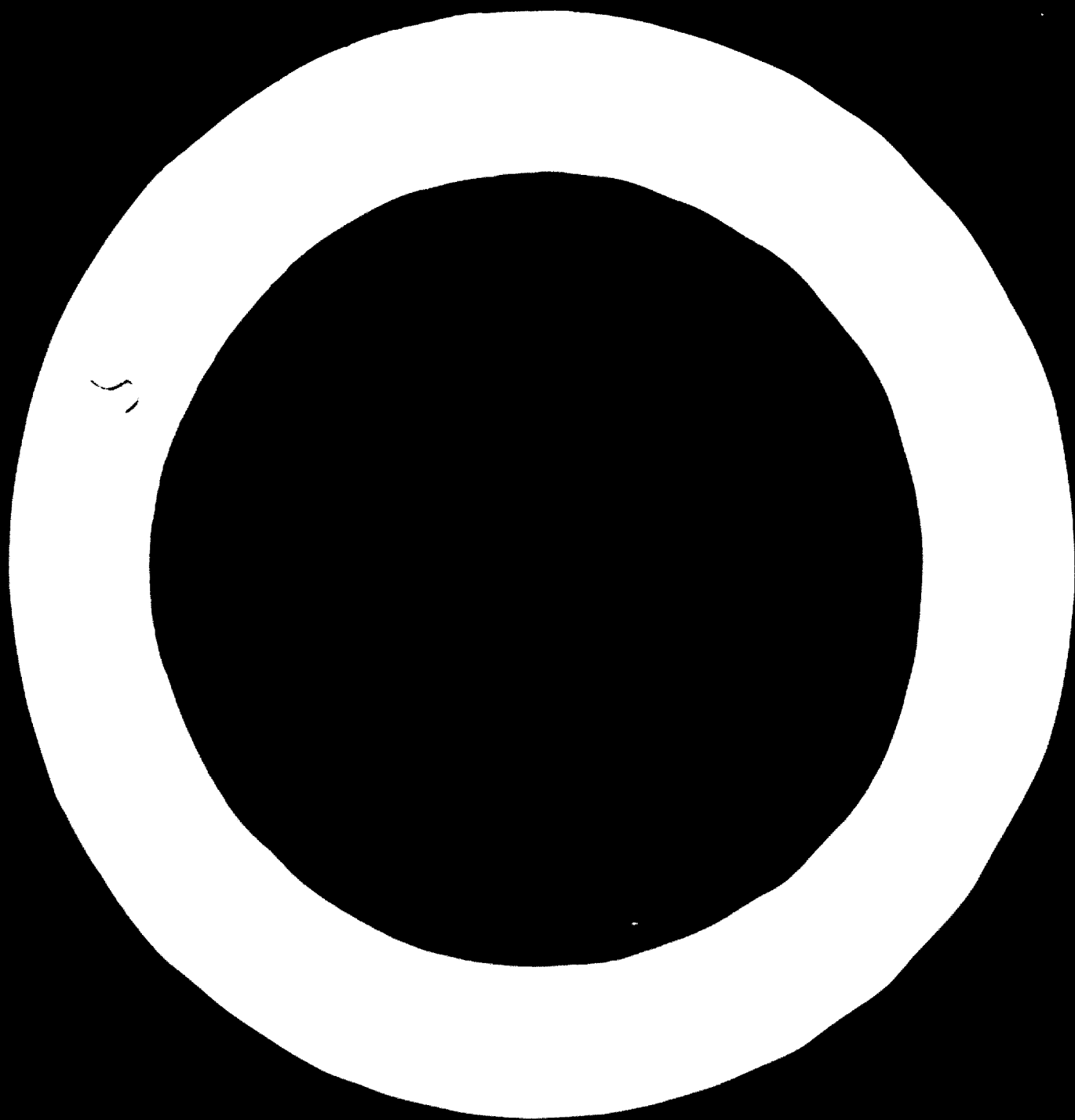
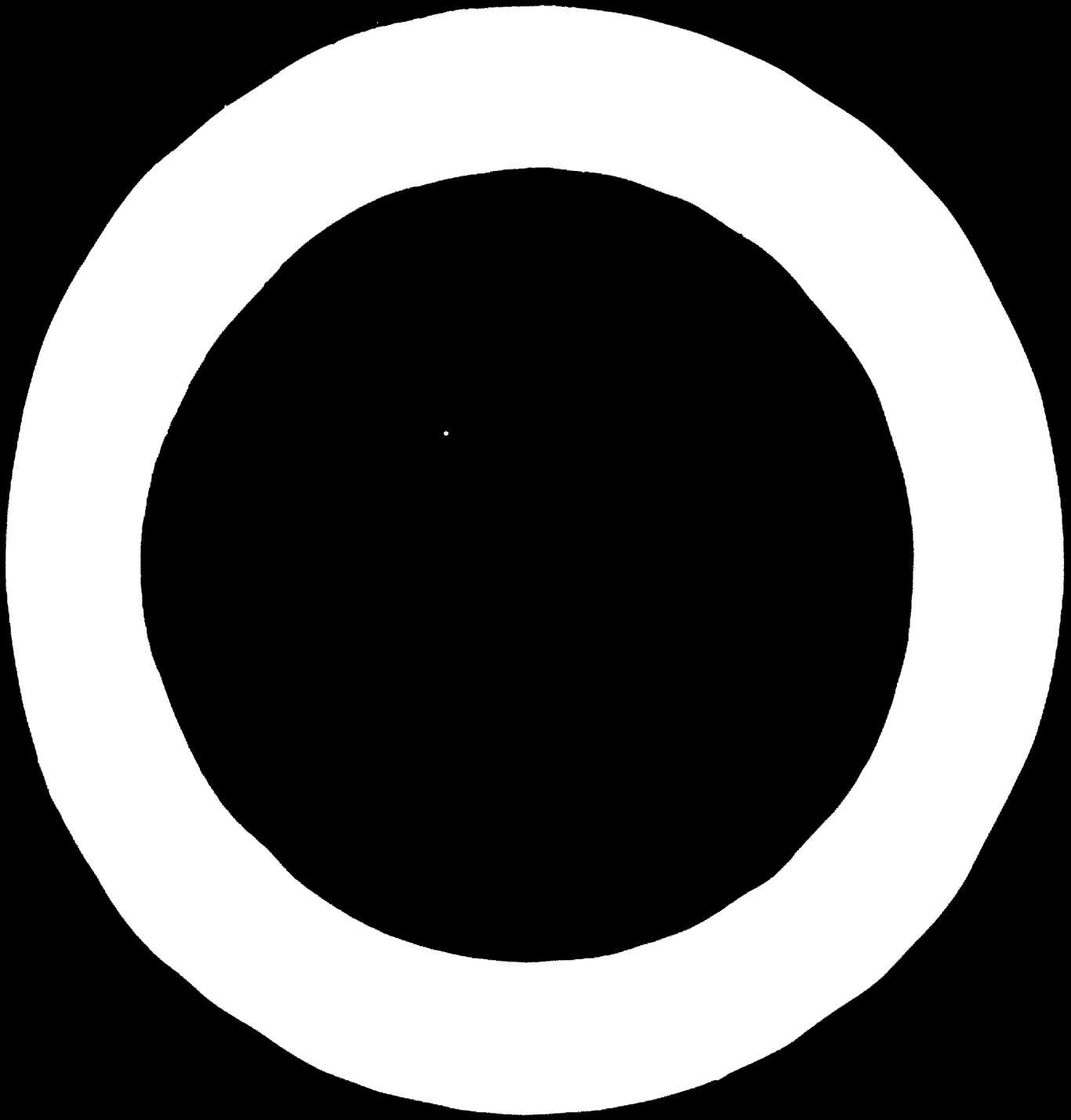by

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ABSTRACT

Current operating practices and proposed new techniques for hydrometal-
lurgical treatment of copper ores and concentrates in the United States
of America are discussed from the viewpoint of possible application in
the developing countries. Examples from industrial practices include
(1) sulfuric acid leaching of oxide and mixed oxide-sulfide ores in vats
and heaps in conjunction with cementation, with direct electrowinning, or
with solvent extraction and electrowinning; (2) dump and inplace leaching
in conjunction with cementation for long-term dissolution of copper
sulfide minerals; and (3) former ammonia leaching practice for native
copper and copper carbonate ores. Also described and discussed are a
variety of laboratory and pilot plant developed processes that have not
been commercially employed. These include (1) sulfur dioxide leaching of
oxide ores; (2) calcining and ammonia leaching of copper silicate ores
that have a high lime content; (3) oxidation and sulfation of sulfide
concentrates via roasting, acid baking, or autoclave treatment, followed
by leaching and cementation or electrowinning of the copper; and (4) a
speculative process for integrated processing of oxide and sulfide ores
involving roasting of the sulfide concentrate to make acid for leaching
the oxide ore, and preparation of sponge iron from the calcine for
cementation of the copper from the oxide leach liquor.

