SUBJ
MNG
NCT I

New copper technology is winning the ore

Metal recovery from low-grade and hitherto worthless stocks is near. And as for the copper industry's bread-and-butter ores, a competitive new hydrometallurgical process does not generate air-polluting sulfur dioxide.

MARK. D. ROSENZWEIG,
Editorial Assistant

The copper industry is entering the nuclear age. If a recent proposal by Kennecott Copper Corp. is approved by the Atomic Energy Commission, a 20-kiloton nuclear device will be detonated some 1,200 ft. below ground-level at a site near Safford, Ariz. The blast would crush a deposit of low-grade ore, now uneconomic to mine, creating a chimney through which it is hoped that copper can be recovered by in-place leaching with sulfuric acid.

And there are other important, though not earth-shattering, developments. Indeed, the copper industry is in the midst of intense technological activity. Some conventional operations are being improved and new techniques are emerging.

▶ **Active Duo**—There are presently two widely used commercial techniques to recover copper from ore. One is for the plentiful sulfide ores, the other for the deposits of oxide, mixed oxide-sulfide and native (unfettered copper) ores.

Smelting Sulfides—Sulfide ores are generally floated and smelted, then electrorefined. Deposits usually are low grade, containing from a fraction to several percent copper. For economic processing, the metal content of the ore is concentrated.

After being crushed, ore is ground to loosen mineral particles from the gangue. This mass is then carried to a cell where most of the minerals are removed from the worthless rock by froth flotation, then dewatered to form a concentrate assaying 15 to 30% copper.

Fed to the smelting circuit, this
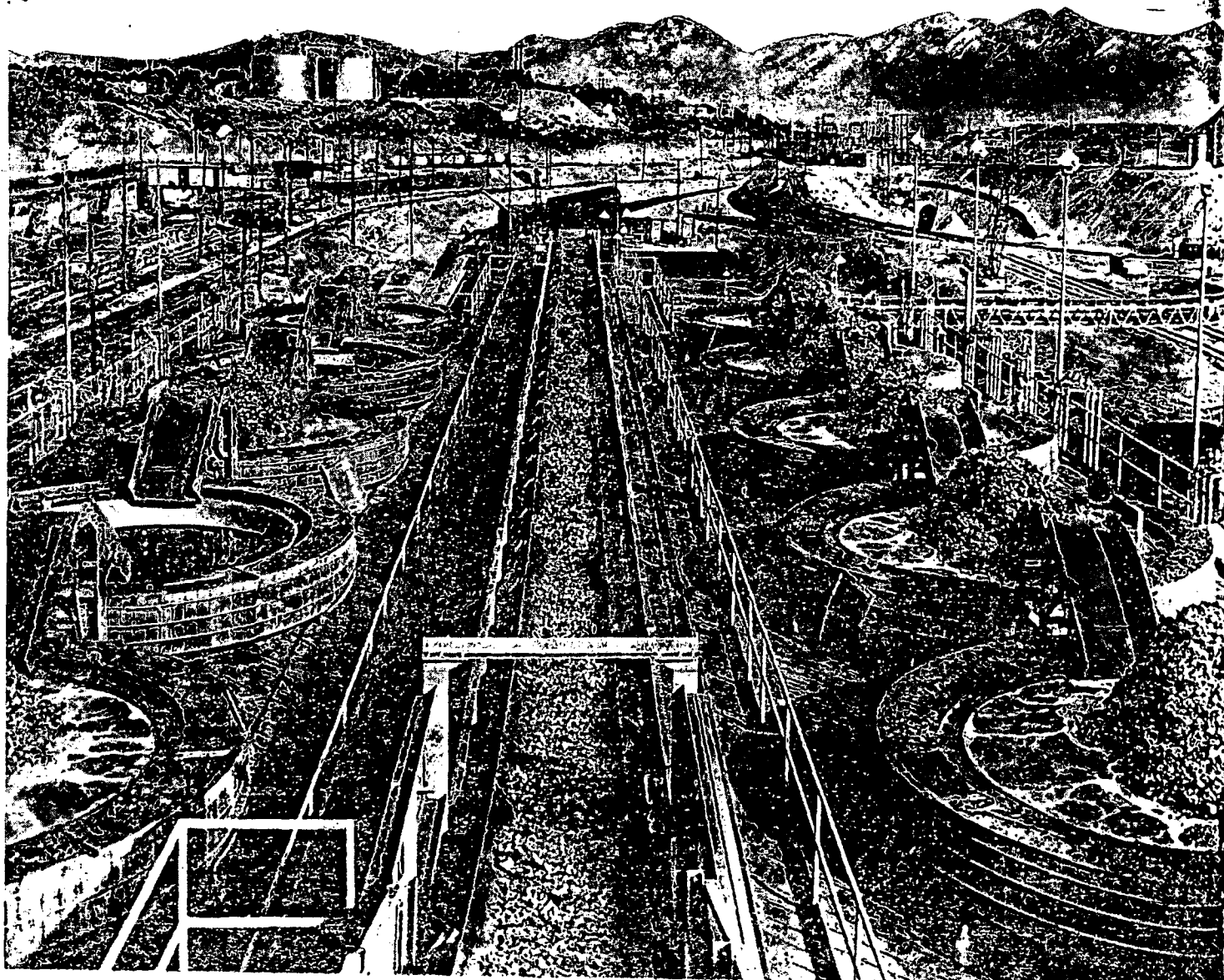
concentrate normally is first roasted: enough sulfur is oxidized and driven out to leave a desired balance of copper, iron and sulfur. In a reverberatory smelter, iron oxides in the ore combine with siliceous flux to produce a slag. Copper sulfide, iron and some sulfur are left as matte, which is then reduced to copper in two stages of air-blowing in a converter.

The resultant more-than-95% pure metal is known as blister copper. Used as anodes in an electrolytic cell, along with pure copper starting-sheet cathodes, the blister ebbs away as copper ions migrate to the cathodes. The pregnant, high-purity-copper cathodes are then melted down and cast into ingots, wirebars or other shapes.

Loaded Liquor — Hydrometallurgical treatment is the prime means used to recover copper metal from oxide, mixed oxide and sulfide, and native ores. It is also used, in some instances, to process sulfide tailings and overburden.

Ores first are leached with an appropriate solvent. For sulfides, this is generally water or dilute sulfuric acid. (In some cases, natural bacterial action converts the sulfides to oxides, forming sulfuric acid. The acid then extracts copper to produce the metal sulfate.) Dilute sulfuric is also favored for the leaching of oxide and mixed ores. The scarce native ores are usually treated with a solution of ammonia and ammonium carbonate. The leach liquor can be handled by either of two methods:

Classically, it is contacted with iron scrap. Iron goes into solution. Copper precipitates. Once dewatered, this finely divided "cement" copper, seldom over 90% pure, is shipped to a smelter for further processing, or is sold.

The other method handles the leach liquor, after some purification, in an electrowinning cell. Ex-

WS OF CONE PRECIPITATORS at Utah have upped cement-copper production ost threefold. Each unit can process 00 gpm. of copper-rich leach solution.

Continental Copper and Steel Industries photo

ELECTROWINNING CELL of new design can tolerate higher levels of impurities in its feed. And it operates at 2 to 3 times present cells' current densities.

cept for insoluble anodes and about four times greater electrical energy requirements, the unit is similar to that used for electrorefining of blister. Heavy, pure-copper cathodes are grown. Again, they are melted and cast.

▶ **Busy Cones**—Important developments in copper-ore leaching processes have been coming to light at a fast clip.

Researchers at Kennecott's Western Mining Division, Salt Lake City, have devised a cone precipitator that is said to make cement copper with much greater efficiency than the conventional method of passing liquor through troughs filled with scrap iron.

In one installation, cone precipitators more than doubled metal production, from 150,000 lb./day to 400,000 lb./day.

Each precipitator can reclaim 20 to 30 lb. of red metal a minute, depending on copper content and the flow rate of solution through the cone. And, according to the company, the units lend themselves

to a higher degree of instrument control than do troughs.

▶ **Selective Solvent**—But boosters of high-purity-copper recovery by hydrometallurgy have been active, too. Fundamental to all of their plans is the need for, or advantage of, using refined copper-rich solution.

The Chemical Div. of General Mills, Kankakee, Ill., has developed a water-insoluble organic reagent, called LIX 64, that can be used to purify leach liquor through solvent extraction.

Already in use at several pilot plants, the liquid ion-exchange reagent will be applied commercially for the first time at the Ranchers Exploration and Development Corp. plant being built in Miami, Ariz., to eliminate cementation and let liquid go into electrowinning.

In use, a 7 to 10% solution of LIX 64 in a carrier such as kerosene gives up two hydrogen ions in exchange for each copper ion in the acidic leach liquor. Then, in a second step, the copper is stripped

from the reagent by an acidic electrolyte in exchange for hydrogen ions.

▶ **Unexcelled Cell**—Just as ion-exchange may make pure copper-rich solution readily and economically available, Continental Copper and Steel Industries of New York has devised a cell that is said to be less sensitive to solution impurities than present electrowinning units. Of course, it functions best with a pure solution.

This unusual cell, called the CCS. deposits red metal smoothly at the cathodes. In conventional units, by comparison, metal is unevenly distributed on the sides of the cathodes facing away from the direction of solution flow. Dendrites of copper build up, sometimes to the point where they short-circuit against an anode.

While present commercial cells operate at a current density of 11 to 20 amp./sq. ft. of cathode surface, the CCS unit has optimum performance in the range of 30 to

Anglo American Corp. of South Africa photo
COPPER FROM REFRACTORY ORE is isolated from gangue in chamber at African plant. Metal then passes on for concentration and refining operations.

45 amp./sq.ft. and has run as high as 60 amp./sq.ft. However, at this higher value, copper is produced as powder. (Harlan Metals Corp., Phoenix, Ariz., is piloting a cell that works at a "significantly higher" current density to make copper powder). Power efficiency is between 90 and 92%.

Increases in current density decrease the cathode surface necessary for a given copper recovery, and reduce the number of electrolytic tanks needed. As a consequence, CCS cell installations would allow lower capital expenditures.

Another plus claimed for the CCS cell is that lower copper concentrations in solution can be used economically. And as much as four times more copper is taken out of solution than in conventional cells.

▶ **Gas Task**—Phoenix-based Arizona Chemcopper Co., a joint venture of Bagdad Copper Corp. and Chemetals Corp., has demonstrated a hydrogen reduction process for producing highly refined copper from leach liquor. The company has had a plant in Bagdad, Ariz., onstream for more than a year.

Feed material for this plant is impure "cement" copper. Sulfuric acid leaches out copper in the form of copper sulfate. Once insolubles are filtered out, the acid solution is sent to agitated autoclaves where it contacts hydrogen gas at about 300 F. and 425 psi. The product is copper powder and dilute sulfuric acid. An acrylic-based dispersing agent prevents agglomeration of the metal particles.

The copper slurry is washed and dewatered, with the acid recycled back for reuse in leaching. The powder, either loose or compressed into briquettes, is sintered to remove traces of sulfur, oxygen and other impurities. This plant caters to the metal-powder market, but its high-purity copper could just as well be melted down and cast into the regular shapes.

There is no doubt, notes a Chemetals spokesman, that the present cement-copper step could be eliminated. Leach liquor, extracted with a reagent such as LIX 64, would provide a sulfate solution pure enough to go directly to hydrogen

reduction. This would put the hydrogen reduction process squarely in competition with electrowinning in conventional tank houses or in cells using the CCS development.

Chemetals' estimates indicate that hydrogen reduction followed by powder melting and casting is slightly cheaper than electrowinning where cathodes are cast. However, the savings are not significant enough to create a major switchover. The relative advantages of the two processes vary, in fact, from location to location, depending on individual circumstances.

▶ **Cyanide's Side**—To further complicate matters, another technique may eventually provide a third alternative.

Though its process is still under development (a pilot plant has not yet been built), Treadwell Corp., New York, intends to take refined copper-sulfate solution and react it below 212 F. with hydrocyanic acid and sulfur dioxide. Copper cyanide and sulfuric acid form. The cyanide, insoluble in the acid, precipitates and is separated from the barren liquor by conventional means.
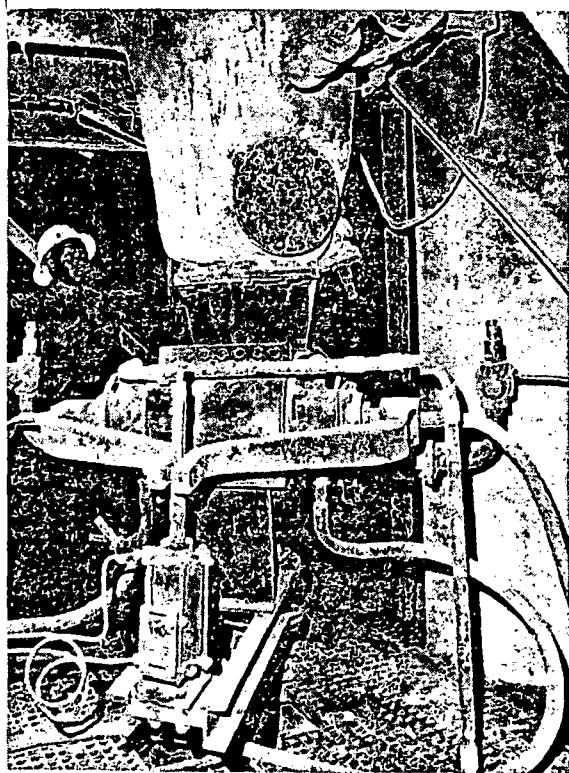
The copper cyanide is contacted with hydrogen gas at 570 to 750 F. to produce pure copper powder and hydrocyanic acid for recycle.

According to the inventor, the process should yield copper more cheaply than electrowinning or hydrogen reduction of copper sulfate, and at less cost than for smelting and electrorefining.
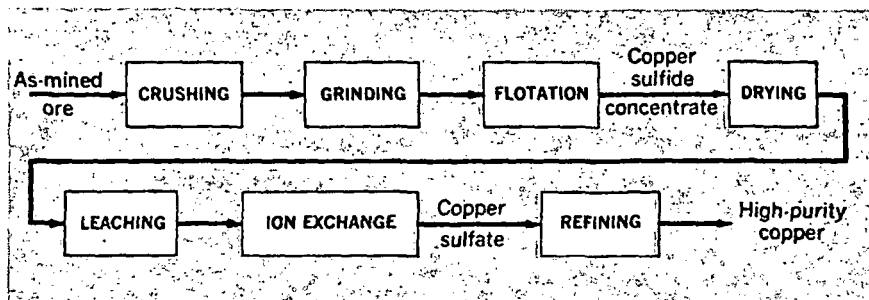
▶ **Refractory Recovery** — While much work has been done to improve the processing of ores from which copper already can be recovered, means for winning metal from hitherto worthless refractory deposits also have been developed.