INTRODUCTION

Copper production in 1969 from ores mined in the United States was 1.5
million tons. Another 300,000 tons of copper was made in U.S. smelters
from imported concentrate, and 1.25 million tons of copper was reclaimed
from scrap. A total of about 3 million tons of copper thus was available
to and was used by industry in the United States last year.

Almost 90 percent of the mined copper came from open-pit operations in disseminated deposits. The remainder came principally from two underground mines--one used a room-and-pillar method in mining a bedded deposit; the other used block caving in a disseminated ore body. Ore mined and processed averaged 0.6 percent recoverable copper. About 2 tons of rock containing about 0.2 percent of copper was mined and piled in waste dumps for each ton of open-pit ore that was mined and processed.

Sulfide copper ores were processed by flotation, smelting, and refining to yield 1.3 million tons copper, 25 million pounds of molybdenum sulfide, 300,000 ounces of gold, and 5 million ounces of silver. Only 30,000 tons of copper was recovered from oxide copper minerals by leach-precipitation-flotation processing of mixed oxide-sulfide ores. About 2,500 tons of sulfuric acid per day was made from copper smelter gases, and perhaps half of this acid was used in leaching copper ore and waste dumps. The pressure on copper smelters to reduce air pollution from emission of sulfur dioxide and planned increases in leaching of mine strip wastes and oxidized ores suggest that much more acid will be produced from smelter gas in the future.

Byproduct metals and acid were recovered only in processing of sulfide ores. The importance of byproducts varies greatly among the individual plants. Almost all the gold was produced at a single plant. About 10 plants recovered molybdenum, but at only a few of these was molybdenum recovery a significant economic factor. Recovery of silver, selenium, tellurium, and other byproduct metals was not of appreciable economic importance to individual plants. Over half the sulfuric acid was made by one smelter, largely for sale to nearby industrial customers. Copper can be produced efficiently and cheaply from suitable deposits by large-scale mining, milling, and smelting of sulfide ores. Hundreds of millions of dollars are needed to provide the plant and thousands of skilled people are needed to conduct the operation. In opening up a new sulfide deposit, such factors as the location, size, grade, and nature of the ore body, available smelting capacity, projected markets, available capital, and organizational competence determine whether a fully integrated facility or only a concentrator will be provided. Sulfide copper concentrators and smelters in the United States are often located on contiguous sites. Rail haulage is used to transport concentrate when mills are at a distance from smelters.

In 1969, dump leaching of waste rock from open-pit mining yielded about 120,000 tons of copper in the form of cement copper by precipitation on iron. Most of this cement copper was further processed in conventional smelters. A few thousand tons were converted to copper powder for market by redissolving, pressure hydrogen reduction, sintering, and grinding. A new plant scheduled to start operating in 1970 is designed to produce 8,000 tons of copper per year from mine dump leach solution by solvent

extraction in conjunction with electrolysis. This will be in lieu of former practice which was to cement the copper on iron and have the cement copper treated on toll by a custom smelter.

Oxide copper ores that were processed by sulfuric acid leaching, followed by cementation on iron, electrolysis, or solvent extraction in conjunction with electrolysis, yielded about 100,000 tons of copper. Perhaps 30,000 tons of this copper was electrowon in two plants that leached crushed and sized ore in vats to make rich solution for the electrolytic cells. One plant used heap leaching of unsized ore and the solvent extraction-electrolysis combination process to produce 5,000 tons of copper for market. The remaining 65,000 tons of copper from oxide ore was produced by leaching in vats, heaps, and agitators followed by cementation on iron and smelting of the cement copper.

Growing concern with environmental pollution problems has stimulated much laboratory work on methods for removing sulfur dioxide from smelter gases. In addition to examining improvements over conventional manufacture of sulfuric acid and liquid sulfur dioxide, the recovery of elemental sulfur from smelter gas is being studied. This is because elemental sulfur offers more flexibility in storage and marketing than sulfuric acid and liquid sulfur dioxide. As an alternative to controlling the smelter emissions, several systems for hydrometallurgical treatment of copper sulfide concentrate are being tested. Many different schemes for chemical processing of concentrate have been developed in the laboratory, but commercial adoption still awaits demonstration of engineering and economic feasibility.

In U.S. practice, hydrometallurgical techniques are being employed only in processing oxide ore and sulfide waste dumps. Some of the hydrometallurgical operations are quite small by smelter standards. A few make only 1,000 tons of cement copper or copper powder per year. One electrolytic plant produces only 5,000 tons of copper per year. By comparison, the smallest copper smelter in the United States produced 25,000 tons of copper last year. The next smallest produced 50,000 tons of copper. This is not to imply that small smelters or large hydrometallurgical plants are necessarily uneconomic in the United States or elsewhere.

Copper deposits in developing countries are likely to be of the same general types as U.S. deposits now being processed or that have been processed in the past. These include high-grade oxide and sulfide ores containing 5 percent or more copper that were formerly smelted directly; carbonate ores such as those in Alaska that were formerly treated by ammonia leaching; and native copper ores in Michigan that were treated by gravity methods and ammonia leaching.

Although there could be notable exceptions, most starting operations in developing countries are likely to be relatively small in terms of copper production. Also, in the absence of an established smelting industry,

alternatives to smelting even for sulfide concentrates and regardless of scale are more likely to receive serious consideration. This paper was prepared to present data and information on U.S. practice and laboratory developments that may be helpful in assessing the merit of certain hydrometallurgical techniques for processing copper deposits in developing countries.

ACID LEACHING OF OXIDE AND MIXED OXIDE-SULFIDE ORES

The term "oxide" embraces copper carbonate and silicate minerals as well as cuprous and cupric oxides. All except cuprous oxide are soluble in dilute sulfuric acid solution. Oxidizing conditions as well as acid are needed to dissolve cuprous oxide. Fine dispersions of copper silicate in a siliceous matrix is a common ore type. Only a part of the copper in such material is liberated and dissolved even by fine grinding and acid leaching. Intimately mixed fine-grained oxide and sulfide minerals constitute another common ore type. These may be processed by a combination of leaching and flotation. Elemental copper is a minor component in many oxide and mixed ore deposits and is the principal mineral in certain deposits that occur in the Great Lakes district. Typical current practices for treating oxide and mixed oxide-sulfide ores are illustrated by operations at Ray and Miami, Ariz., and past practice by operations in Alaska and Michigan.

Copper Silicate Ore Leaching Plant, Kennecott Copper Co., Ray, Ariz.

A leaching and electrowinning plant designed to produce 24,000 tons of copper annually from a copper silicate ore was placed in operation at Ray, Ariz., in March 1969. About 10,000 tons of ore is treated daily. Mine-run ore containing about 0.8 percent copper is crushed to minus-1/2 inch in three stages of crushing. The crushed ore is deslimed at 100 mesh. Spent solution from copper electrolysis is used to agitation leach the slimes and vat leach the sands.

Residue from the agitation leach circuit is washed by countercurrent decantation in thickeners. Copper is precipitated from the clear solution on shredded scrap cans in cone precipitation units, and the cement copper is redissolved to yield rich solution for upgrading the electrolytic cell feed. Barren effluent from the cementation cones is circulated to mine waste dumps for dump leaching. This proves an effective bleed off of aluminum and iron impurities that are leached from the ore in the agitators and vats.