Refractory ores are so completely tied to the worthless gangue that crushing, grinding and flotation cannot free the mineral value. Nor can presently used solvents leach these ores profitably.

Anglo American Corp. of South Africa (Johannesburg) has devised a method to recover metal from such ores at a cost said to compare favorably with that of conventional production. A plant will be completed in Mauritania in about two

| As-mined ore → | CRUSHING | → | GRINDING | → | FLOTATION | Copper sulfide concentrate → | DRYING |
| LEACHING | → | ION EXCHANGE | Copper sulfate → | REFINING | → High-purity copper |

NEW ROUTE FOR SULFIDE ORES is being investigated. Chemical process, unlike conventional hot-smelting operations, would win metal without venting harmful sulfur dioxide into the air. And it may require only half the capital.

years. Similar ones may be started shortly in Zambia and Italy.

In Anglo-American's Torco (treatment of refractory copper ores) process, dried ores are sent to a vessel to react with a secret ingredient at a high temperature. (Other investigators, in previous ill-fated attempts, tried sodium chloride and carbon; and in one case, salt and llama dung.) Copper is released as metal particles. The mixture is then cooled in water, and a 55% or higher copper concentrate is extracted by flotation.

Leaching with alkaline cyanide solution is being mentioned by several companies as a way to recover copper from refactory ores in tailings, overburden and other low-grade material.

Copper Range Co. of New York, for one, is planning a plant around such a process. Its pilot tests indicate that much normally lost metal can be recovered profitably by alkaline cyanide leaching.

▶ **Smokeless Smelting**—About 88% of U.S. copper production involves hot-smelting of sulfide ores. However, as a byproduct of the process, enormous quantities of noxious sulfur dioxide fumes are spewed into the air (although some is recovered as sulfuric acid). As an outcome, hydrometallurgical techniques that cause little or no air pollution are being groomed to challenge hot-smelting.

Leaching would do away with the large amounts of fuel, and the fluxes for slagging gangue, as well as the dust and fumes of smelting. In many steps, liquids would be handled instead of more-bothersome

solids. And such a process probably would not have a cement-copper production step—this would eliminate the problem of getting rid of the water-polluting ferrous sulfate made along with the precipitate.

On the other hand, the liquids would be corrosive, so that efficient washing of treated ores would be difficult. Moreover, no such leaching system has proved economical.

Yet, today's materials, equipment and technology can surmount the drawbacks—at least judging from what is being piloted and proposed.

In one plan, copper-sulfate concentrate from a flotation circuit would undergo a controlled roasting. Off-gas would be rich enough in sulfur dioxide so that it could be used directly in the manufacture of sulfuric acid. Not only would this cut down on the amount of baneful gas vented to the atmosphere, but the sulfuric acid would then be used to leach the sulfide-oxide mix produced by the roasting.

The resulting copper-sulfate solution would be purified and then refined by electrowinning or other means to yield pure metal.

Arizona Chemcopper has already run a pilot plant using a completely smokeless method. With a special solvent, ore is leached directly at a low temperature and pressure and under essentially noncorrosive conditions. Then the solution is purified by ion exchange. Copper is recovered by hydrogen reduction or electrowinning.

Sulfur is recovered as sulfuric acid. This could serve to leach oxide ores, if any, or could be converted to gypsum (calcium sulfate)

and sold. It also could be used to treat phosphate ores for making phosphate fertilizers.

For large plants, the cost of operating such a process is estimated to be about the same as for hot smelting. Capitalization is only about one half as much.

So, for plants either just being planned or now without a smelter, the technique is considered worthwhile. Its adoption at other locations is precluded by existing investments in smelting facilities.

However, with tightening pollution regulations, such a chemical means for winning copper may win industrywide acceptance.

New Relief for the Thirsty: Fresh Water from Wet Air

Fresh water from the air may solve the water-supply shortages for many islands and coastal regions of the world, and at a lower cost than from seawater desalting.

The method as proposed by Robert D. Gerard and J. Lamar Worzel, Columbia University oceanographers, requires a coastal location in the regular path of humid, maritime winds, with cold ocean water offshore. These conditions are met in most of the Caribbean islands, and in numerous other coastal regions of the world. An estimated 300 million gal. of water vapor in the lower atmosphere sweep across every mile of island shoreline exposed to the humid trade winds, according to the two scientists.

Cold ocean water from a depth of approximately 3,000 ft. would be piped to a condenser set up on shore to intercept the humid winds. Resultant cooling of the water-laden air would produce liquid condensate to be drawn off and stored as a fresh-water supply.

Calculations show that a 3-ft.-dia. pipe running 1 mi. from deep water in the Virgin Island Basin to an onshore condenser could produce 1-million gal. of fresh water a day. The cost could be kept low by using wind-driven generators to pump the ocean water.

**UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.**

NEW DEVELOPMENTS IN MINERALS AND ENERGY

WASHINGTON STATE

1980

by

Bonnie Butler Bunning

State of Washington
Department of Natural Resources
Division of Geology and Earth Resources
Olympia, Washington   98504

December 1980

METALLIC MINERAL EXPLORATION

SUMMARY

The 1980 level of mining and exploration in Washington varied with each commodity (table 1). While 20 to 30 companies explored for uranium in 1978, only an estimated 16 were active in 1980 and of those, 50 percent were either seeking venture partners or pulling out of Washington entirely. Many have been discouraged by the relatively low U_3O_8 price and the uncertain political future of nuclear power generation. Gold and silver activity, for obvious reasons, showed a dramatic increase both in new hard rock mining projects and prospector activity, including small dredging operations on the upper Columbia River and in the Cascades, and substantial recreational gold panning. Copper exploration attracted few newcomers this year and operations have been carried at the maintenance level on several projects since 1979. Some new molybdenum exploration was initiated and several molybdenum targets were drilled across the state. New zinc-lead exploration remained at a minimum, while at several old lead-zinc mines, geologists drilled new ore extensions to buoy proven reserves while waiting optimistically for the zinc price to rise to a 50 cent minimum.

Okanogan County saw the most activity with 14 companies reported working in the area, followed by at least 13 in Stevens County, 9 in Ferry County, 6 in Pend Oreille County, 2 each in Chelan, Spokane, Skamania, Snohomish and Whatcom Counties and at least 1 in Pierce and King Counties (table 2). Many others worked generally in the Okanogan Highlands and north and south Cascades.

Washington Public Power Supply has permanently discontinued all exploration in the state, Reserve Oil and Minerals has left Northeast Washington for Albuquerque, New Mexico, and Pathfinder Mines will be gone by 1981. Cyprus Mines has been taken over by Amoco. Rocky Mountain Energy has recently opened

a Spokane office and is aggressively pursuing uranium targets in the northeastern part of the state.

Altogether a minimum of 47 different companies were active in exploration and mining of metallic minerals in the 1980 season, in addition to countless small placer operations (table 3).

An estimated several hundred leases were held on state lands for mineral exploration. Hundreds more were committed to oil and gas efforts.

MINERAL EXPLORATION AND MINING ACTIVITY

Chelan County

Reported activity in Chelan County was minimal in 1980. Bethex is known to have dropped interest in its Basalt Peak property on the Chiwawa River after drilling in 1979 (figure 1).

No activity reported at the Gold King mine near Wenatchee.

Ferry County

Gold. — Day Mines Inc. continued production at the Knob Hill mine in Republic (figure 2). Reserves of 128,745 tons of 0.43 oz/T gold and 1.63 oz/T silver are published on this epithermal vein and breccia deposit, (table 4). Drilling and limited mining is continuing to increase reserves on productive vein extensions.

Wheelbarrow, shovel, and hand-held drill were the tools of Matt Obersbee in his constant quest for gold at the Never Fear mine in the Republic district. No production is reported in the mineralized greenstones of the mine.

A 100-ton cyanide plant produced gold this year at the Valley View (Golden Valley) mine near Curlew Lake. Ore was mined from low-grade gold-silver bearing quartz veins by Ruby Mines, Inc.

Houston International Minerals Co. conducted extensive drilling and exploration this year in the Republic district.

Plans for a 60,000 ton-per-day mine on Mount Tolman are progressing smoothly toward a late 1983 early 1984 startup date. Final agreement with the Colville Federated Tribes is imminent and a final draft E.I.S. will be submitted this December. Construction of the mine and mill complex, a 2½-year project, is slated to begin in mid-1981. Training programs for employees are already underway with help from CETA and Indian Action Program funds through

Spokane Community College. Reserves published are 900 million tons of 0.1 percent MoS_2 and 0.09 percent copper (table 4).

Base Metals And Uranium. — Homestake, BurWest, Rocky Mtn. Energy, Western Nuclear, and others explored in the county for uranium as well as lead and zinc.

Lincoln County

Rexcon was active again in the Sand Flat area, which was drilled as a uranium target by Anaconda in 1978 (figure 2).

Okanogan County

Silver And Gold. — Rocky Mines Co. of Republic, Washington began mining at the Silver Bell mine with 150,000 tons of drilled reserves, grading 5.5 oz/T silver and 0.02 oz/T gold (table 4). It is the first major metal mine to begin production in Okanogan County in at least 25 years. The mine is located in brecciated volcanics of the Klondike Mountain Formation (figure 1). Gangue consists of quartz, fluorite, and sanidine, with pyrite and dustlike inclusions of silver. The ore is milled at the Dankoe mill north of Nighthawk, Washington, and is smelted in Trail, British Columbia.

JNT and GPM Enterprises has leased the Silver Mountain (Silver Star) property in the Loomis mining district. Silver, gold, and lead values are reportedly found in a 4-foot quartz vein bearing galena and arsenopyrite. The Alder mine, a major past producer of gold in the Twisp district, was under investigation this season. Geochemical studies and short core drilling were conducted. The 300-foot shaft of the Ivanhoe mine was pumped out this year, and the mine was sampled for silver by Wallace Diamond Drilling. Cyprus has been investigating the old American Rand mine for gold. Other companies have also been active in precious metal searches this season.

Base Metals and Uranium. — Bear Creek Mining Co. drilled the Sherman property for copper and molybdenum, while AFM Exploration from Canada conducted approximately 5,000 feet of drilling at the Starr Molybdenum locality.

Quintana was looking for partners for its Mazama area copper-molybdenum prospect. Other companies maintaining a copper-molybdenum position were Bethex on Thunder Mountain, and United Mines at the Copper Glance prospect. Cyprus, Duval, and Amax, among others, also conducted molybdenum and copper exploration in the county. Drilling was completed on the Starr-Molly prospect west of Tonasket by an undetermined party. Denison Mines, Duval, Phillips Uranium, and Chevron explored for uranium in the Okanogan County area.

Pend Oreille County

Plans to open pit 2½ million tons of lead-zinc-silver ore are being proposed for 1981, at Rocky Creek mine by operators Joe McNamee, and others (figure 2). The mine is located on the southwest side of Seldom Seen Mountain, 12 miles by road from Tiger townsite.

Gulf Resources Co. explored extensions of the Pend Oreille mine in a modest drilling and mapping program.

Joy Mining Co. drilled a lead-zinc prospect in the county this year and BurWest, Homestake, and Conoco, among others, continued evaluation of both hard and soft rock uranium occurrences.

Reserve Ore and Minerals, formerly working in the Tiger Formation, has dropped all interest concurrent with a move out of the area.

Pierce County

The sole reported exploration group in Pierce County was Amoco Minerals, which worked on its copper-molybdenum, gold-silver property on the Carbon River north of Mount Rainier (figure 3).

Skamania County

Amoco Minerals optioned their claim group to Denison Mines, who is reported to have drilled the property during the 1980 field season. The copper-molybdenum prospect lies on the north side of the Silver Star stock (figure 3).

Snohomish County

Exxon and Occidental maintained a low-level position at their respective copper-molybdenum properties — the Silver Creek show on the Skykomish River and the Sunrise-Vesper Peak prospect (figure 4).

Spokane County

At the start of the year, Westinghouse in conjunction with Mineral Associates of Seattle had plans to begin an in-situ leach test of certain autunite deposits on Mount Spokane (figure 2). Both companies have since shelved interest.

Stevens County

Uranium. — Midnite mine, run by Dawn Mining Co. in turn controlled by Newmont Mines, continued production on the Spokane Indian Reservation through 1980. Rock was processed at the rate of 21,000 TPD from the mine, while 960 TPD of ore was handled. Ore grade in mine and stockpiles is 0.153 percent U_3O_8. Mine geologists prospected the surrounding holdings of Dawn Mining in an effort to discover additions or extensions to present reserves (table 4).

A few miles to the south the Sherwood Project run by Western Nuclear maintained its target 2,000 TPD; mill feed ran 0.089 percent U_3O_8 (table 4). Current thinking suggests that the Sherwood deposit is an eroded portion of the Midnite deposit, laid down as mineralized boulders in the Sherwood conglomerate.

Sabine Products through Joy Mining Company continued plans to heap leach uranium from a bog on Flodelle Creek northeast of Colville (figure 2). Activity is expected as soon as the various permits are obtained and agencies responsible are satisfied. Western Nuclear's Spokane Mountain uranium find described in the December 1978 issue of Economic Geology is scheduled for production at some unspecified future date.

Western Nuclear and Rocky Mountain Energy drilled uranium prospects in the county, in addition to general exploration joined by Homestake, Minatome, and others.

Gold-Silver. — Charleston Resources of Vancouver shipped three carloads of silver ore from a newly discovered vein at the Melrose mine near Northport, Washington this past season. Irregular polymetallic ore shoots are mined from a 6-foot quartz vein in argillite; ore averages 24 oz/T silver (table 4). An agreement between Charleston Resources and Arbor Resources, also of Vancouver, has been signed. Arbor Resources will initiate an in-depth study of the mine area, to include soil and stripping surveys, in an attempt to block out sufficient proven reserves.

On the Canadian border, also in the Northport district, a group of prospectors is doing limited development on the Simons property, a free gold-bearing quartz vein. Farther south in the Kettle Falls district, an Olympia company explored the Vanasse property; a deposit of silver, copper, lead and antimony sulfides in quartz veins that mineralize arkose and quartzite units. Gold-silver and base metal work is also underway at the First Thought mine near Orient. A new mill has been set up in Laurier to handle local gold ore.

Base Metals. — Eagle Mountain Mining Co. has re-opened the Copper King mine northeast of Chewelah to geologically define new exploration targets. The company has also recently leased the adjacent Blue Star claims of Chewelah Eagle Mining Co.

An Oregon group has initiated predevelopment exploration in the Deer Trail Group of mines. Underground mapping, sampling, etc. is being considered.

Limited tungsten production is reported again from the Blue Grouse mine near Springdale.

Copper-tungsten exploration was carried out on Mineral Mountain near Orient. Work in 1980 consisted of geophysical surveys and drilling.

In the Northport area, Toledo Resources Ltd. ran a magnetometer survey on their Copper Find claim group to evaluate the porphyry copper potential of this chacopyrite-bornite-molybdenite occurrence.

Zinc exploration was also conducted near Northport by Houston International Minerals Corp. (formerly Houston Oil and Minerals). Geologic mapping and sampling was done at projects in the Leadpoint and Flagstaff Mountain areas.

Whatcom County

At the New Light gold mine in the Slate Creek district, Lions Mines continues limited mining of stockpiles and work on a new mill to expand production from 100 TPD to 200 TPD (table 4). This mine has reserves of 200,000 tons, the grade of which is not known.

A Bellingham group is re-evaluating the Lone Jack mine, a major past producer of free-milling gold ore (figure 4). Other reported activity in Whatcom County is centered at the Great Excelsior mine, a silver-mineralized breccia, under control of U.S. Borax.

GOLD PLACER MINING AND SMALL-SCALE GOLD OPERATIONS

Along with countless weekend gold panners and prospectors there were many placer gold mining operations in the Cascade region, and northern Stevens County.

Kittitas County

The Liberty district saw several small 5 TPD free-milling gold operations producing throughout the summer. Ore averaging 0.33 oz/T was processed using ball mills, amalgamation plates, tables, etc.

Goodfellow Construction Co. of Wenatchee mined 150 yards per hour in Williams Creek of the Liberty district, using dragline, dozer, and ripper with a washing plant on the bank. Numerous other part-time concerns operated on Swauk and Williams Creeks.

In the Blewett district summer placer operations were active on Shasser, Peshastin, and Negro Creeks. Bill Priestly mined lode gold on a small scale in Culver Gulch.

Okanogan County

In Okanogan County the Similkameen River saw numerous floating suction dredges up to 8" diameter. Nuggets recovered were sold to local jewelers.

Stevens County

At least eight new leases were taken for gold dredging on the upper Columbia River this year. A minimum of four new leases were operating in the Sheep Creek drainage north of the Columbia River as well.

Whatcom County

Ruby Canyon and Slate Creeks saw a flurry of small-scale panning, sluicing, and dredging operations throughout the summer.

NONMETALLIC MINERAL PRODUCTION

Production in dollars of the nonmetallics industry remained relatively constant over the past 5 years (figure 5). While figures for 1980 production are not available yet, it is expected that many nonmetallic efforts will show a downturn this year due to the uncertain state of the economy and high cost of new building starts.

Crushed Rock and Building Stone

The crushed rock/building stone industry statewide has been hurt by the slow-down in building activity during 1980. While several companies reported "holding steady" since 1979, others commented that the economy was hard on business in 1980. As one operator put it "the quarry is used on an as-needed basis and we haven't needed it yet this year." The largest crushed stone operator in the state is the state's Department of Transportation. Another big producer-user is the Burlington Northern railroad.

Table 5 shows the change in company activity for various crushed rock products from 1979-1980.

Silica Sand

Silica sand was produced by at least three operators in Washington State. They are Industrial Mineral Products of King County, Wenatchee Sand and Silica of Chelan County, and Lane Mountain Silica of Stevens County. Silica is mined mostly from quartzite, crushed and treated to remove iron, etc. The silica sand product is then used for glass making or smelter flux. Producers report that business in 1980 had increased from 1979 levels.

Barite

Of the nonmetallic commodities, barite was the only one with significant new development. Washington Barite Corporation continued production from their newly opened barite mine on Flagstaff Mountain near Northport in

Stevens County (table 4).

Barite is shipped to Montana for use as drilling additives. In addition, Washington Barite Corporation also conducted exploration in the O'Toole Mountain and Bruce Creek areas of Stevens County.

Wallace Diamond Drilling explored for high grade barite in the Eagle Mountain area. Other individuals are known to be assessing the barite occurrences of Washington State.

Olivine

Two companies presently mine olivine from the Twin Sisters Mountain area in Whatcom and Skagit counties. Olivine Corporation, in Whatcom County, tripled business in 1980 from 10,000 tons in 1979 to 30,000 tons so far this year. Together the two companies make Washington one of the top two olivine producers in the nation.

Diatomite

Washington is also a leading (top 3) producer of diatomite. Witco Chemical Corp. produces diatomite from two pits near George in Grant County. Business remains essentially unchanged since 1979. The diatomite is used exclusively as a filtering agent and insulating medium.

Limestone, Dolomite, Marble

Production of dolomite was off an estimated 20 percent in 1980, though the total number of mines remains unchanged. The production of limestone and marble did not differ substantially from production in 1979.

Clay

Clay operations held their own as long as they weren't suppliers for the hard-hit building industry. Production in the building-related clay industry, however, was way down in 1980.

Magnesium

Northwest Alloys, Inc., a subsidiary of Alcoa, continued to produce magnesium from dolomite mined in Stevens County. All production goes into making Alcoa products elsewhere in the nation, so the Addy plant is unaffected by market

conditions which are slightly off this year. The silicon furnace shut down in the fall of 1979 and remains inoperative.

A reliable supply of inexpensive energy would likely bring the metallic silicon operation back into business again, though no projections are being made at this time.

Feldspar, Gypsum, Jade, Talc and Peat

Other commodities mined in Washington contribute little to the overall economy of the state. Intermittent mining of jade, gypsum, and feldspar continues. Talc operators largely mine soapstone for carving. Some small-scale talc mining was carried out in the Springdale, Wenatchee, and Marblemount areas of Stevens, Chelan and Skagit Counties, respectively. Several "Mom and Pop" peat operators, active in the past, maintained a low profile in 1980 due to retirement and general low production.

ENERGY ACTIVITY

OIL AND GAS

Drilling

Two drilling permits have been approved for oil and gas efforts in the state this year. Shell Oil has both permits located in NW¼NW¼sec. 33, T. 15 N,R. 19 E. and SW¼SW¼ sec. 34, T. 15 N.,R.19 E. of Kittitas County. Only the first site is currently being drilled. Target depth is 15,000-20,000 feet.

Leasing

Leasing activity reached a high level in 1980, with 300 applications for 40,000 acres by eleven different companies in Benton County alone, during the last week in October. Shell is the major lessee. Companies and individuals not willing to reveal their position in the leasing race are not recording their private leases. (Total leased acreage figures are minimum estimates based on knowledge of state leases and minor information obtained on fee or federal leases.)

Shell is by far the largest land holder with a minimum of 500,000 acres in Grant, Benton, Kittitas, and Yakima Counties. Shell is currently securing new leases in those four counties, as well as in Walla Walla County.

Texaco is reported to have 640 acres in Grant County and is actively working on more acreage in that county.

Night Royal, a Denver company is also active in Grant County. Along with applications to the BLM, Night Royal has at least 20,000 acres in the county.

Union Oil joins the others in the Columbia Basin, holding 6,000-7,000 acres in Grant, Kittitas and Yakima counties.

Gulf Oil, working also in the eastern Washington area, maintains at least 16,000-17,000 acres.

Champion Oil, a Denver-based independent has a known 12,000-acre position in the Basin as well.

Dolores Yates, who has published an Oil and Gas Information Circular from Portland for several years, has now turned speculator with 30,000 acres of Columbia Basin land under lease, much on BLM controlled ground.

Another area attracting oil and gas activity in 1980 was the extreme southwestern corner of the state, across the Columbia River from the newly discovered Mist, Oregon gas field.

Snyder Oil has a 27,000-acre minimum position in Wahkiakum and Cowlitz Counties. Rushing Minerals is also working in Wahkiakum County. Between Wahkiakum and Pacific Counties, Rushing Minerals maintains a 23,000-acre position in the state.

Cardinal Oil, the large independent who leased the Mist, Oregon area before productive gas was discovered, also maintains an undetermined position in southwest Washington.

Getty Oil holds 18,000 acres in Grays Harbor County. As yet, no other companies have made leases public there, but several are known to be considering the area.

Jerry Ryan of May Petroleum in Jefferson and Benton Counties has leases totaling 74,000 acres.

Eagle Exploration is active in Adams, Whatcom, Kittitas, and Yakima Counties, with 8,000 acres tied up. A section (640 acres) of state land in Jefferson County is also leased to Eagle Exploration.

Reports have been received of oil and gas activity in the Wenatchee River area, but no confirmation of Chelan County activity could be made.

COAL

Interest in Washington coal resources remains fairly high, although no new coal mining operations started in 1980.

Washington Irrigation and Development remains the largest coal producing entity in the state (table 6). Approximately 5 million tons per day are produced at the open-pit mine near Centralia; total production is used to generate power at the adjacent thermo-electric plant. Confirmation drilling of reserve holdings and seam characterization prior to mining continue; present reserves are estimated to be approximately 60 million tons.

The only other coal producer in the state at the present time is Palmer Coking Coal of Ravensdale. Palmer produces approximately 20,000 tons of bituminous coal per year, mostly for small institutional contracts and domestic use.

Burlington Northern maintains an active mapping and drilling program in the Green River district of King County. In addition, they are actively evaluating other BN lands in western Washington where higher rank coal is known to occur.

Several timber companies are active and many Rocky Mountain and Midwestern coal companies showed increased interest in the state's coal resources. Exploration drilling work was concentrated in the Chehalis, Green River, Wilkeson-Carbonado, Fairfax-Ashford, and Grande Ronde coalfields of King, Pierce, Lewis, and Asotin Counties. Companies known to be actively drilling and exploring are listed in table 6.

In 1979 and 1980 Sandia Corporation conducted drilling and site characterization studies for a proposed underground coal gasification project in northern Lewis County, 3 miles east of the Widco Mine. A test for that basin is yet to be designed and no concrete plans for the project have been made.

The State of Washington and Gulf Research & Development Co. have jointly submitted a proposal to the U.S. Department of Energy for a cooperative underground coal gasification project in Washington State lands. A specific site has yet to be selected. The decision on the DOE grant request is not expected until mid-January of 1981.

GEOTHERMAL ENERGY

Several private companies have shown interest in Washington's geothermal potential, including Burlington Northern, Seattle City Light, and Washington Public Power Supply System. Phillips and Chevron are examining the situation with a less active interest at the present time. More aggressive exploration is expected within the next few years.

WASHINGTON DIVISION OF GEOLOGY AND EARTH RESOURCES
1980 ENERGY AND·MINERAL ACTIVITY

Eleven of the seventeen Division of Geology and Earth Resources' geologists worked on energy and mineral projects in 1980. In March a new field office was opened in eastern Washington. Projects conducted from that office include coal geology of the Grouse Creek interbed, Columbia River Basalt, Asotin County, Washington, and the geologic potential for uranium deposits, including a catalog of radioactive occurrences, in Washington State.

The state's western coal resources and coal geology are being mapped and evaluated by several state geologists. Work has been concentrated in King and Kittitas Counties with plans to study Cowlitz, Whatcom, and Lewis Counties. The first results of that effort, "The geology and energy resources of the Cle Elum - Roslyn area", is now on open-file (80-1) in the division. In addition, concentrated exploration on state lands is being conducted on selected sections in the Centralia - Chehalis basin.

The Division of Geology and Earth Resources is continuing to evaluate the state's geothermal potential under a renewable contract from the U.S. Department of Energy. Eight temperature gradient holes are planned along the crest of the Cascades including the Stevens Pass, Snoqualmie Pass, White Pass, Mount Rainier, and Wind River areas. Specific state studies include a hydrothermal investigation of Yakima County warm water aquifers, a mineralogic and temperature evaluation of springs across the state, and a well temperature study throughout eastern Washington. Other investigations sponsored by the program are the geology and geothermal potential of Quaternary volcanics in the Bumping Lake area, age dates of Quaternary volcanics in the southern Cascades, a time-composition model of Quaternary volcanics in the Cascades, and lineament mapping in the southern Cascades.

Special attention is being paid to Mount St. Helens where three temperature gradient holes were drilled in 1979. One of the 1979 holes was destroyed in the May 18th blast, one was remeasured with no apparent change, and a third was isothermal and of no further interest.

Division of Geology and Earth Resources publications for 1980 include the following citations related to energy and minerals:

Bulletin 72	"Myers Creek and Wauconda districts of northeastern Okanogan County," by Wayne S. Moen
Information Circular 69	"Directory of Washington mining operations-1979," by Carl McFarland, Glennda McLucas, James Rigby, and Keith Stoffel.
Information Circular 70	"Theses on Washington geology, 1901-1979,"compiled by Connie Manson
Open-File 80-1	"Geology and energy resources of the Roslyn-Cle Elum area, Washington,"by Charles Walker
Open-File 80-4	"Bibliography of geothermal resource information for the State of Washington," by Mike Korosec
Open-File 80-6	"Quaternary volcanics and volcanic centers in the State of Washington," by Michael Korosec and Glennda McLucas
Open-File 80-7	"Well temperature information and locations in the State of Washington," by Michael Korosec and Keith Kaler
Open-File 80-8	"Geology of the White Pass - Tumac Mountain area, Washington," by Geoff Clayton
Open-File 80-9	"Heat flow and geothermal gradient measurements in Washington to 1979, and temperature depth data collected during 1979," by David Blackwell
Open-File 80-11	"Table of thermal and mineral spring locations in Washington," by Michael Korosec

LEGISLATIVE ACTIVITY AFFECTING MINING

Regulations adopted this year under Washington Administrative Code 402-52 govern uranium and thorium mill tailing piles, and set a schedule of fees for their licensing and inspection. The Department of Social and Health Services is the designated radiation control agency responsible for making inspections, granting licenses, and writing environmental impact reports when necessary. The specific sections address the siting of tailings in order to protect human population, drinking water, air quality, and wildlife; and to prevent wind and water erosion, toxic seepage, and fault disruption or flooding either while piles are active or abandoned. Table 7 summarizes the maximum fees charged for licensing. If the actual cost of making major or minor amendment or renewal is less than the maximum, reimbursements will be made.

The moratorium on leasing state lands for coal operation will remain in effect for the next 6-8 months while regulations controlling leasing are being rewritten.

TABLE 1.— 1980 Commodity Index of Metallic Mineral Exploration & Mining Activity

Washington State

COPPER AND MOLYBDENUM

Amoco

Bear Creek Mining Co.

Bethex

Denison Mines

Duval

Eagle Mountain Mining, Inc.

Exxon

Joe McNamee

Lowell Warner

Occidental

Quintana

Toledo Resources

United Mines

LEAD AND ZINC

BurWest

Gulf Resources Corp.

JNT-GPM Enterprises

Joe McNamee

Joy Mining Co.

Lowell Warner

MOLYBDENUM

AFM Exploration

AMAX Exploration

Rexcon

SILVER AND GOLD

Amoco Minerals

Arbor Resources Ltd.

Charleston Resources

Cominco American, Inc.