Sands are leached by upflow percolation in 14 vats on a 10-day leach and 4-day wash cycle. Each vat holds 10,000 tons of ore. Ore is bedded in the vats, and the spent residue is removed for discard by automatic mechanical equipment. About half of the tankhouse feed solution, which

contains 30 grams of copper per liter, is electrolyzed to 10 grams of
copper per liter and then recycled to vat leaching. The remainder is
electrolyzed to 5 grams of copper per liter and used to leach the ore
slimes. Current density ranges from 16 amperes per square foot at the
feed end of the circuit to 5 amperes per square foot for depleted
electrolyte. Overall current efficiency is 70 percent, and the power
consumption averages 1.5 kwhr per pound of copper. Innovations at the Ray
tankhouse include use of perforated lead anodes containing 30 percent less
lead than conventional cast anodes and the use of an anionic surfactant
to produce a froth that inhibits the discharge of acid mist from the cells.

Acid consumption is about 100 pounds per ton of ore or 500 tons of acid
per day. This acid is produced in a 750-ton-per-day plant at the nearby
Hayden smelter. A fluosolids reactor system roasts copper sulfide con-
centrates from the Hayden concentrator to produce rich SO_2 gas that is
combined with lower strength gas from the copper converters in the smelter
to provide a suitable feed gas for the acid plant.

Leaching and Flotation of Mixed Oxide-Sulfide Ores, Inspiration Copper Co., Miami, Ariz.

Until the mid-1950's, Inspiration practice comprised vat leaching of
the sand fraction of the mixed oxide-sulfide ore and a combination of
flotation and agitation leaching of the fine ore fraction. Copper was
recovered from solution by electrowinning, and the spent electrolyte was
recycled to the vat and agitation leach units. Chalcocite, the easiest
of the copper sulfides to leach, was the chief sulfide mineral. With
deeper mining depth, the proportion of sulfide minerals increased and the
principal copper mineralization shifted to chalcopyrite, the least soluble
of the copper sulfides. To cope with the changed mineralization, the
Inspiration flowsheet was altered to encompass (1) flotation of selectively
mined sulfide ore containing about 0.5 percent copper, (2) vat leaching
of selectively mined oxide ore containing about 0.5 percent copper as
oxide and 0.1 percent copper as sulfide, and (3) vat leaching of mixed
ore containing 0.8 percent copper about evenly divided between oxide and
sulfide, followed by grinding and flotation to recover the undissolved
copper sulfides.

The current operating level is 13,000 tons ore per day of sulfide ore,
4,000 tons per day of oxide ore and 8,000 tons per day of mixed oxide-
sulfide ore.

For vat leaching, the ore is crushed to 3/8 inch, then deslimed at 200
mesh. Slimes from the oxide ore are agitation leached directly; slimes
from the mixed ores are first floated to remove a sulfide concentrate, and
then the flotation tailings join the oxide slimes in agitation leaching.
Leached slimes are washed by countercurrent decantation in thickeners, and

the residue is discarded. Copper is removed from the agitation leach
liquor by cementation on iron in launders. A part of the cement copper
is dissolved in hot, aerated acid solution to yield strong copper solution
for enriching the electrolytic cell feed. The remainder of the cement
copper is upgraded by flotation to make copper powder for market, or
charged to the converters in the smelter.

Oxide and mixed ore in the vats are leached in 4 days to dissolve only
the oxides, compared to the 8 days needed when dissolution of sulfides
was attempted. Solution from the vats after further enrichment with
copper from dissolved cement copper is electrolyzed, and the depleted
electrolyte is used for leaching. About 8,000 tons of copper per year,
analyzing 99.7 percent copper, is made by electrowinning. Overall copper
recovery from the three ore types is 80 percent.

Leaching, Solvent Extraction, and Electrowinning at Ranchers', Bludbird Mire, Miami, Ariz.

Ranchers' Exploration and Development Corp. is treating an oxide copper
ore at the Bluebird mine near Miami, Ariz., by heap leaching, solvent
extraction, and electrowinning to produce 15 tons copper per day (10).[1]
The ore, containing about 0.5 percent copper, is composed of chrysocolla,
malachite, and some azurite in schist and granite porphyry host rocks.
About 6,000 tons per day of ore is mined by ripping, hauled to the heaps
by scrapers, and leveled by graders. The heaps are built up in 20-foot
lifts with fresh ore added to build a new lift after about 180 days of
leaching.

Raffinate, containing 0.2 gram of copper per liter, from the solvent
extraction circuit is fortified with makeup acid to a concentration of
10, 20, or 50 grams of H_2SO_4 per liter and used for leaching. The
strongest acid solution is used for the first 20 days of a new lift. Next,
the intermediate-strength acid solution is used for 30 days. Finally, the
weakest solution is used for 130 days. The raffinate flow of 1,150 gallons
per minute is augmented by a leach circuit recycle of 200 gallons per
minute. Solution is distributed over the heaps through perforated polyvinyl
chloride pipes at the rate of 1,350 gallons per minute, equivalent to about
5 gallons per square foot of leach area per day. Effluent from the heaps,
containing 2.5 grams of copper per liter, is solvent extracted by a 7-percent
solution of General Mills Reagent LIX 64N[2] in kerosine. Three mixer-
settler contact stages yield loaded organic containing 1.2 grams of copper
per liter and raffinate containing 0.2 gram of copper per liter.

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[1] Underlined numbers in parentheses refer to items in the list of
references at the end of this report.
[2] Reference to trade names is made to facilitate understanding and does
not imply endorsement by the Bureau of Mines.

Spent electrolyte containing 31 grams of copper and 155 grams of H_2SO_4 per liter is used in stripping the organic. Two mixer-settler contact stages yield strip liquor containing 35 grams of copper and 150 grams of H_2SO_4 for electrolysis and organic containing 0.12 gram of copper per liter for recycle to the extraction circuit.

The strip liquor is electrolyzed at a current density of 17 to 20 amperes per square foot to produce cathode metal analyzing 99.9 percent copper. Current efficiency is 83 percent and power consumption 0.9 kwhr per pound of copper. Organic loss in the solvent extraction circuit is 0.16 gallon of the 7-percent LIX 64N solution per 1,000 gallons of leach solution. Assuming the cost of the LIX-kerosine mixture to be $1.40 per gallon, the organic loss is equivalent to about 1 cent per pound of copper recovered.

Ranchers' Bluebird formerly recovered copper from heap leach liquor by cementation on iron. Advantages stated for the current solvent extraction-electrolysis circuit are that a higher grade copper product is made for market, impurities in the electrolyte are maintained below troublesome levels by the selective extraction of copper from the leach liquor, and less plugging of the heaps is expected because iron from cementation no longer enters the leach liquor.

DUMP AND CAVED MINE LEACHING OF SULFIDE MINE WASTE

Long-term leaching of sulfide and mixed sulfide-oxide copper minerals in mine waste dumps on the surface is practiced at about 15 locations in the United States. Underground leaching formerly was practiced at the Ohio mine in Utah, the Ray mine in Arizona, and the Anaconda mine at Butte, Mont. The only current example of inplace leaching from caved workings is the Miami mine in Arizona. Although copper extraction is slow and incomplete, plant investment and operating costs may be modest and, hence, attractive in developing countries.

The solution used to dissolve copper from mine dumps and caved mine areas is dilute sulfuric acid containing iron sulfates. After percolating through the broken rock, the solution is passed over iron to precipitate the copper. Acid is then added as needed, and the solution is recycled to mine dumps or caved rubble by spraying, by flooding, or through perforated pipes driven into the dump. Solution flow rates vary with the height, permeability, and copper content of the rock pile but are ordinarily adjusted to yield an effluent containing about 1 gram of copper per liter or 8 pounds of copper per 1,000 gallons. After several weeks or months of leaching and decreasing copper yield, leaching is recessed and this section of the dump or mine is allowed to drain and oxidize for several months. Dissolved copper that impregnates the rock migrates from the interior of the rocks during the draining period and is recovered during the next leach cycle.

Dumps and caved mine areas settle and compact on aging and leaching.
Acid leaching of broken rock is akin to accelerated weathering. Rock
fragments slowly disintegrate, clays are formed from alumina-bearing
minerals, and iron and aluminum sulfates hydrolyze and precipitate. All
these factors tend to plug the dumps or caved material or sections thereof.
The permeability of new dumps may range up to 240 gallons per square foot
per day, whereas old dumps that have been leached for several years may
allow passage of only 5 gallons per square foot per day.

Although solution composition data from operating dumps are variable, the
analyses in table 1 generally characterize dump influent and dump effluent
solutions.

TABLE 1. - Analysis of dump solutions

| | Chalcocite mineralization | | | | Chalcopyrite mineralization | | | |
| | grams per liter | | | | grams per liter | | | |
	pH	Cu	Fe^{+2}	Fe^{+3}	pH	Cu	Fe^{+2}	Fe^{+3}
Dump influent	3.0	0.01	2	0	2.8	0.05	7	0
Dump effluent	2.4	1.2	0.1	1	2.4	1.2	3	1.5

Of significance in these data is that ferrous iron is oxidized and acid
generated concurrent with copper dissolution as the solution flows through
the dump. This is indicative of widespread air penetration into the dump
to effect the oxidation of sulfides and ferrous ion. Oxygen dissolved
in the solution entering the dump is too low to be of importance in the
oxidation reactions. Over 1 pound of iron goes into solution for each
pound of copper cemented. Unless holding tanks or reservoirs are provided
on the surface for oxidation, precipitation, and removal of the added
iron, hydrolysis with precipitation of the added iron occurs in the dump.

Air is the oxidizing medium in conventional dump and caved mine leaching.
In addition to the direct oxidation of sulfides, oxygen from the air
converts ferrous to ferric ion, and the ferric sulfate in turn oxidizes
copper sulfide minerals. Oxidation by injection of liquid oxygen into
dumps has been tried experimentally but has not been adopted in practice.
Bacteria present in all dumps and mines accelerate the oxidation of
sulfides by air. These are most effective at temperatures of 35° C and
a solution pH of 2.0 to 2.5 (7,13). Current typical dump leach practice
is illustrated by operations at Silver Bell and Miami, Ariz.

Dump Leaching at AS&R Co.'s Silver Bell Mine

Waste material, stripped during the open-pit mining of the sulfide ore
from the Oxide and El Tiro pits at Silver Bell, is piled in multimillion-
ton dumps and leached to extract the copper. The operation is described

by Sheffer (11). Waste rock containing chalcocite and chrysocolla, with
minor amounts of chalcopyrite, azurite, malachite, and cuprite, is hauled
by truck and deposited on the existing unprepared terrain to form dumps
about 200 feet high. Bulldozers and front-end loaders level the rock
and form ditches and ponds for distribution of leach solutions. An
irrigation-type system is employed to distribute about 2,000 gallons of
solution per minute. Precipitation plant effluent is delivered through
plastic pipe, discharging into open ditches from which solution flows
into irregular ponds of about 2,500 square feet area each. Several ponds
are continuously flooded with leach solution until the copper content of
the effluent solution drops to less than 0.5 gram per liter. Flooding
of that particular dump area then is discontinued, and the leach solution
is diverted to other ponds. After an inactive period ranging from 6
months to 1 year, the rested ponds are flooded again. This alternate
flooding and resting produces the most efficient dissolution and removal
of copper from sulfide dumps.

Effluent solution collection dams are placed across drainage canyons at
the base of the dumps. Leach liquor from the dumps, containing from 0.4
to 1.4 grams of copper per liter, is pumped to a conventional launder
system for precipitation and recovery of the copper by cementation on
detinned scrap cans. Unlike conventional practice of acidulating the
barren solution after copper cementation, Silver Bell practice is to
acidulate the leach liquor before cementation. Lowering the pH from 2.6
to 2.3 speeds cementation and improves the grade of the cement copper.
The barren precipitation effluent is stored briefly in a collecting
reservoir and then pumped to the dumps for further leaching. Some iron
salts precipitate and settle in the barren solution storage reservoir,
but more of the iron salts precipitate on the pond bottoms. During the
resting cycle, the iron precipitate dries and cracks, presenting little
resistance to solution flow when flooding is resumed. At other dump
leaching operations, periodic ripping or scraping of the surface is
required because of the impermeable layers that form. The dump leaching
operation at Silver Bell produces about 10 tons per day of cement copper
analyzing 82 percent copper.

Inplace Leaching at Miami Mine of Miami Copper Co.

Miami Copper Co. employs inplace leaching to recover copper from an
underground worked-out mine that had been mined by block-caving methods.
Copper is leached from the oxide capping, from low-grade material left
in the stopes below the capping, and from crushed pillars in the mine.
The principal copper mineral is chalcocite, with chalcopyrite, bornite,
covellite, malachite, azurite, chrysocolla, cuprite, and native copper
occurring in minor quantities. Mineralization occurs in seams, veinlets,
and disseminated particles. A description of the leaching operation is
given by Sheffer (11). Barren effluent from the cementation plant is
acidified to pH 1.4 and sprayed on the surface of the caved area. The

olution percolates downward through 400 feet of broken ground. Most
of the copper is contained in the bottom 160 feet of the rock column.
Pregnant liquor drains to an underground collecting system in the old
mine haulage way at the 1,000-foot level. From 3 to 4 weeks are required
for leach solution introduced on the surface to emerge on the 1,000-foot
level. The copper-bearing liquor is pumped to the surface where the
copper is recovered by precipitation with detinned shredded scrap cans
in a conventional launder system. Solution flow rate is 2,500 gallons
per minute, and the copper content of the leach liquor is about 1.5 grams
per liter. Twenty tons of copper is produced daily in the form of cement
copper analyzing 77 percent copper.

Past Ammonia Leaching Practice on Copper Carbonate and Native Copper Ores and Proposed Application to Copper Silicate in Limestone Gangue

Kennecott Copper Co. operated a combination gravity-flotation-ammonia
leach plant for treating copper ore in Alaska from 1916 to 1931 (3).
The ore contained chalcocite, covellite, malachite, and azurite in a
dolomitic gangue. Jig tailings and coarse sand table tailings, containing
about 1 percent copper, mostly in the form of carbonates, were treated
by ammoniacal-ammonium carbonate leaching in a 800-ton-per-day plant.
The sands first were flooded by upward percolation of leach solution to
displace contained water and then were soaked in ammoniacal solution
containing 10.5 percent NH_3, 12.4 percent CO_2, and 6.3 percent copper for
12 hours without circulation. Subsequently, leaching was continued by
downward percolation and recirculation of solution for 36 to 48 hours.
After draining the leach solution, the sands were washed with dilute
ammonia solution and then purged with low pressure live steam to flush
out the remaining ammonia. Sand residue was discharged by opening doors
in the bottom of the tanks. Strong liquor from the leach circuit, contain-
ing 10.3 percent NH_3, 12.2 percent CO_2, and 7.9 percent copper, was treated
in the evaporators by steam distillation to drive off ammonia and carbon
dioxide and precipitate copper oxide analyzing 75 percent copper. The
ammonia vapor was condensed and recycled to the leaching circuit. Copper
recovery by ammonia leaching was about 80 percent.

From 1916 until 1968, Calumet and Hecla operated an ammonia leaching plant
in Michigan to recover native copper from gravity beneficiation tailings (1).
About 8,000 tons of coarse jig and table tailings containing about 0.7
percent copper were leached daily in 1,000-ton-capacity steel tanks by
downward percolation of cupric ammonium carbonate solution. The presence
of cupric ion was essential to the dissolution of elemental copper in
ammonium carbonate solution. The leaching tanks were equipped with water-
seal covers, cocoa matting filter bottoms, and central cone discharges.
After leaching, the sands were washed twice and purged with live steam
to remove the remaining ammonia. The advancing wash solution used in the

leach contained 5.5 percent NH₃, 3.8 percent CO₂, and 2.8 percent copper. About 95 percent of the copper in the advancing wash solution was oxidized to the cupric form by air in tower reactors.