Cyprus Mines (now Amoco)

Day Mines

Houston International Minerals

JNT-GPM Enterprises

Joe McNamee

Lowell Warner

Matt Obersbee

Rocky Mines

Ruby Mines, Inc.

U. S. Borax

Wallace Diamond Drilling

TUNGSTEN

Joe McNamee

URANIUM

BurWest

Chevron

Denison

Energy Fuels

Homestake Mining

Houston International Minerals

TABLE 1. — 1980 Commodity Index of Metallic Mineral Exploration & Mining Activity

Washington State

URANIUM (Cont'd)

Joy Mining

Midnite Mines

Minatone

Mineral Associates

Pathfinder

Phillips Uranium

Rexcon

Rocky Mtn. Energy

Sabine Products

Teton Exploration

Western Nuclear

TABLE 2. —   1980 COUNTY INDEX OF METALLIC MINERAL EXPLORATION & MINING ACTIVITY

WASHINGTON STATE

COUNTY	COMPANY	COMMODITY
Chelan	Bethex	Au
	Cyprus Mines	Au
Ferry	Amax	Mo
	BurWest	Pb-Zn
	Day Mines, Inc.	Au, Ag
	Homestake Mining Co.	U
	Houston International Minerals Co.	Au, Ag
	Matt Obersbee	Au, Ag
	Rocky Mtn. Energy	U
	Ruby Mines, Inc.	Au, Ag
	Western Nuclear	U
King	Cominco American Inc.	Au
Lincoln	Rexcon	U
Okanogan	AFM Corp.	Mo
	Amax	Mo
	Bear Creek Mining Co.	Cu/Mo
	Bethex	Cu/Mo
	Chevron	U
	Cyprus	Au
	Denison Mines, Inc.	U
	Duval Corp.	Cu, Mo
	JNT-GPM Enterprises	Au,Ag,Pb,Zn
	Pathfinder	U
	Phillips Uranium	U

TABLE 2. —   1980 COUNTY INDEX OF METALLIC MINERAL EXPLORATION & MINING ACTIVTY

COUNTY	COMPANY	COMMODITY
Okanogan	Quintana	Cu-Mo
	Rocky Mines	Ag
	United Mines	Cu-Mo
Pend Oreille	BurWest	U
	Conoco	U
	Gulf Resources Corp.	Pb/Zn
	Homestake Mining Co.	U
	Joe McNamee	Pb/Zn,Cu,Ag
	Joy Mining Co.	Pb/Zn
Pierce	Amoco Minerals	Au/Ag,Cu/Mo
Skamania	Amoco Minerals	Cu/Mo
	Denison Mines,Inc.	Cu/Mo
Snohomish	Exxon	Cu/Mo
	Occidental	Cu/Mo
Spokane	Mineral Associates	U
	Westinghouse	U
Stevens	Arbor Resources Ltd.	Ag
	Charleston Resources	Ag
	Eagle Mountain Mining, Inc.	Cu
	Homestake Mining Co.	U
	Joe McNamee	Cu,W,Au
	Joy Mining	U
	Lowell Warner	Ag/Au,Pb,Sb,Cu
	Minatome	U
	Newmont	U
	Rocky Mountain Energy	U
	Sabine Products	U
	Toledo Resources Ltd.	Cu,Mo

(24)

TABLE 2: —— 1980 COUNTY INDEX OF METALLIC MINERAL EXPLORATION & MINING ACTIVITY

COUNTY	COMPANY	COMMODITY
Stevens	Western Nuclear Inc.	U
Whatcom	U.S. Borax	Ag
	Lions Mines	Au
Unidentified Locations	Cominco American, Inc.	Au
	Minatome	U
	Teton Exploration	U

TABLE 3. — __Mining Companies Active in Washington, 1980__

AFM Exploration	Lions Mines Ltd.
Amax	Midnite Mines, Inc.
Amoco	Minatome Corp.
Bear Creek Mining Co.	Mineral Associates II
Bethex	Occidental Petroleum
BurWest	Pathfinder Mines
Charleston Resources	Phillips Uranium
Chevron	Quintana Minerals Corp.
Cominco American Inc.	Rexcon
Conoco	Rocky Mines
Cyprus Mines	Rocky Mountain Energy
Dawn Mining Co.	Sabine Products, Inc.
Day Mines, Inc.	St. Joe American Corp.
Denison Mines, Inc.	Teton Exploration
Duval Corp.	Toledo Resources Ltd.
Eagle Mountain Mining	Union Carbide
Energy Fuels	United Mines
Exxon	U.S. Borax
Gulf Resources Co.	Utah International
Homestake Mining Co.	Wallace Diamond Drilling
Houston International Minerals Corp.	Washington Barite Corp.
JNT and GPM Enterprises	Western Nuclear, Inc.
Joy Mining Co.	Westinghouse
Kimmer Coal Co.	

TABLE 4. — Mine Production, Reserves, Grade

Washington State

MINE	COUNTY	COMMODITY	PRODUCTION	RESERVES	GRADE
Knob Hill mine	Ferry	Au,Ag	Production for 1979 - 16,260 oz. Au, 58,045 oz. Ag	128,745 T	0.43 oz/T Au 1.63 oz/T Ag
Melrose mine	Stevens	Ag	45T Av. 24#oz. Ag/T, shipped in 1980.		Av. 24 oz/T
Midnite mine	Stevens	U	Present production rates 21,000 T/day (ore + waste) 960 TPD (ore)	766,000 T 1,600,000 T	0.153% U_3O_8 0.05% U_3O_8
Mount Tolman[1]	Ferry	Mo/Cu	Planned rate of 60,000 (TPD)	900 mT	0.1% MoS 0.09% Cu
New Light mine	Whatcom	Au	Plans to upgrade production capacity from 100 to 200 TPD	200,000 T	NA
Sherwood mine	Stevens	U	Present ore production rate 2,000 TPD	8 mT	.089% U_3O_8
Silver Bell	Okanogan	Ag	10,000 tons in 1980	150,000 T	5.5 oz/T Ag 0.02 oz/T Au
Flagstaff Mtn. mine	Stevens	Ba	Production 1979-1980 22,500 T	8,000 T proven 24,000 inferred (1960)	Present statistics not available

[1] Scheduled for Production 1983-1984

TABLE 5.- Crushed Rock/Building Stone

PRODUCT	1979 NUMBER OF OPERATORS	1980
Andesite	5	3
Basalt	76	62
Diorite	2	0
Felsite	1	1
Granite	3	1
Rhyolite	1	0
Sandstone	3	2
Shale	2	1
New Operators (of all products)	7	6
TOTAL	100	76

TABLE 6. —   COAL EXPLORATION COMPANIES ACTIVE IN WASHINGTON, 1980

|	
ABCON Engineering (Luscar Ltd.)	Gulf Research and Development Corp.
Amax Coal	Gulf Resources Exploration Corp.
AMCA Coal Leasing	Kemmerer Coal Co.
ARCO Coal	Kimmer Coal Co.
Bear Creek Mining	Palmer Coking Coal
Burlington Northern Inc.	TKW Corp.
Exxon	Utah International
Gulf Mineral Resources	Washington Irrigation & Development Corp.

A.	Application fee	$ 27,000
B.	License fee	165,000
C.	Amendment fee	
	Major	10,000*
	Minor	800*
	Administrative	85
D.	Renewal fee	10,000*
E.	Annual Inspection fee	90,000
*	Maximum fee allowed - may be less	

EXPLANATION

▲ GOLD AND / OR SILVER
■ MOLYBDENUM AND / OR COPPER
● LEAD AND / OR ZINC
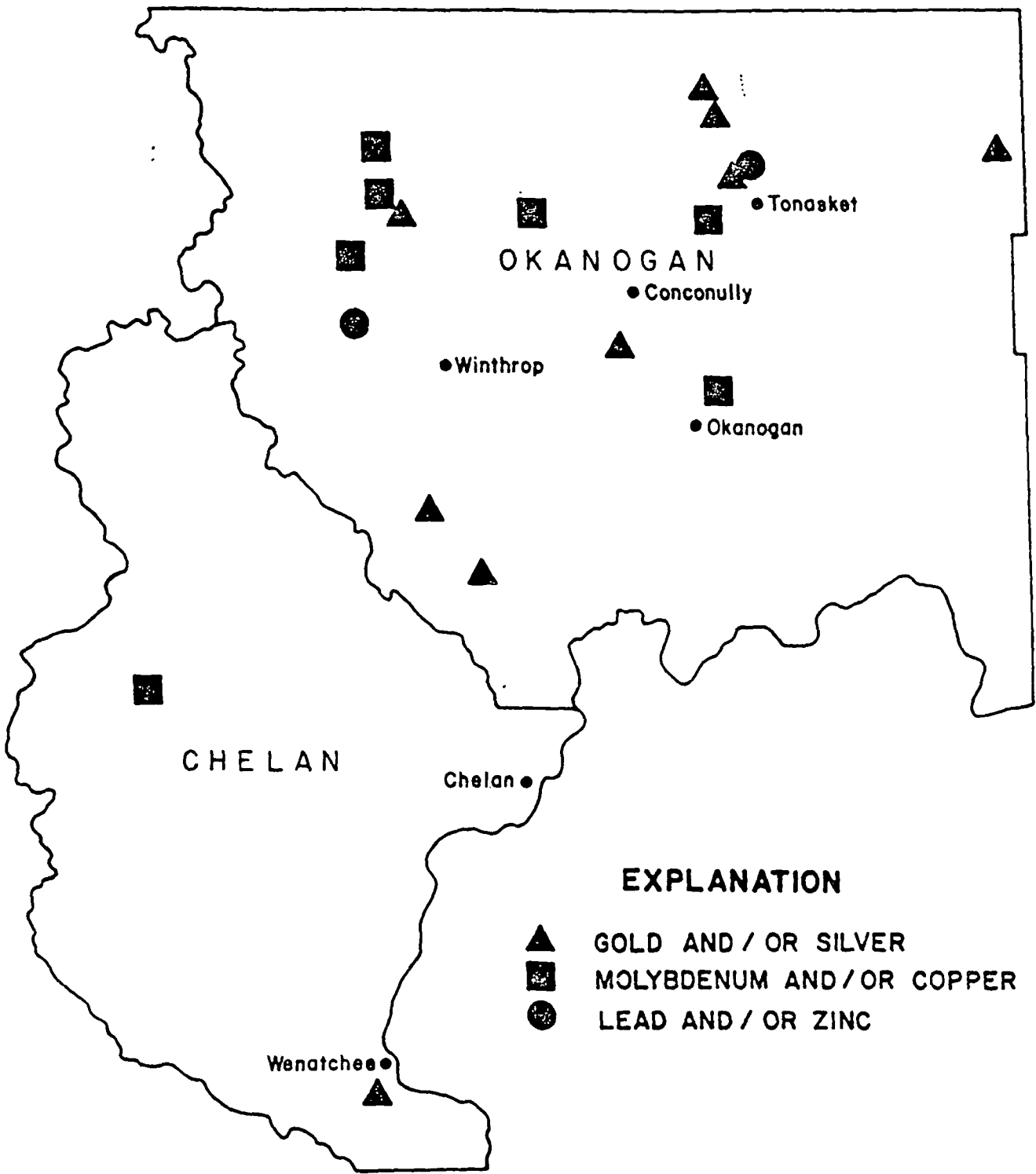
1980 MINERAL EXPLORATION AND MINING ACTIVITY

IN OKANOGAN AND CHELAN COUNTIES

FIGURE 1
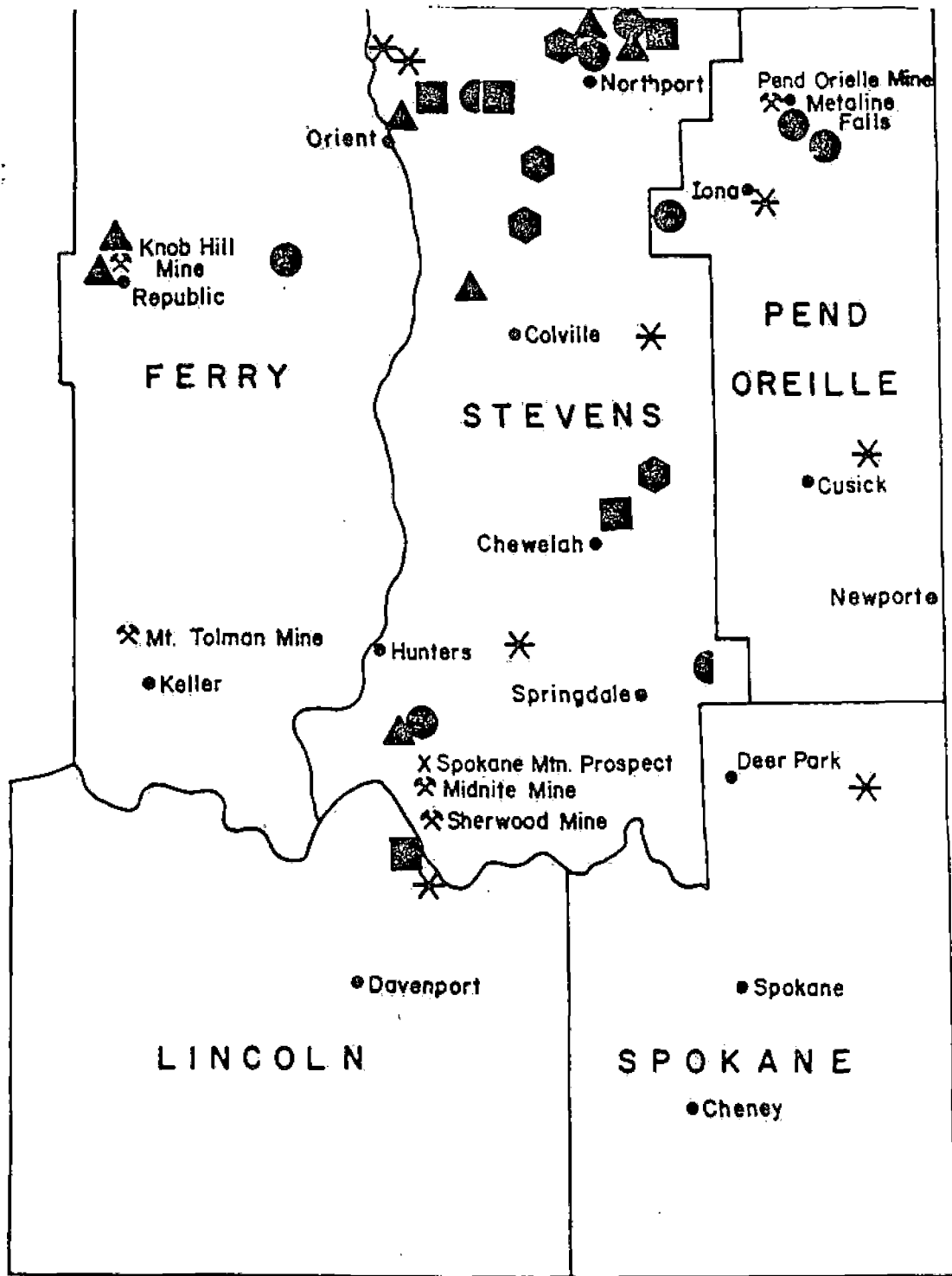
EXPLANATION

▲ GOLD AND / OR SILVER	✳ URANIUM
▦ MOLYBDENUM AND / OR COPPER	⬡ BARITE
● LEAD AND / OR ZINC	◗ TUNGSTEN

1980 MINERAL EXPLORATION AND MINING ACTIVITY IN PEND OREILLE, STEVENS, FERRY, LINCOLN, AND SPOKANE COUNTIES

FIGURE 2
(32)