Copper was recovered from the leach effluent liquor containing 5.5 percent NH₃, 3.8 percent CO₂, and 5.4 percent copper, by steam distillation to drive off ammonia and carbon dioxide. These were subsequently condensed for recycling as ammonium carbonate while the copper precipitated out as CuO and Cu₂O analyzing 80 percent copper. Reagent loss was made up by adding aqueous ammonia and carbon dioxide from the burning of coke.

Reduction Roasting and Ammonia Leaching of Chrysocolla Ore

Ores containing oxide copper minerals in a limestone or dolomitic gangue are not amenable to conventional acid leaching because of the prohibitive amount of acid consumed. One plant in Arizona uses the segregation method (8) for processing 650 tons per day of high-limestone ore containing 1.7 percent copper, mostly as chrysocolla. Ore crushed to 1/4 inch is mixed with salt and coke and heated in a direct-fired rotary kiln to 800° C. After quenching in water to prevent reoxidation of the elemental copper formed in the kiln, the calcine is ground and the copper floated. The segregation process also is used on noncalcareous oxide ores at the Torco plant of Rhokana Corp. in Zambia. There the ore is preheated to about 650° C in a fluidized-bed furnace then reacted with salt and coal in a segregation chamber. As at Lakeshore, the calcine is quenched, ground, and floated.

As the cost of roasting makes the segregation method too expensive for ores containing only about 1 percent copper, an alternative ammonia leach process is being investigated by industry. Experiments are being conducted on a laboratory bench scale and in a 1-ton-per-hour pilot plant. The ore is roasted under reducing conditions at 500° to 700° C to convert the copper silicate to ammonia-soluble copper oxide and metallic copper. After leaching, the copper can be recovered from the ammoniacal leach liquors by steam distillation or by solvent extraction-electrowinning. Unless suitable reduction can be obtained by a relatively low temperature-short time roast, the proposed roast-ammoniacal leach system does not appear to offer any significant advantage over the segregation-flotation process for high-limestone oxidized copper ores.

PAST AND PROPOSED PROCESSES FOR SO₂ LEACHING OF OXIDE ORE

Sulfurous acid formed by the solution of SO₂ in water, although a comparatively weak and unstable acid, is an effective solvent for copper carbonate and oxide minerals. In the presence of air and iron salts, some of the SO₂ is readily converted to sulfuric acid which is more effective than SO₂ alone in leaching copper silicates.

SO_2 and air were used in 1903 to leach copper from Comstock Lode tailings in a 350-ton-per-day plant at Virginia City, Nev. After copper removal, the tailings were cyanided for gold and silver recovery. The oxide copper minerals were readily dissolved, but the high clay content of the tailings precluded an effective liquid-solids separation.

In 1908, a small commercial-scale plant utilizing the Neill-Hurfeind process (2) was operated at Coconino, Ariz. This process featured the use of oxygen-free sulfurous acid to form copper sulfide and subsequent precipitation of insoluble cupro-cupric sulfite from solution by driving off the excess SO_2. Difficulties encountered included premature precipitation of the copper, resulting in high copper loss in the leach residue and formation of some copper sulfate, which required separate precipitation with iron or limestone.

Based on extensive testing, a plant (15) to process 250 tons per day of low-grade, oxidized copper ore was operated in 1916 and 1917 at Ludwig, Nev. The process featured SO_2-air sulfating and leaching of ore crushed to 1 inch and screened to 10 mesh. The coarse fraction was bedded in 21-foot-tall closed towers and wet with water; then a hot dilute SO_2-air mixture was forced up through the tower while recycled leach solution was sprayed on top of the ore. The fine ore fraction was processed by recycling a pulp of minus-10-mesh ore and leach liquor through a closed slatted tower against a rising current of SO_2 and air. Overall extraction of copper was over 90 percent. However, difficult problems with corrosion, liquid-solids separations, and materials handling made the process uneconomic.

The difficulties inherent in the tower leach method indicated the need to devise a simple mechanical method for achieving adequate contact of gas and ore pulp. By 1919, the U. S. Bureau of Mines, after testing several alternatives, had developed a process (14) that minimized the problems encountered in prior plants. Leaching was performed in a wooden or wood-lined rotary drum provided with special lifters to enable intimate contact of a thick, cool slurry of minus-30-mesh ore with dilute hot SO_2 gas and air. Countercurrent flow of gas and slurry was employed to promote dissolution of SO_2 and copper at the cool feed end of the drum, and allow discharge of a warm leach pulp essentially free of SO_2.

The Miami Copper Co. subsequently built and operated for 11 months a 100-ton-per-day plant for leaching the oxidized copper minerals from a flotation mill tailing using the Bureau-developed process. Dissolution of the 0.6 to 1.0 percent nonsulfide copper in the leach feed ranged from 70 to 80 percent, using 50 percent pulp solids and a 2- to 4-percent SO_2 gas in the leach drum. The relatively low extraction was attributable to the presence of 0.1 to 0.2 percent copper as chrysocolla diffused in siliceous gangue. Prior to plant shutdown, because of depressed markets for copper

in 1921, sulfuric acid was tried for leaching in lieu of SO_2. Use of 42 pounds of sulfuric acid per ton of tailing enabled extracting 90 percent of the copper in the rotary drum. Subsequent research by the Bureau of Mines showed that recycling part of the solution after iron precipitation of dissolved copper provided enough dissolved iron in the leach pulp to catalyze the formation of sulfuric acid by reaction of air with SO_2.

The leaching of nonsulfide copper minerals from low-grade ores and tailings by the SO_2 rotary drum method has several advantages over leaching with dilute sulfuric acid, particularly in undeveloped countries. The plant is compact and relatively inexpensive, and much of the equipment can be constructed of wood. The operation is simple and easy to control. Excellent contact of gas and ore particles is achieved; hence, leaching is relatively rapid, with good utilization of reagents. If dilute SO_2 gas can be made from locally produced pyrite, the gas would be comparatively cheap; hence, ores containing relatively large amounts of acid-consuming constituents may be economically processed. The process is applicable to small-scale operations without undue increase in operating cost.

PROPOSED HYDROMETALLURGICAL PROCESSES FOR COPPER SULFIDE CONCENTRATE

Because of claimed economic and pollution control advantages, numerous proposals have been advanced to substitute hydrometallurgical methods, in whole or part, for smelting of copper sulfide concentrates. These are usually based on acid or alkaline autoclave leaching, sulfation by acidulating and baking, sulfation roasting, or roasting to oxide.

Alkaline pressure leaching of nickel sulfide concentrate containing cobalt and copper is practiced on a commercial scale in Canada. Small production scale operations have been tried in the United States for (1) acid pressure leaching of cobalt concentrate containing nickel and copper, (2) concentrate containing about 5 percent each of nickel, cobalt, and copper, and (3) lead concentrate containing zinc and copper. Operating results were less satisfactory and costs higher than predicted by laboratory studies. A pilot plant for sulfation by acidulating and baking with a design capacity of 6 tons of copper sulfide concentrate per day is being constructed in Tucson, Ariz. Sulfation roasting on a semicommercial scale was tried at Bagdad, Ariz., and abandoned. Experiments with dead roasting to the oxide, followed by leaching of the calcine, have not extended beyond the bench scale.

A common feature of hydrometallurgical processing of copper concentrate is that byproduct recovery of precious metals would require reprocessing of the leach residue. Summary descriptions of the technology and limitations of several proposed hydrometallurgical processes for sulfide copper concentrate may be useful in assessing possible applications in developing countries.

Ammoniacal and Acid Autoclave Leaching

Alkaline and acid leaching of copper sulfides in autoclaves has been investigated by a number of researchers (6,12). In general, metal values are dissolved at elevated temperatures under air or oxygen pressure and recovery from solution is made by hydrogen reduction, electrolysis, or chemical precipitation. An example of successful commercial application of pressure leaching is the refinery of Sherritt Gordon Mines, Ltd., at Fort Saskatchewan, Alberta, Canada. About 300 tons per day of sulfide concentrate, containing 10 percent nickel, 1.2 percent copper, and 0.2 percent cobalt, is pressure leached with ammonia and air at 80° to 95° C, and a total pressure of 115 to 128 psig. Soluble ammine complexes of the metals are formed. Nickel and cobalt are separately recovered by pressure hydrogen reduction after several intermediate purification steps. Sulfur in the concentrate is recovered as ammonium sulfate, which is a marketable byproduct in that area. Copper is recovered from solution as Cu_2S, which is shipped to a smelter. This marketing of copper as the sulfide is noteworthy because the process is technically capable of converting copper sulfides to ammonium sulfate and copper powder.

Laboratory studies show that chalcopyrite is readily dissolved in ammoniacal-ammonium sulfate solutions under oxidizing conditions (4). Finely ground concentrate was almost completely dissolved in 1 hour at 150° C and an oxygen pressure of 100 psi. Pressure hydrogen reduction, direct electrolysis, and solvent extraction-electrolysis have been examined for recovering the copper from ammoniacal sulfate solution. All are workable but involve complicated and potentially troublesome operations. Advantages of alkaline pressure leaching are that leaching conditions are relatively mild, iron remains in the leach residue, and sulfur compounds are recovered as potentially salable byproducts. Conversely, recovery of copper from solutions appears complicated and expensive, and a large quantity of ammonia and a market for ammonium sulfate are needed.

More severe conditions of temperature and oxygen pressure are required for rapid autoclave leaching of copper sulfide concentrate in the absence of ammonia. At a temperature of 250° C and oxygen pressure of 100 psi, finely ground chalcopyrite in a vigorously stirred dilute pulp was dissolved in about 1 hour in laboratory tests. Recovery of copper from solution by either hydrogen pressure reduction or electrowinning results in formation of an equivalent quantity of sulfuric acid that must be neutralized. Results in commercial-size equipment have fallen far short of those obtained in the laboratory. A possible cause for the failure to achieve satisfactory scale-up may be the difficulty of effectively distributing oxygen through the pulp in large autoclaves. Despite the extensive use of titanium and stainless steel, corrosion in the large autoclaves proved troublesome and expensive.

An alternative acid pressure leaching process for chalcopyrite has been proposed that recovers part of the sulfur in elemental form (2). A temperature of 110° C and 500 psi oxygen overpressure were employed in laboratory tests to dissolve part of the chalcopyrite and make elemental sulfur. An excess of chalcopyrite must be present, and this necessitates subsequent flotation of the leach residue to recover the sulfur and unreacted chalcopyrite. These can be separated by hot filtration or by dissolving the sulfur in a suitable organic liquid. To avoid oxidation of the sulfur to acid during leaching, the temperature must be maintained at under 115° C. This relatively low temperature in turn adversely effects the chalcopyrite dissolution rate. Controlled pressure leaching has not been attempted on a commercial scale.

Because of the probable high costs for equipment, operation, and maintenance, the extensive auxiliary supplies that must be available, and the close control needed, pressure oxidation leaching is of doubtful applicability to copper operations in developing countries.

Sulfation of Copper Sulfide Concentrates
by Acidulation and Baking

The Anaconda Co. currently is investigating a hydrometallurgical method for processing copper flotation concentrates containing chalcopyrite, chalcocite, and pyrite to replace conventional smelting with its concomitant air pollution problems. The process, based on a patent and patent application owned by the Treadwell Corp., will be investigated in a pilot plant having a capacity of 6 tons per day of flotation concentrate (2). In the proposed process, the copper concentrates are pugged with strong sulfuric acid to form a slurry which is fed along with preheated quartz pebbles to an externally heated kiln. At a temperature of 230° C copper and iron sulfides are converted to sulfates and sulfur, and the iron sulfate simultaneously decomposes to form iron oxide. Sulfur dioxide gas from the kiln is converted to oleum for recycle to the acid pugging step. The pebbles coated with reaction products from the kiln are washed to remove the water-soluble copper sulfate and the insoluble residue. Any precious metals present in the original sulfide concentrate remain in the residue.

To recover copper from solution, HCN and SO_2 are added to the sulfate solution at a temperature of 40° to 70° C to precipitate cuprous cyanide and regenerate sulfuric acid for recycle to the acid bake. The cuprous cyanide is reduced with hydrogen, yielding copper powder and HCN gas for recycle. However, copper could be recovered from the copper sulfate leach liquor by conventional electrowinning and the sulfuric acid generated by electrolysis recycled to the acid pugging step.

Sulfation by Roasting in Controlled SO_2 Atmospheres

Research is currently in progress at the Salt Lake City Metallurgy Research Center of the U.S. Bureau of Mines to investigate the feasibility of

processing copper sulfide flotation concentrates by roast-leach techniques
to recover both metal values and byproduct sulfur. Ideally, the process
would comprise roasting of the sulfides to oxides with evolution of strong
SO_2 gas suitable for conversion to elemental sulfur, acid leaching of the
copper oxide, and electrowinning to recover the copper. Unfortunately,
an oxidizing roast produces acid-insoluble copper ferrites whenever iron
is present in the sulfide concentrate. Recent investigations showed that
copper ferrite formation could be inhibited by roasting in high SO_2
atmospheres. However, copper and iron sulfates were formed with the
result that considerable water-soluble copper and acid-soluble iron were
produced. A copper sulfate product and an off-gas containing 85 percent
SO_2 were made by roasting a chalcopyrite concentrate at 700° C in a gas
initially containing 70 percent SO_2, 21 percent oxygen, and 9 percent
nitrogen. Complete copper extraction from the sulfated calcine requires
dilute acid leaching. More acid is made in the subsequent electrowinning
step than needed for leaching the sulfated calcine. Perhaps the excess
can be decomposed in the roaster to yield more SO_2 for conversion to
sulfur. Another alternative being tested is to crystallize copper sulfate
from the leach liquor, followed by a decomposition roast to convert the
copper to an acid-soluble oxide while generating SO_2 for recycle to the
initial sulfation roast. Copper could then be recovered by electrowinning
with the resultant acid used to dissolve more copper oxide.

Bagdad Roast-Leach-Electrolysis Plant

A semicommercial plant employing sulfation roasting of concentrate was
operated by Bagdad Copper Co. in Arizona in the mid-1950's (5). Five
tons per day of chalcopyrite concentrate from the Bagdad mill and up to
750 pounds per day of cement copper from dump leaching were processed by
sulfation roasting, leaching of the water-soluble copper sulfate, and
electrodeposition of the copper from the leach liquor. Feed to the
fluidized bed reactor averaged 28 percent copper, 23 percent iron, and 26
percent sulfur. The roasting temperature had to be accurately regulated
at about 685° C; if the temperature was too low, excessive iron was
solubilized, while if the temperature was too high, some copper became
insoluble. At the proper temperature, about 95 percent of the copper in
the calcines was water soluble and 98 percent was acid soluble.

After agitation leaching of the roast calcines and countercurrent
decantation washing in thickeners, the pregnant liquor, containing about
46 grams of copper and 40 grams of H_2SO_4 per liter, flowed to 22 concrete
lead-lined cells in the tankhouse. The liquor passed through starting
sheet tanks, commercial cathode tanks, and finally stripping tanks where
sponge copper was produced. Spent liquor contained 0.2 gram of copper
and 100 grams of H_2SO_4 per liter. This acid was partly consumed by
leaching oxide ore in a separate circuit. In the absence of enough oxide
ore to consume all the acid, the excess was neutralized with limestone

before the spent electrolyte was used in leaching of calcine. About 96 percent of the copper was recovered by electrowinning. Cathodes assaying 99.92 percent copper were produced. Current efficiency was 88.5 percent.