Map showing:

- Tacoma
- PIERCE
- Olympia
- THURSTON
- Mt. Rainier
- Chehalis
- LEWIS
- COWLITZ
- Kelso
- Mt. St. Helens
- Mt. Adams
- SKAMANIA
- CLARK
- Stevenson
- Vancouver

EXPLANATION

▲ GOLD AND / OR SILVER

▨ MOLYBDENUM AND / OR COPPER
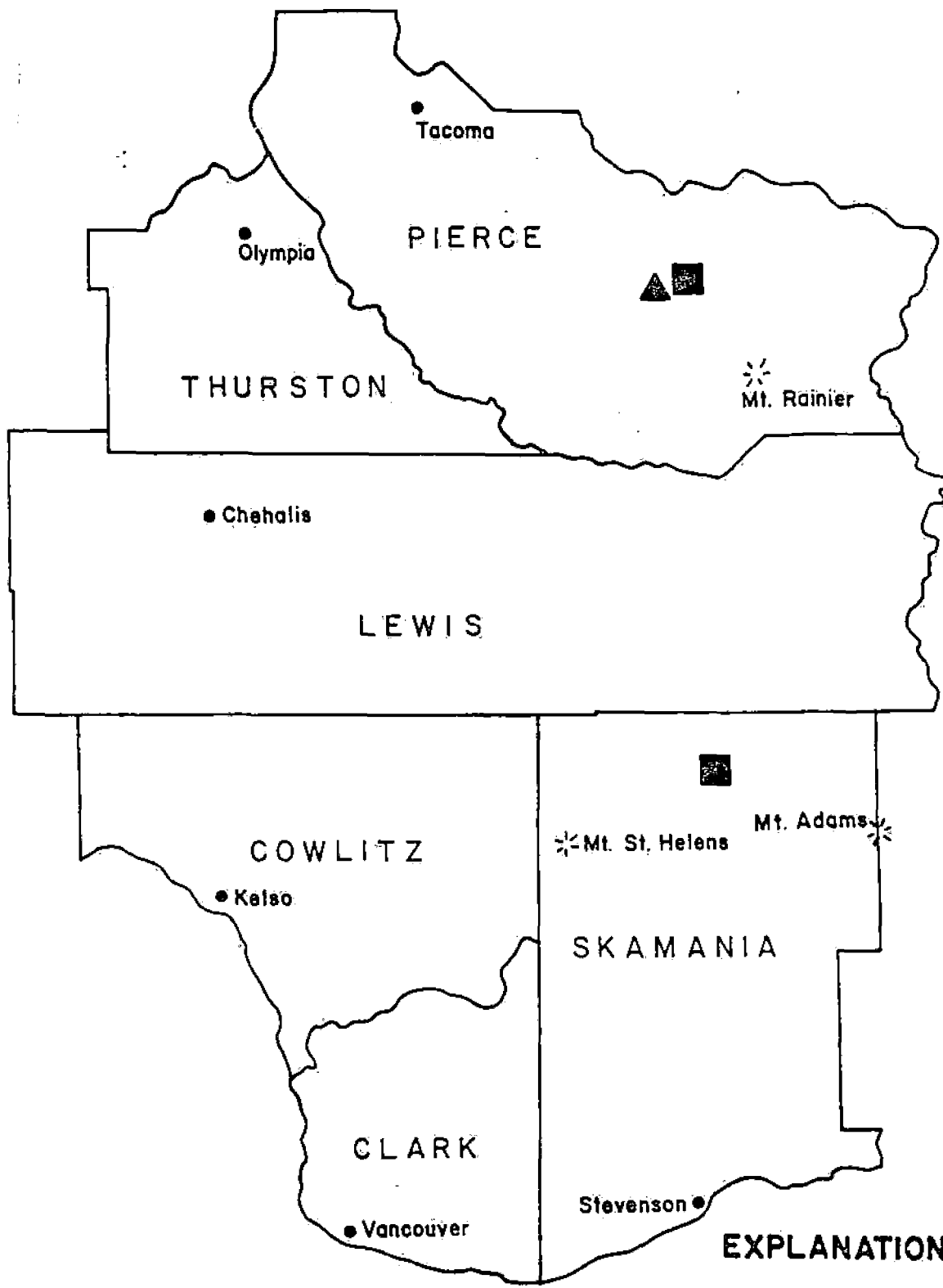
1980 MINERAL EXPLORATION AND MINING ACTIVITY IN PIERCE, THURSTON, LEWIS, COWLITZ, CLARK, SKAMANIA, AND YAKIMA COUNTIES
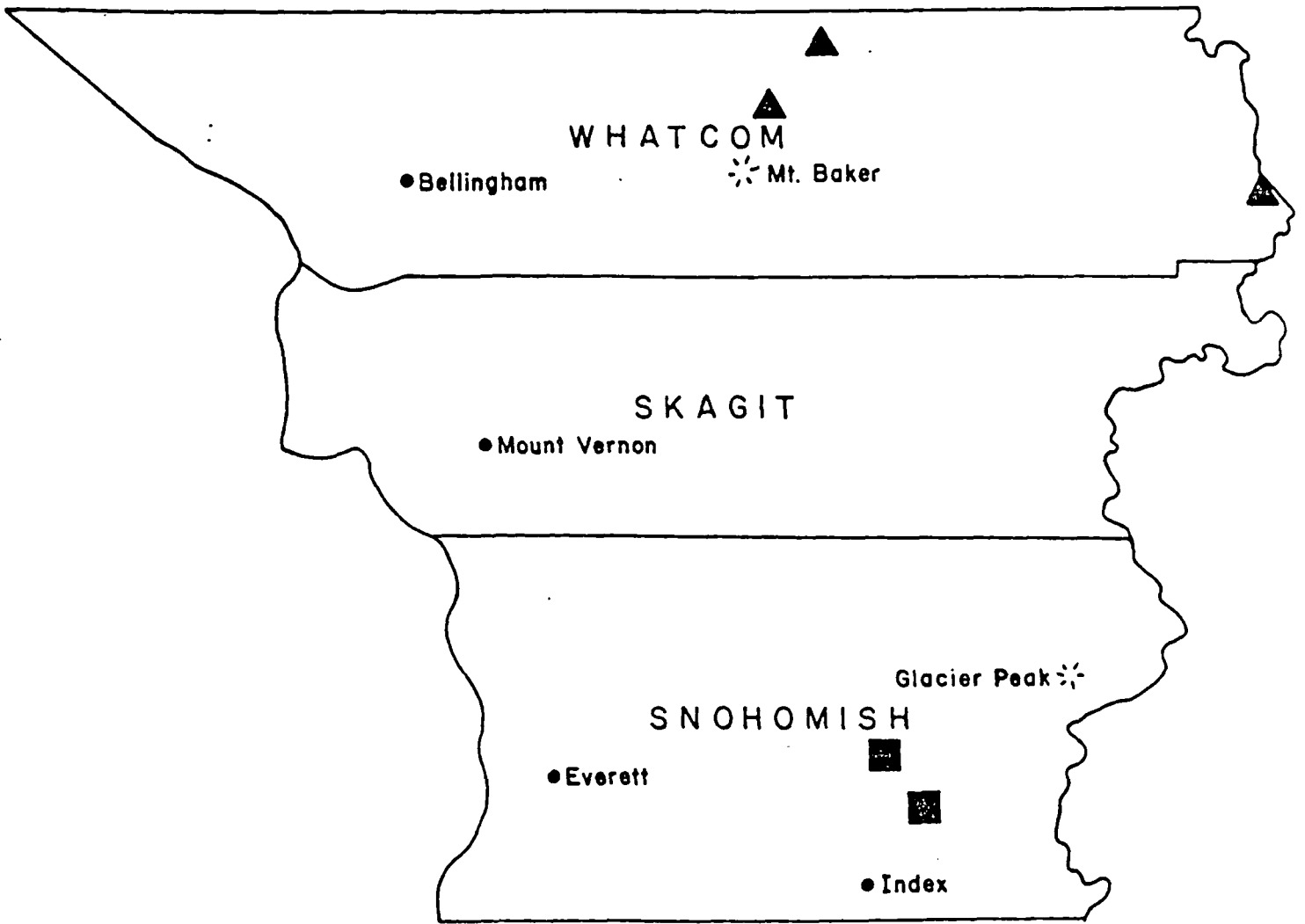
FIGURE 3

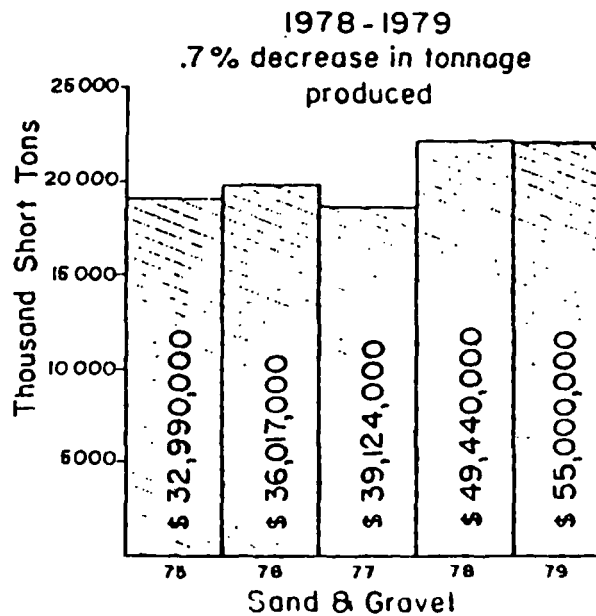WHATCOM

●Bellingham

☼ Mt. Baker
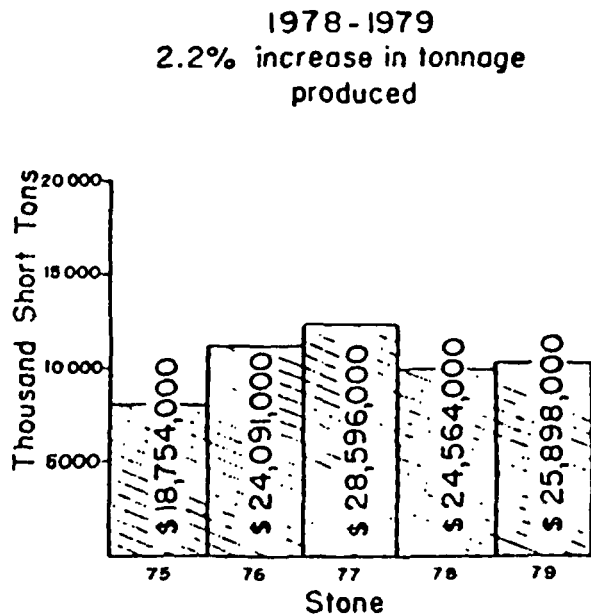
SKAGIT

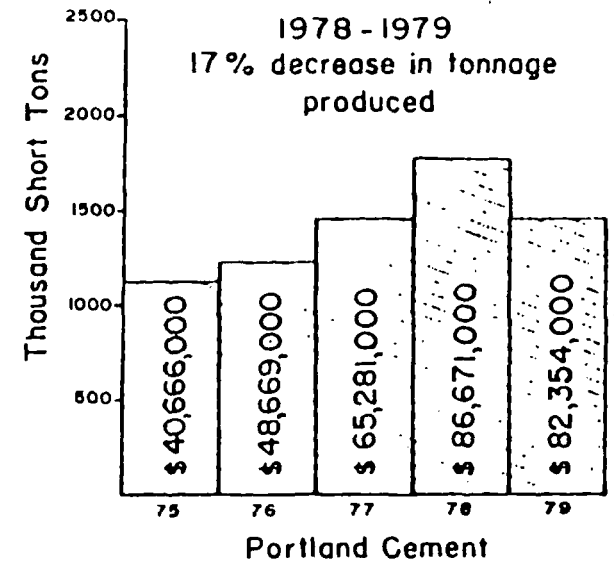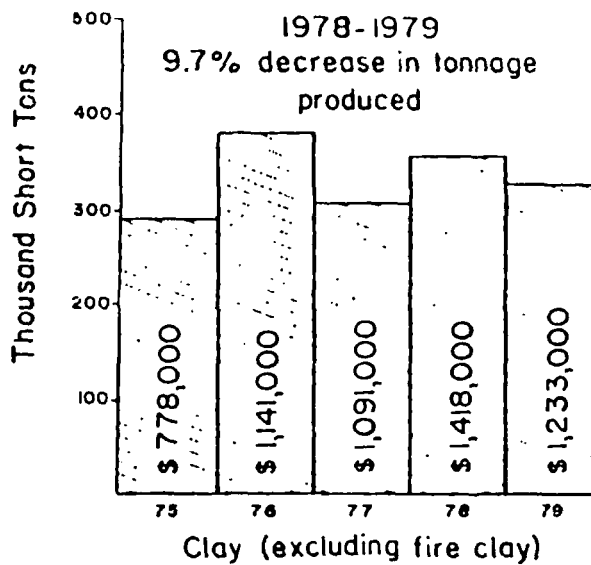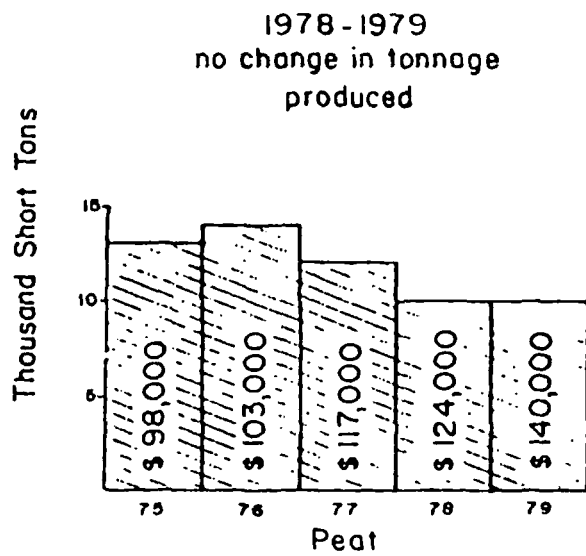●Mount Vernon