The principal problems in the operation appeared to be bed defluidization owing to the sticky nature of the copper sulfate at roaster temperature, control of the iron solubility which caused problems in electrowinning, and the consumption or neutralization of the acid generated during electrowinning.

Sulfation roasting processes are still in an experimental stage of development and are not presently suitable for use in developing countries.

Oxidation Roasting of Copper Sulfide Concentrates

As cited in the section on sulfation roasting, oxidation roasting of copper-iron sulfides results in the formation of considerable acid-insoluble copper ferrite. Methods for processing copper oxide ferrite calcines are being examined at the Salt Lake City Metallurgy Research Center. A chalcopyrite concentrate was roasted at 825° C in a fluidizing gas containing 20 percent SO_2, 21 percent O_2, and the remainder N_2. The resultant stack gas contained 35 percent SO_2 and should be readily convertible to elemental sulfur. Sulfur elimination from the calcine was essentially complete. About 40 percent of the copper was in the form of acid-insoluble ferrite. Experiments are being made to convert copper oxides and ferrites to metallic copper by a reducing roast. Cupric ammonium carbonate leaching would dissolve the copper that then could be recovered either by steam distillation to produce cupric oxide or by solvent extraction-electrowinning to produce electrolytic-grade copper.

PROPOSED INTEGRATED PROCESS FOR SEPARATELY MINEABLE OXIDE AND SULFIDE ORES

A process that uses oxide ore leaching and sulfation roasting of sulfide concentrates has been proposed for processing a major deposit of separately mineable, roughly equal tonnages of oxide and sulfide copper ore. A few of the unit operations, such as leaching of the oxide ore and flotation of the sulfides, are being tested in an industrial laboratory, but no comprehensive integrated system study is underway. The conceptual plan is presented here to illustrate the kind of technology that may be considered for a new operation. Principal provisions of the flowsheet are as follows:

1. Sulfide ore is floated to produce a sulfide concentrate and the tailings are discarded.

2. Sulfide concentrate is roasted under conditions that produce a rich SO_2 gas for acid making, and a calcine containing copper in a form leachable in spent solution from copper electrowinning. The iron in the calcine must be substantially insoluble in the spent electrolyte. Precious metals are insoluble and remain in the iron-rich leach residue.

3. Acid made from the roaster gas is used to leach oxide ore in heaps or in vats and agitators. Chrysocolla is the main copper mineral present in the oxide ore.

4. Residue from leaching of calcine is reductively roasted to yield sponge iron, and the iron in turn is used to cement copper from the oxide ore leach solution. The cement copper, containing precious metals that were present in the initial sulfide concentrate, is sold to a smelter or smelted on toll.

5. Rich solution from the leaching of calcine is electrolyzed to produce copper metal for market and spent acid solution for reuse in leaching calcine.

These are the bare bones of the conceptual process. Unanswered are such questions as how to roast concentrate that will yield calcine in which all the copper but little of the iron is acid soluble; how to prepare reactive sponge iron from leached calcine residue; how to cope with iron in the electrolytic circuit; and how to obtain high copper dissolution by dilute acid leaching of refractory chrysocolla ore. These and other considerations would pose worrisome problems in planning a copper operation in developing countries.

SUMMARY

This review has covered U.S. current and past hydrometallurgical practices for treating oxide and mixed oxide-sulfide ores, proposed processes for treating high-lime oxide ores, and nonsmelting processes for treating sulfide flotation concentrate. A choice of methods appear available for oxide and mixed oxide-sulfide copper deposits in developing countries from among the processes used commercially in the United States. The situation with regard to sulfide flotation concentrate is different. Processes that have been proposed are based on laboratory or pilot plant studies of varying scope. In the absence of commercial experience, these methods are regarded as experimental and should be so considered for any application in developing countries.

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SUMMARY

Copper production in the United States now is based mainly on smelting of sulfide concentrates in large plants. Less copper is made by leaching, but the technology is widely practiced at numerous locations. Growing concern with environmental pollution from smelter gas has stimulated process development work on hydrometallurgical methods for processing sulfide concentrate. These methods for treating concentrates, as well as past, present, and proposed hydrometallurgical procedures for oxide ores and mining wastes, are described and discussed from the viewpoint of possible application in developing countries.

Pattern of U. S. Copper Production

Copper production in 1969 from ore mined in the United States was 1.5 million tons. Sulfide copper ores were processed by flotation, smelting, and refining to yield 1.3 million tons copper, 2.5 million pounds molybdenum sulfide, 300,000 ounces of gold, 5 million ounces of silver, and lesser amounts of selenium, tellurium, and other byproduct

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metals. About 2,500 tons sulfuric acid a day was made from copper smelter gas, and perhaps half of this was used in leaching copper ores and mine waste dumps. The pressure on copper smelters to reduce air pollution from emission of sulfur dioxide and planned increases in leaching oxidized ores and mine strip wastes suggests that much more acid will be produced from smelter gas in the future.

Leaching of waste rock from mining sulfide ores yielded 120,000 tons of copper in the form of cement copper by precipitating the dissolved copper on iron. Most of this cement copper was further processed in conventional smelters. Leaching of oxide copper ores followed by cementation on iron, electrolysis, or solvent extraction in conjunction with electrolysis yielded 100,000 tons of copper.

Acid Leaching of Oxide and Mixed Oxide-Sulfide Ores

United States' practice for oxide and mixed ores are illustrated by descriptions of the plants operated by Kennecott at Ray, Ariz.; Inspiration at Miami, Ariz.; and Ranchers' Bluebird at Miami, Ariz. Past practice for oxide and native copper ores are illustrated by descriptions of plants operated by Kennecott in Alaska, and by Calumet and Hecla in Michigan.

Kennecott at Ray, Ariz., treats 10,000 tons copper silicate ore a day by acid leaching the sand fraction in vats and the slimes in agitators. Copper is recovered from the vat leach solution by electrolysis. Copper in solution from the agitators is cemented on iron, then redissolved to make strong copper solution used to fortify the electrolytic cell feed. Spent solution from electrolysis is used in leaching.

Inspiration at Miami, Ariz., treats a total of 25,000 tons of ore a day by three different methods: (1) Selectively mined sulfide ore is floated and the concentrate smelted; (2) selectively mined oxide ore is leached in vats and the leach solution electrolyzed; and (3) mixed ore containing 0.4 percent each of oxide (mostly chrysocolla) and of sulfide (mostly chalcopyrite) is leached in vats, followed by grinding and flotation of the residue to recover the undissolved copper sulfides. Slimes made in crushing the ore for the vats are leached by agitation, followed by cementation of the copper on iron.

Ranchers at Miami, Ariz., treats 6,000 tons a day of chrysocolla ore by heap leaching, followed by solvent extraction in conjunction with electrolysis to produce 15 tons of copper a day. Cementation on iron was formerly used to recover the copper from solution. Advantages stated for the solvent extraction-electrolysis circuit are that a higher grade copper product is made for market, impurities in the electrolyte are maintained below troublesome levels, and less plugging of the heaps is expected because iron from cementation no longer enters the leach liquor.

Dumps and Caved Mine Leaching of Sulfide Mine Waste

Long-term leaching of sulfide and mixed sulfide-oxide copper minerals is practiced at about 15 locations in the United States. Underground leaching of copper from caved mine workings is practiced at the Miami mine in Arizona. The leach solution used is dilute sulfuric acid containing iron sulfates. After percolating through the broken rock, the solution containing about 1 gram Cu per liter is passed over iron to

precipitate the copper. Acid is then added as needed and the solution recycled to the mine dump or caved rubble by spraying, flooding, or through perforated pipes driven into the dumps. After several weeks or months of leaching, and decreasing copper yield, leaching is recessed and the dump or mine area is rested for several months. The rubble remains moist and oxidation by air, aided by the presence of bacteria, continues during the rest period. Dissolved copper that impregnates the rock migrates from the interior of the rocks during the rest period and is recovered during the next leaching cycle. Most of the acid required for copper dissolution is provided by oxidation of sulfide minerals in the dump or mine. Iron requirements for precipitation of the copper is 2 to 3 pounds per pound of recovered copper.

Past Ammonia Leaching Practice and Proposed Application to Copper Silicates in Limestone Gangue

Ammonia leaching in both Alaska and Michigan was on sand tailings from gravity concentration of ore. The sands were percolation leached with ammoniacal carbonate solution. Strong leach liquor was heated to drive off the ammonia and carbon dioxide for recycle, and recover a copper oxide precipitate containing 75 to 80 percent copper.

An ammonia leach process is being investigated for treatment of copper silicate ore containing too much limestone for economical acid leaching. The ore is roasted under reducing conditions at 500° to 700° C to convert the copper silicate to ammonia soluble copper oxide and metallic copper. Unless suitable reduction can be obtained in a low temperature-short time roast, the proposed roast-leach system may be economically applicable only to relatively high-grade ore.

SO_2 Leaching of Oxide Ore

Sulfurous acid formed by solution of SO_2 in water, although a comparatively weak and unstable acid, dissolves copper carbonates and some of the oxides and silicates. In the presence of air and ferrous salts, part of the SO_2 is converted to sulfuric acid which is more effective than SO_2 alone in leaching copper silicates. Satisfactory leaching of oxide copper was obtained using a rotary drum constructed of wood and featuring special lifters for countercurrent contacting of ore pulp with hot dilute, SO_2-bearing gas.

Proposed Hydrometallurgical Processes for Copper Sulfide Concentrate

Processes that have been proposed for hydrometallurgical treatment of copper sulfide concentrates usually are based on ammonia or acid autoclave leaching, sulfation by acidulating and baking, sulfation roasting, or roasting to oxide. Ammonia pressure leaching is successfully practiced in Canada, but on nickel sulfide rather than copper sulfide concentrate. Laboratory tests show chalcopyrite, the most resistant of the copper sulfides, to be readily dissolved in ammoniacal ammonium sulfate solution at elevated temperature and oxygen pressure. Equipment and operating costs appear to be high and a large quantity of ammonia and market for byproduct ammonium sulfate is needed.

Much higher temperature and oxygen pressure is needed for acid than for alkaline autoclave leaching, and corrosion problems are more severe. Small commercial scale plants that operated in the United States on cobalt, nickel, and lead concentrates proved uneconomic.

Sulfation of copper sulfide concentrate by acidulating and baking at 230° C is being investigated by The Anaconda Copper Co. on a pilot plant scale. Copper and iron sulfides are said to be converted to sulfates and sulfur, and the iron sulfate simultaneously decomposed to form iron oxide and SO_2. Sulfur dioxide from the kiln is converted to oleum for use in the acidulating step.

Sulfation roasting followed by dissolution by the copper sulfate and electrolysis of the leach solution was practiced on a semicommercial scale by Bagdad Copper Co. in Arizona about 15 years ago. Close temperature control was required to obtain a calcine in which most of the copper but little of the iron was soluble. A principal problem appeared to be bed defluidization owing to the sticky nature of the copper sulfate at roaster temperature of 685° C.

Recent laboratory experiments on oxidation roasting of copper sulfide concentrate have been directed at methods of treating the calcine that contains up to 40 percent of the copper as acid insoluble copper ferrite. One approach being examined is to convert the copper oxide and ferrite to metallic copper by a reducing roast, and follow with ammonia leaching.

Proposed Integrated Process for Separately Mineable Oxide and Sulfide Ores

A process that uses oxide ore leaching and sulfation roasting of sulfide concentrates has been proposed to treat a major deposit of separately mineable oxide and sulfide ore. The oxide fraction would be leached using acid made in roasting the sulfide concentrates. Calcine
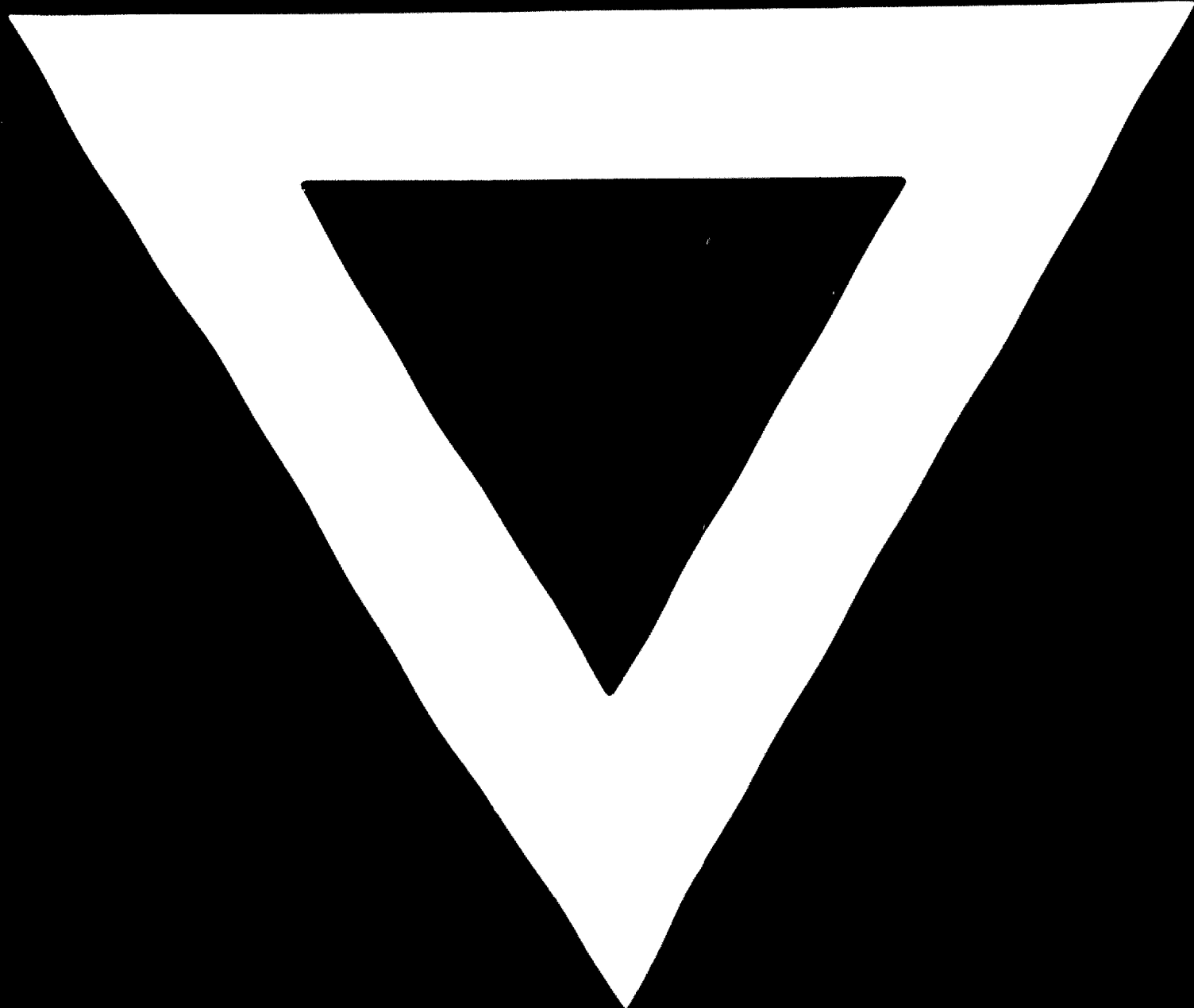
from the roaster would be leached in spent cell electrolyte to make strong copper solution for electrowinning. Sponge iron would be made from the leached calcine residue and used to precipitate the copper from the oxide ore leach solution. Unresolved problems are foreseen especially in controlling the roasting step.

CONCLUSIONS

A choice of methods appear available for oxide and mixed oxide-sulfide copper deposits in developing countries from among the process used commercially in the United States. The situation with regard to hydrometallurgical treatment of sulfide flotation concentrate is different. Processes that have been proposed are based on laboratory or pilot plant studies. In the absence of commercial experience, these methods are regarded as experimental and should be so considered for any application in developing countries.

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