Glacier Peak ☼

SNOHOMISH

●Everett

● Index

EXPLANATION

▲ GOLD AND / OR SILVER

▨ MOLYBDENUM AND / OR COPPER

1980 MINERAL EXPLORATION AND MINING ACTIVITY

IN WHATCOM, SKAGIT, AND SNOHOMISH COUNTIES

FIGURE 4

(34)

1978-1979
no change in tonnage
produced

Thousand Short Tons

$ 98,000 — 75
$ 103,000 — 76
$ 117,000 — 77
$ 124,000 — 78
$ 140,000 — 79

Peat

1978-1979
9.7% decrease in tonnage
produced

Thousand Short Tons

$ 778,000 — 75
$ 1,141,000 — 76
$ 1,091,000 — 77
$ 1,418,000 — 78
$ 1,233,000 — 79

Clay (excluding fire clay)

1978-1979
17% decrease in tonnage
produced

Thousand Short Tons

$ 40,666,000 — 75
$ 48,669,000 — 76
$ 65,281,000 — 77
$ 86,671,000 — 78
$ 82,354,000 — 79

Portland Cement

1978-1979
2.2% increase in tonnage
produced

Thousand Short Tons

$ 18,754,000 — 75
$ 24,091,000 — 76
$ 28,596,000 — 77
$ 24,564,000 — 78
$ 25,898,000 — 79

Stone

1978-1979
.7% decrease in tonnage
produced

Thousand Short Tons

$ 32,990,000 — 75
$ 36,017,000 — 76
$ 39,124,000 — 77
$ 49,440,000 — 78
$ 55,000,000 — 79

Sand & Gravel

(35)

FIVE-YEAR PRODUCTION TRENDS
IN WASHINGTON

For Clay, Peat, Sand & Gravel,
Portland Cement, Crushed & Dimension Stone

1975-1979

From USBM annual data

FIGURE 5

NICKEL ELECTROLYSIS FROM SULFATE-CHLORIDE SOLUTIONS USING CURRENT OF VARIABLE POLARITY

UDC 669.243.87

A. I. Semenova and I. N. Piskunov

Modern nickel electrolysis practice involves the use of sulfate-chloride solutions at current densities of 250-350 A/m^2. Nickel electrolysis can be intensified by using current of variable polarity. Increasing the current density in the cells by reversal will increase cell capacity by several times. Research on nickel electrolysis using reversal has been carried out at the Leningrad Mining Institute. The electrolyte used was nickel sulfate-chloride solution after removal of impurities with the following composition (g/liter): 80 Ni (as $NiSO_4$), 90 NaCl, 60 Na_2SO_4, and 6 H_3BO_3; the medium is slightly acid. The experiments were carried in the 600-1400 A/m^2 range of current densities with various reversal times and total electrolysis periods. Electrolyte circulation into the cathode compartment was 60 ml/(A-hr).

Electrolytic nickel was used as the anode and a nickel starting sheet with a slightly polished surface was used as the cathode. The experiments were conducted with a diaphragm.

Preliminary experiments established that the optimum total electrolysis period T = 3 sec.

It was also established during the research that increasing the reversal time from 0.063 to 0.446 led to a sharp reduction in cathodic current efficiency and yielded a cathodic nickel deposit of poor quality. Satisfactory cathodic nickel quality with high current efficiency (99%) were obtained at a reversal time τ_a = 0.139 sec.

The maximum permissible current density was determined in the next series of experiments. Satisfactory cathodic nickel quality was obtained in the range D_c = 600-1200 A/m^2. Raising D_c to 1400 A/m^2 led to damage to the deposit. The cathodic current efficiency in terms of nickel fell from 99 to 93% when current density increased from 600 to 1400 A/m^2.

In conclusion, a crude nickel electrolytic refining experiment of many hours' duration was carried out. No difficulties in anode dissolution occurred during the experiment. Cathodic current efficiency was 97.50%, the slime yield was 3.72%, extraction of non-ferrous metals from the anode into solution was high, and the quality of the cathodic nickel was satisfactory.

The cathodic current efficiency in terms of nickel in experiments with reversal was calculated by the formula

$$\eta_e = \frac{m \cdot 100}{q(I_t \tau_c - I_a \tau_a)}.$$

where m is the amount of nickel evolving on the cathode, g, q is the electrochemical equivalent of nickel, 1.095 g/(A-hr), and $I_c \tau_c$ and $I_a \tau_a$ are the periods of cathode operation in cathodic and anodic routines.
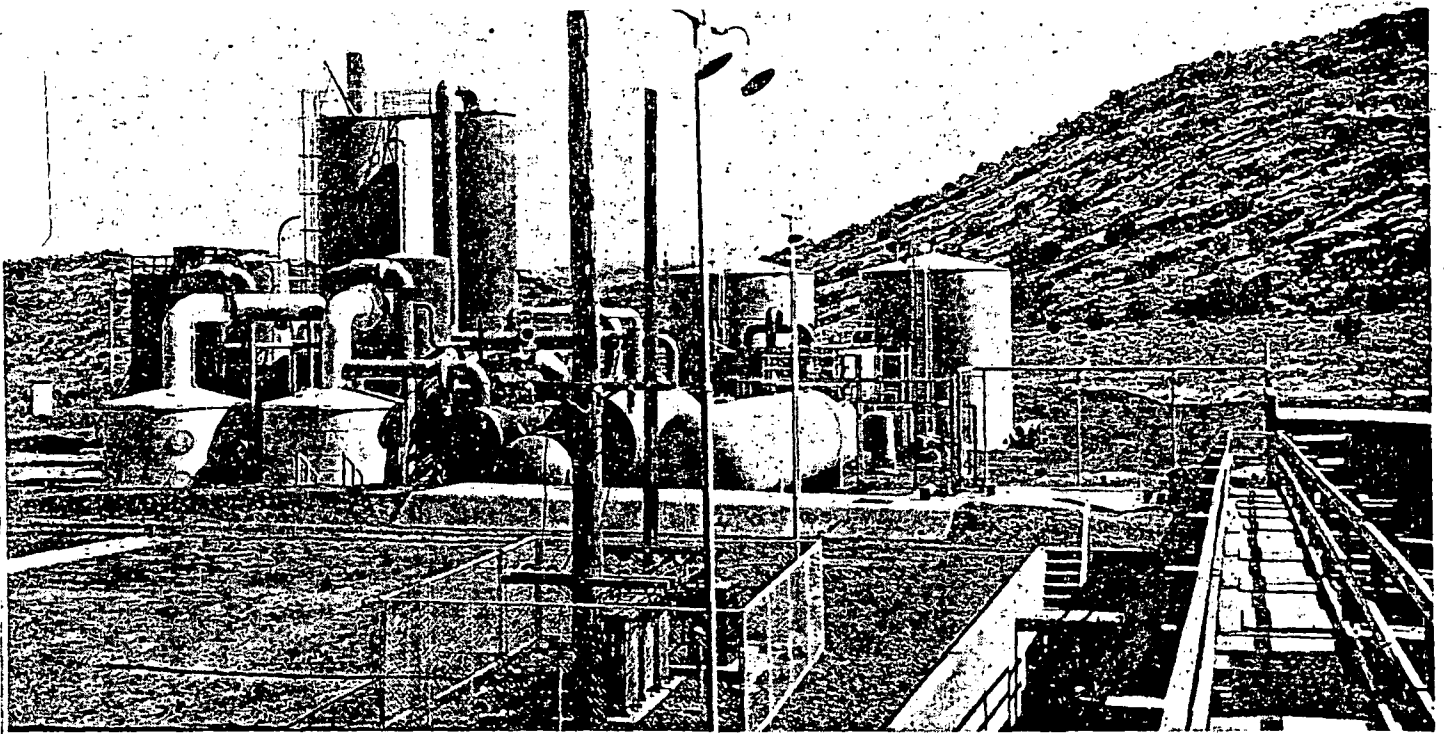
SULPHURIC ACID PLANT converts molten Texas sulphur to 98 percent pure H_2SO_4 at rate of 200 tons per day. Plant, pre- cipitating launders, and surge pond are located on a small mesa two miles northwest of Bagdad open pit.

New Leach Plant Ups Bagdad's Copper

A $2,000,000 acid-leach-precipitation plant recently increased production for Bagdad Copper Corporation to about 100,000 pounds of copper per day. Oxide stockpiles are now irrigated with dilute acid, and the solution pumped to launders where tin cans precipitate 40,000 pounds of cement copper daily

by John R. Bogert

Field Editor, Mining World

Last year copper production in the State of Arizona reached an all-time high of 539,300 tons—and in 1961 it will probably be higher. Contributing in no small way to this greater output will be the Bagdad Cooper Corporation of west central Arizona who recently upped copper production from 60,000 to 100,000 pounds a day—a whopping 67 percent increase! This big production jump is due solely to round-the-clock output of a new cement copper operation that includes the largest sulphuric acid plant in Arizona, and the largest Koroseal

plastic-lined surge pond in the world. These and other aspects of this modern recovery operation have attracted the attention of engineering men from all parts of the United States.

Bagdad operations have always been based on disseminated sulphide ore which occurs in a relatively thin irregular zone underlying oxidized capping. A 5,000 ton-per-day flotation mill effectively concentrates this ore, and concentrates are sold to the American Smelting and Refining Company's smelter at Hayden, Arizona. However, minor copper values in the extensive oxidized overburden has always been noticed and appreciated.

As early as 1926 J. W. Hutchinson in a report on the then undeveloped

Bagdad prospect made special note of the 70,000,000 tons of oxidized overburden carrying at least six to eight pounds per ton of acid soluble copper, and said it was "of fundamental economic importance to your company." Thus, it is no wonder that starting in 1946, when mining operations at Bagdad were converted from underground to open pit, that the oxidized stripping was carefully stockpiled in two dumps. However, it was not until 1959 that a method of heap leaching was decided on, and the decision made by management to go ahead.

At Bagdad, since there are no sulphide minerals in the dumps, it is impossible to successfully leach with water alone. Thus, an acid plant was
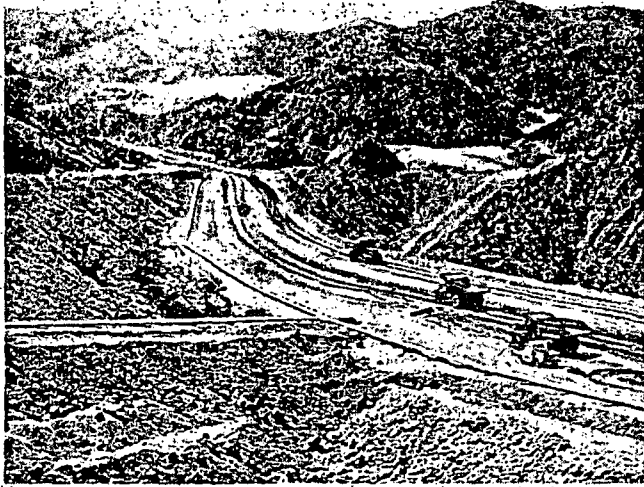
PIPELINES carry acid solutions to and from dumps in background—Mineral Creek to left, Alum Creek to right.
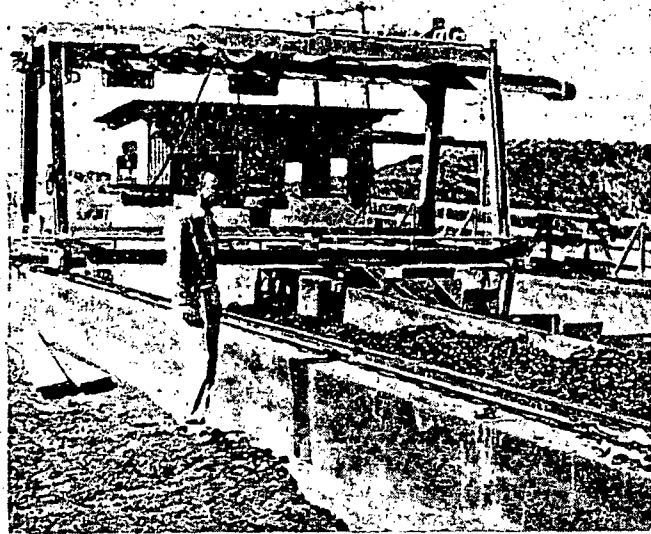
PRECIPITATING CELLS, charged with shredded tin cans by automatic loading device, are inspected by Bob Bogart.

Production by 67 Percent

the main item of the new project.

The sulphuric acid plant construction was begun in 1960 by the Fisher Contracting Company of Phoenix, with design and engineering work done in collaboration with the engineering staff of Bagdad. The 200 tons-per-day plant was completed in March, and started operating in May. The plant, nearby precipitating launders, and surge pond are all located on a small mesa approximately two miles northwest of the Bagdad open pit. This was the only flat area available reasonably close to the dumps.

Heap leaching at Bagdad has its beginning with the purchase of molten sulphur in Louisiana from the Texas Gulf Sulphur Company. This is delivered in tank cars to the Santa Fe railroad siding at Hillside, Arizona, 28 miles southeast of Bagdad. Since the sulphur becomes partly solidified in transit, a special steaming plant at Hillside is used to empty the tank cars and return the sulphur to a molten state. Dickie Trucking Company trailer tank trucks then carry the molten sulphur to underground storage at the acid plant at Bagdad. The insulated underground tank has a capacity of 250 tons, and is equipped with steam lines to keep the sulphur continually molten.

The process of converting the sulphur to sulphuric acid is semi-automatic. It is controlled by one man from a Minneapolis-Honeywell color-guided schematic instrument panel where flow, temperatures, and pressures are automatically and continually recorded.

Produces 200 Tons Acid Daily

Molten sulphur from underground storage is transferred by air pressure to a horizontal charge tank. It is then pumped to a sulphur burner where, together with dry air from a vertical drying tower, SO_2 gas is generated. This gas goes to a waste heat boiler, through a heat exchanger, and to the first converter. This converter has two masses of vanadium pentoxide which act as a catalyst in converting the SO_2 to SO_3. After returning through the heat exchanger, this last step is repeated through a second converter when conversion to SO_3 gas is theoretically complete. The SO_3 gas then passes through a cooler to an absorption tower where moisture (from the drying tower) is absorbed until sulphuric acid of 98 percent purity is attained. Excess SO_3 is released into the atmosphere. Operating continually this efficient plant produces 200 tons of H_2SO_4 acid per day which is stored in two 750-ton storage tanks.

Sulphuric acid from the storage tanks starts its work in the leaching operation at two small 890,000 gallon conditioning ponds near the precipitating launders. Here, acid is added to barren solution coming from the launders, bringing it up to a strength of seven and a half grams acid per liter of water. This lixiviant then flows by gravity through a 4,500-foot long, 14-inch diameter pipeline to the leach dump. This pipeline is made of stainless steel lined with polyvinyl chloride plastic.

There are two multi-million-ton dumps at Bagdad that will eventually be treated by heap leaching. The largest dump is the Mineral Creek; the smallest the Alum Creek. Dump material is altered monzonite porphyry; mine run in size, containing approximately 0.435 percent acid soluble copper in the form of malachite, azurite, and a little chrysocolla. Present plans call for leaching only the Alum Creek dump.

The top of the dump is divided into a series of connected ponds 100 feet square and approximately one foot deep. These shallow ponds control the distribution of the dilute sulphuric acid solution. By a system of rotating the flooding of the various ponds an even application of leach solution is applied which percolates through the dump.

Although the dump material is relatively free from acid-consuming constituents other than copper miner-

als, it is anticipated that approximately 30 percent solution losses will occur. Thus, of 4,800 gallons a minute irrigated on top of the dump, only approximately 3,350 gallons of copper-bearing pregnant solution reaches the collecting pond at bottom. This is because of natural evaporation, absorption by the dump material, and seepage into the ground.

The collecting pond at the bottom of the dump is formed by a small concrete dam which also supports a pumping station. On top of the dam two United States pumps are presently installed, with two more to be added when leaching of the nearby Mineral Creek dump begins. The existing pumps are equipped with 400 horsepower vertical turbine Ideal electric motors, and each pump up to 1,800 gallons per minute.

From the collecting pond, the copper-bearing solution is pumped uphill through another plastic-lined pipeline to the leach plant on the mesa. The pumping distance is 4,500 feet and the vertical lift 650 feet. Here, close to the sulphuric acid plant, the pregnant solution (containing copper sulphate) is discharged from the pipeline into a special plastic-lined surge pond.

The 1,400,000-gallon pond is unique and the largest of its kind in the world in industrial use. It is 264 feet long, 114 feet wide, 7 feet deep, and the bottom completely covered with an aluminum-coated Koroseal polyvinyl plastic sheet made by B. F. Goodrich. The pond was simply scooped out of the earth, and has no special base other than the plastic sheet which is 280 feet long, 130 feet wide, and 8 mills thick. It is impervious to most chemicals, mildew resistant, and will last indefinitely with proper care.

From the plastic-lined surge pond

the copper-bearing solution flows by gravity to the nearby precipitating launders. Here, at a flow rate of 3,350 gallons per minute, the solution containing copper sulphate circulates through a series of cells containing shredded tin cans. Since the iron has a greater affinity for the sulphate radical than the copper, the iron is slowly dissolved and the copper precipitated in the form of the dark brown mud called cement copper. There are a total of 10 double precipitating cells 9½ by 10 by 30 feet deep, made of reinforced concrete. A stainless steel screen is placed 13 feet down from the top of each cell to hold the shredded tin-can scrap.

Launders Charged Automatically

The cells are charged with an overhead three-ton semi-automatic loading device made by Shaw Box. Two 48-inch Schrader magnets designed for shredded iron move back and forth keeping the cells filled, from a three-day storage supply alongside the launders. Each magnet has a load cell which sends information to a totalizing device that keeps a record of the tonnage deposited in the individual cells. The loading device requires an operator for starting and stopping only.

For each pound of cement copper produced one-and-one-half to two pounds of burned, shredded tin cans are needed. These are purchased from Las Vegas, Nevada (300 tons a month); Phoenix, Arizona (100 tons a month); and Los Angeles, California (6,700 tons a month.

As the shredded tin in the cells is replaced by copper, the mud precipitate settles to the bottom and is pumped to a holding cell at the head of the launders. This pumping is done with 10 Worthington pumps

(one for each two cells) powered by General Electric Tri-Clad induction motors. From the holding cell the cement copper mud is then pumped by another Worthington unit to a 2,200 revolution-per-minute Bird centrifuge that dewaters the precipitate to 15 percent moisture. Overflow from the centrifuge goes back to the precipitating cells.

From the centrifuge the dewatered cement copper drops onto an 18-inch wide Hewitt-Robins conveyor that carries it 20 feet to a concrete loading pad. Here, a 1¼-yard Hough Payloader loads tractor-trailer trucks that take the cement copper (averaging 70 to 80 percent Cu) to the Hillside railroad siding. From there it is shipped to the American Smelting and Refining Company smelter at El Paso, Texas.

At the end of the launders the barren acid solution, now devoid of copper, flows by gravity to two 500,000 gallon conditioning ponds. Here fresh sulphuric acid is added to bring it up to a strength of 7½ grams acid per liter of water, and the dilute solution is again sent to leach the oxide dump. Acid consumption in the circuit is approximately 10 pounds acid for each pound of copper.

Water for the acid-leach-precipitation operations is piped from Burro Creek, some seven miles away. During dry summer months, though, this small creek dries up, so deep wells in the area have become the sole source of supply.

The entire operation is run by supervisor Edward S. Howell with one man each at the control panel, acid plant, and precipitation cells; plus two maintenance men, and one clean-up laborer. The general manager of all Bagdad operations is George W. Colville, assisted by Robert C. Bogart. END
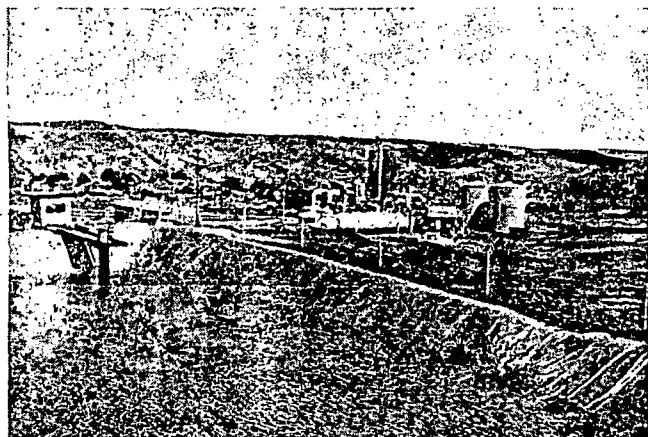
UNIQUE plastic-lined surge pond holds 1,400,000 gallons, is largest of its kind in the world, and is estimated to have lowered construction costs by about $24,000.

ALUM CREEK DUMP is smallest of the two large stripping dumps that contain an estimated 0.435 percent acid soluble copper. Photo taken prior to leaching operations.

New Technology

of Leaching

Waste Dumps

Higher extraction of copper from mine dumps is achieved with warm leach solutions, indicating the desirability of recycling effluents heated in percolating through large waste dumps.

By E. E. MALOUF
Project Development Engineer

and

J. D. PRATER
Chief, Hydrometallurgical Section
Kennecott Research Center
Kennecott Copper Corp.

HERETOFORE, leaching of copper from mine waste has been more of an art than a science. Long ago, the blue tinge of waters flowing from some copper mines and the freshets coming down the draws during spring runoffs where mine waste was dumped showed that water-soluble copper—$CuSO_4$—was going to waste. Moreover, where these copper-bearing waters flowed over tin cans or bits of scrap iron, the red color of precipitated metallic sponge copper was evident. What could be more logical insofar as mine waste dumps were concerned—simply supplement the natural spring runoff by pumping water into ponds on top of the mine waste dumps, collect the water flowing down the gulch from the bottom of the gulch, let it pass over metallic iron (detinned scrap) in a concrete launder, collect the copper precipitates and then pump the water back up to the ponds to be recycled. The practical result was a simple process by which some of the low-cost copper was produced with a small capital investment. Indeed, what could be simpler?

Object is to Replace a Random System

Some years ago, S. R. Zimmerley, research director at Kennecott Research Center, was concerned about the huge amounts of copper gradually accumulating in these very low-grade mine waste dumps as compared to the relatively small amount that was being retrieved annually by this simple, lucrative and empirical process—"sort of letting nature take its course." Also, he was concerned about a critical problem as to how insoluble copper sulfide minerals such as chalcopyrite and chalcocite were changed into $CuSO_4$, which was soluble in water and hence could be leached from the mine dumps. In this instance, his hunch that bacteria, re-

motely hinted to in previous scientific literature, are the catalyst for the necessary oxidation to render the copper soluble in water proved to be correct.

Further considerations of the overall project to permit long-range planning and to yield the maximum economic return, led to systematic studies in basic research, bench testing, mathematical models, pilot plant leaching and field experiments on experimental dumps at the mines. These investigations embraced the study of bacteria-accelerated reactions, chemical reactions, chemical kinetics including the temperature effect, the theories of permeability and tortuosity related to the flow of water through random and altered rock, the mineralogy of the copper-bearing waste material, and the effect of constituents such as limestone on the solubilization of copper. These efforts have been supplemented by studies whereby the leaching systems may be automated and the precipitated copper may be made at a lower cost and yield a higher grade product.

To date, we certainly do not have all the answers. We are in the midst of trying to convert an apparently simple, random process into one that can be controlled, engineered and designed to produce low-cost copper to create a maximum cash flow to the corporation. Our research indicates that our findings may not be confined to copper. Also, bacterial oxidation of pyrite might have some bearing on the prime problem of low sulfur in coal.

To return to our basic thesis, we are concerned with the development of a new technology for the recovery of copper from the low-grade, multimillion ton reserves resulting from the segregation of sub-marginal copper mine waste in dumps amenable to leaching processes.

Controlled pH Aids Process

By controlling the pH of the recycled solutions it was found that accretions in the pipelines were dissolved, the surface of the dump kept pervious, and the ready percolation of solutions into the dump permitted the inspiration of air, thereby accelerating the bacterial oxidation of ferrous to ferric iron.

Controlling the pH of the leach solutions not only keeps the pipelines and surface of the waste dump open, but also keeps the ferric iron in solution, thereby forming an effective lixiviant for the copper sulfide minerals.

Oxidizing
A study of dicated the pr teria that act copper solution only thrive i accelerate th minerals to copper and i of bacteria, tl utilizes the o the sulfides as another strain oxidans, oxid ric iron as i bacterial str other, in that which keeps tion that is thereby forn viant for cop ferric sulfate. This bacte to ferric iron faster than d tion reaction temperatures tions without

Bacterial form sulfuric can be used waste dump lixiviant for This approa waste dumps erals or whe tent of the w ment of the l dump.

In waste d ment is suita of the bacteri that under pH of the so iron present formed in the through whi Sufficient ox obtained fro over the ro cycle of the dized to fer oxidizes the iron again b iron to agai repeated seve permeate thr fect will con teria obtain ture in the d Pasteurizatio

Sunlight N
Bacterial but are not t to direct su been made

Oxidizing Bacteria Found in Mine Waters

A study of various mine waters indicated the presence of oxidizing bacteria that actually thrive in high-acid copper solutions. These bacteria not only thrive in this environment, but accelerate the oxidation of sulfide minerals to form acid and soluble copper and iron sulfates. One strain of bacteria, thiobacillus thio-oxidans, utilizes the oxidation of the sulfur of the sulfides as its energy source, while another strain, thiobacillus ferro-oxidans, oxidizes ferrous iron to ferric iron as its energy source. These bacterial strains complement each other in that the one produces acid which keeps the ferric iron in solution that is produced by the other, thereby forming the powerful lixiviant for copper minerals of acidified ferric sulfate.

This bacterial oxidation of ferrous to ferric iron occurs a thousand-fold faster than does the chemical oxidation reaction by aeration at ambient temperatures under similar conditions without bacteria.

Bacterial oxidation of pyrite to form sulfuric acid and ferric sulfate can be used in "breeder" tanks on a waste dump to generate a low-cost lixiviant for the copper in the waste. This approach can be used where waste dumps are low in sulfide minerals or where a high limestone content of the waste prevents the development of the bacterial oxidation in the dump.

In waste dumps where the environment is suitable for the promulgation of the bacteria, it has been determined that under conditions of controlled pH of the solutions and with ferrous iron present, ferric iron is readily formed in the first 20 to 50 ft of waste through which the solutions trickle. Sufficient oxygen for the bacteria is obtained from the solutions trickling over the rocks in the dump. The cycle of the ferrous iron being oxidized to ferric iron, which in turn oxidizes the sulfide minerals, with the iron again being reduced to ferrous iron to again enter the cycle, can be repeated several times as the solutions permeate through the waste. This effect will continue as long as the bacteria obtain oxygen and the temperature in the dump does not exceed the pasteurization temperature.

Sunlight Makes Bacteria Inactive

Bacterial cultures become inactive, but are not destroyed, when exposed to direct sunlight. Experiments have been made to evaluate bacterial activity in open ponds with solution depths up to two ft. Virtually no bacterial oxidation was noted in these ponds, even though the solutions were in nighttime darkness during 50 percent of the time and viable bacterial cultures were present. The bacteria are extremely sensitive to ultraviolet light, for only short exposure to this radiation will completely sterilize a culture.

Temperature has been found to exert a very pronounced effect on the rate of the bacterial conversion of ferrous to ferric iron with maximum bacterial activity occurring at 35°C; temperatures above 50°C have been found to destroy the bacteria; below 35°C the rate of bacterial action decreases non-linearly as the temperature is reduced.

The oxidizing bacteria are active only in acid media. Bacterial action is most pronounced in a media having a pH between 2.0 and 3.5. Both above and below this pH range, the rate of bacterial oxidation decreases and at pH values above 6.0 bacterial action is almost completely inhibited. In alkaline media (pH 9) the bacteria are destroyed.

Warmed Solutions Increase Recovery

With the use of controlled pH leach solutions on the large mine waste dumps, it was noted that copper content of the effluent solutions increased two to four lb of copper per 1000-gal over and above that obtained previously. This was attributed not only to the formation of the ferric sulfate lixiviant, but also to maintaining a pervious condition on the waste dump which permitted the penetration of air necessary for the bacterial oxidation to proceed.

As these conditions were maintained on the waste dump, the temperature of the effluent solutions increased 25°F over the temperature of the solutions entering the waste dump. Solutions that were entering the waste at 85°F temperature were draining from the waste with a 110°F temperature.

On an experimental basis, the leach solutions were first heated to the 100 to 110°F range before being discharged on the waste dump to determine the effect of recycling these warm solutions through the dump. The effect of these warm solutions was to double the copper content of the solutions from the dump.

Even though the temperature of the leach solutions had approached the point where pasteurization of the bacteria could be expected, the rate of chemical dissolution at this higher temperature exceeded that of the bacterial action.

On small dumps, namely those up to 250 ft in depth, the energy generated by the oxidation processes is lost by radiation of heat as fast as it is generated. However, on larger dumps there is an accumulation of this energy sufficient to increase the temperature of the leaching solutions an additional 25°F.

Value of pH Control Demonstrated

Rate of dissolution of a number of sulfide and sulfide-bearing minerals has been determined in laboratory tests. Data obtained from these tests indicate that the copper sulfide minerals, in increasing resistance to dissolution, are chalcocite, covellite and chalcopyrite.

With copper-bearing pyrite, the

Material Leached	Lixiviant	Leaching Time, Days	Percent of Total Extracted			
			Cu	Fe	Zn	Mo
Chalcopyrite sample	Recycled Solution	65	9.2			
Chalcopyrite-flotation concentrate	Recycled Solution	408	47.9			
Chalcopyrite-bearing mine waste	Recycled Solution	287	64.6			
Chalcocite-bearing ore	Recycled Solution	105	95.0			
Chalcocite-bearing flotation tailing	Recycled Solution	89	86.0			
Copper-bearing pyrite	Recycled Solution	42	95.0			
Copper-bearing pyrite*	Synthetic Solution	113	79.8	3.8		
Sphalerite	Synthetic Solution	337			19.6	
Sphalerite and pyrite	Synthetic Solution	337		100	48.6	
Molybdenite concentrate (copper bearing)	Synthetic Solution	123	28.2	9.8		< 0.1
Molybdenite concentrate (copper bearing)	Recycled Solution	78	6.6			

Table 1. Rate of dissolution of sulfide minerals and sulfide-bearing materials using bacterially generated lixiviant

* Synthetic solution refers to a ferrous sulfate solution inoculated with oxidizing bacteria while the recycled solution refers to the acidified ferric sulfate solution resulting from the bacterial oxidation.

Leaching began at the Utah Copper Division in 1923 when a test plant was erected in the bottom of the pit at Bingham Canyon to recover copper from meteoric waters. There are now four leaching water distribution systems, and a fifth one is projected after installation of a tunnel in Dry Fork. A 20,000,000-gal reservoir was recently completed to conserve run-off water so as to assure full operation of the existing leaching systems at all times
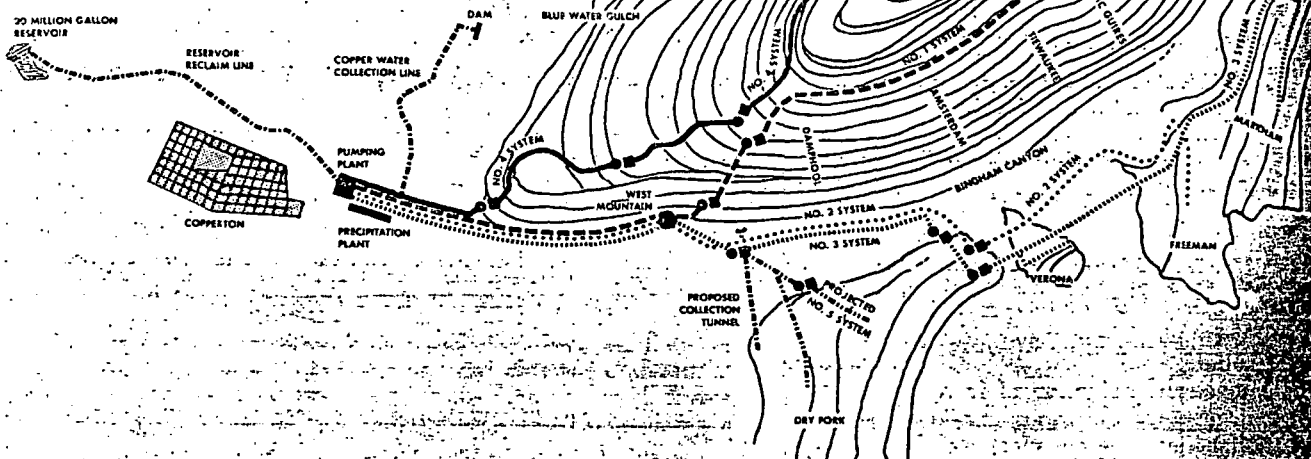
copper was selectively extracted. In 113 days of percolation leaching of copper-bearing pyrite, containing four percent copper, using a synthetic nutrient solution inoculated with bacteria, 80 percent of the copper was extracted while only four percent of the iron was solubilized. However, when a pH controlled, bacterial generated lixiviant of ferric sulfate was used, virtually all the copper was extracted in 42 days. The second solution was much more effective because of its higher content of solubilized ferric sulfate.

Copper and iron minerals can be selectively leached from molybdenite concentrates. Twenty-eight percent of the copper, ten percent of the iron and virtually no molybdenum were extracted in 123 days of percolation leaching of a sample of molybdenite concentrate containing 2.17 percent copper and 3.30 percent iron.

Sphalerite was altered and the zinc solubilized when the sample was leached using a synthetic solution inoculated with the oxidizing bacteria. With mixtures of sphalerite and pyrite, the pyrite was preferentially attacked. In one laboratory test in which a mixture of ten grams of sphalerite and three grams of pyrite was used, the iron was completely solubilized together with 50 percent of the zinc in 337 days.

Table 1 lists various products leached and the comparative extraction at various leaching times.

In summary, the order of copper minerals in increasing resistance to attack was chalcocite, covellite, chal-

copyrite. Copper was selectively leached from copper-bearing pyrite; copper and iron were preferentially extracted from molybdenite concentrates. Pyrite was attacked more rapidly than sphalerite when mixtures of the two minerals were leached simultaneously with lixiviant prepared by the use of oxidizing bacteria.

Dump Permeability Varies Widely

The capacity of a formation for transmitting water is measured by its coefficient of premeability which is defined by Meinzer as the rate of flow of water in gallons per day through a cross-sectional area of one sq ft under a hydraulic gradient of one ft per ft at a temperature of 60°F.

Flow of leach solutions through a mine waste dump is affected by the composition of waste; namely, fines or clay minerals that are present, size of the waste, depth and horizontal length of the dump, age of the dump which determines the degree of reconsolidation of the waste, as well as the breaking down of various gangue minerals to form clays or slimes which fill the interstices of the dump. The larger the dump, the faster the alteration due to internal temperatures and pressures.

Data obtained from leaching various size dumps indicate the coefficient of permeability of leach solutions of 30 gal per day per sq ft of area can be expected for dumps 30 or more years old which contain considerable slimes and clay, to 240 gal per day per sq ft of area for a waste dump which has not aged to the point

where considerable reconsolidation has taken place, namely one under 30 years of age.

Leach solutions placed on a 100-ft high waste dump require two to three days before the solutions emerge from the toe of the dump. A 250-ft high dump requires three to four days, a 300-ft dump six days, while a 400 to 500-ft high dump requires 12 days. Of course, this time of percolation is dependent not only on the vertical distance, but also on the horizontal distances through which the solutions must percolate.

Ground water hydraulics can be applied in studying the leaching of mine waste. Although the first studies of the flow of water through capillary tubes by Hagen and Poiseuille indicated that the rate of flow is proportional to the hydraulic gradient, it was Darcy who confirmed and applied this law to the flow of water percolating through filter sands. Darcy's law is applied to the percolation of leach solutions through mine waste and is expressed as follows:

$$v = \frac{PI}{7.48p}$$

where: v = velocity in feet per day
 P = coefficient of permeability in gallons per day per square foot
 I = hydraulic gradient in feet per foot
 p = porosity in percent

In most ground water problems, and this would apply to mine waste dump leaching, the total volume of flow is required rather than the velocity, and consequently Darcy's

equation is n form:

where: Q_d = d
 P = c

 I = h

 A = a

This form use with the cient of tran distinction b that of the c

where: Q_d =
 I = l

 T =

 W =

In applyi ground wat cases of wa the waste d permeabiliti have been t the hydraul proximately height.

Acid Add

The bact iron to the because of ubilization resultant o solutions of precipitatio iron cause and precip fate. Lowei partial plug ing of the c salts result

The add sulfuric ac solution ha in preventi tation of b being used leaching p operation. practiced, with lixivi

Field tes at the Utal ing of sol eliminated furic acid operating ability wa per sq ft per hour. use of th time that under lea dump. O
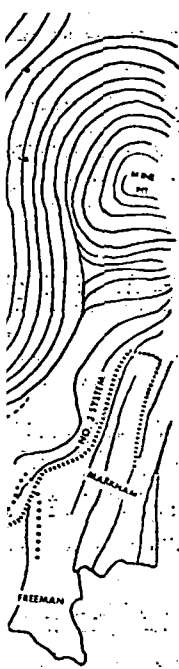
...uation is modified to the following form:

$$Q_d = PIA$$

where: Q_d = discharge in gallons per day
P = coefficient of permeability in gallons per day per square foot.
I = hydraulic gradient in feet per foot
A = area of flow cross section in square feet

This formula may be adapted for use with the more convenient coefficient of transmissibility by noting the distinction between its definition and that of the coefficient of permeability:

$$Q_d = TIW$$

where: Q_d = discharge in gallons per day
I = hydraulic gradient in feet per foot
T = coefficient of transmissibility in gallons per day per foot
W = width of flow cross section in feet

In applying Darcy's equation of ground water hydraulics to several cases of waste dump leaching where the waste dumps have had different permeabilities and heights, the results have been the same so that invariably the hydraulic gradient has been approximately one foot per foot of height.

Acid Added to Depleted Solutions

The bacterial oxidation of ferrous iron to the ferric state is beneficial because of the accelerated rate of solubilization of copper. However, the resultant oxidation of the iron with solutions of a pH value resulting from precipitation of copper with scrap iron caused undesirable hydrolysis and precipitation of basic iron sulfate. Lowered pump capacity due to partial plugging of the lines and sealing of the dump areas by precipitated salts resulted.

The addition of small amounts of sulfuric acid to the copper-depleted solution has been found to be effective in preventing hydrolysis and precipitation of basic iron salts and is now being used as a regular part of the leaching program in the Kennecott operation. Before pH control was practiced, permeability of the dump with lixiviant was very slow.

Field tests in an experimental dump at the Utah mine indicated that ponding of solutions could be practically eliminated by this addition of sulfuric acid. Later tests on one of the operating dumps indicated permeability was increased from two gal per sq ft per hour to 15 gal per sq ft per hour. Another advantage in the use of the acid was the increased time that an area could be maintained under leach without sealing of the dump. Over-all recovery of copper

from the dump was substantially increased because of the longer time that an area could be leached.

The concentration of copper per unit volume of solution was increased about 30 percent in field tests when acid was added to solutions used as lixiviants as compared with solutions to which no acid was added after the copper was precipitated on scrap iron. Substantial savings in the cost of pumping solutions to the dumps were realized because of the larger payload resulting with each cycle.

Reaction is Exothermic

During the course of the experiments on a major mine waste dump, an increase in the temperature of the effluent solution was noted. Oxidation of copper sulfide minerals and of pyrite are exothermic reactions. Because of the increased reactions occurring within the dumps, the temperature of the effluent solutions was increased 25°F compared with background data obtained before acid was added to the solutions. The reactions are synergistic in that with the increased temperature the rate of reaction was increased, thereby liberating additional heat. Laboratory tests under controlled conditions indicated that the rate of solubilization of copper from mine waste was increased two to three fold by raising the temperature of the lixiviant from 70° F to 100°F. The value of the conservation of all heat possible in the leach solution becomes obvious.

Channels Replace Dump Ponds

As a result of the information gained in the tests on a major waste dump, a different method of preparing the dump for leaching has been established. Formerly, ponds were made on the dump surface to impound the water. This was necessary because of the relatively long time required for permeation of the solution into the dump. The preparation of the ponds was time consuming and costly. With the increased rate of penetration because of the addition of acid to the solutions, ponds are no longer necessary on most dumps. Instead, shallow channels are prepared with a bulldozer to provide a strip for leaching. The strips may either be parallel with the edge of the dump or at right angles to it, depending upon the terrain and size of dump under leach. For small dumps, the channels at right angles to the edge are generally preferred, but with large dumps either system may be used. Each system is being employed on different dumps at the Utah mine. Generally a

strip 20 ft wide by 400 ft long will accommodate a flow of 2,000,000 gal per day.

Principal objectives of the leaching tests were (a) to effect higher extraction of copper and at more rapid rates than previously obtained, and (b) to determine a systematic and controlled method for leaching the various dumps. It has been found that differences in leaching characteristics exist between the several dumps with respect to composition of the waste, percent of copper contained in the waste, depth of waste, and time of placement or again of the waste in the dump. Systematic data are required so that the status of each dump under leach may be known. With this information the frequency of change from one strip to the next and the optimum distribution of solution to the different dumps may be planned to achieve the most effective use of the water and to insure constant copper heading to the precipitation plant. Leaching of mine waste thus has become a planned and integral part of the over-all operation contributing substantially to the total copper produced. Reduced costs plus increased recovery of copper at a rate more nearly current with the placing of the copper in the waste dump are goals which may be achieved.

Alternate Methods Under Study

With the increased extraction of copper from the waste, the problem of recovering the copper from solution becomes increasingly important. The historic method for recovering copper from mine and waste leach solutions has been by precipitation on scrap iron. Two alternative methods have been investigated by Kennecott.

According to the first, copper is precipitated in a cone by contacting the solution with a form of powdered iron. The precipitant is maintained in a dispersed state by the upflow velocity of the solution. Advantages of the process include (a) the reaction is rapid and precipitation is complete, (b) control of the process is precise, (c) the operation lends itself to automation, (d) iron consumption per unit of copper precipitated is lower than that in the usual precipitation by flowing the solution over scrap iron. Precipitation of relatively high purity copper powder, for direct fabrication without melting, by electrolytic reduction from mine water is also being studied as a possible means of recovery. Each method or combination of both show considerable promise as a substitute for the historic method.

Left margin fragments:

econsolidation one under 30

d on a 100-ft e two to three s emerge from a 250-ft high four days, a while a 400 uires 12 days. percolation is the vertical he horizontal ch the solu-

ics can be applied of mine st studies of gh capillary iseuille indiflow is proportional gradient, it led and appow of water lter sands. the percoirough mine follows:

per day — rmeability in ly per square nt in feet.

ent

problems. mine waste volume of ian the velocity Darcy's

A Numerical Method for Computing Equilibria in Aqueous Chemical Systems

Francois Morel[1] and James Morgan

W. M. Keck Laboratories, California Institute of Technology, Pasadena, Calif. 91109

■ A general purpose computer program especially adapted to the study of acid–base and coordinative interactions and dissolution and precipitation in aqueous systems has been developed. The program uses the stability constant approach and the Newton-Raphson method for digital computation of equilibria. It is able to handle numerous species and to find the equilibrium set of solids. Gas phases are considered to be at constant partial pressures. The method is explained by use of the aqueous iron(III)–calcium–carbonate–phosphate system as an example. An application of the program to a system of 788 soluble species, 83 possible solids, and one gas-phase component is given as an illustration.

Equilibrium models can be very useful for understanding the various processes—dissolution and precipitation, oxidation and reduction, acid–base and coordinative interactions—which govern the chemical composition of natural waters (Stumm and Morgan, 1970). A classical example of such an equilibrium model is the seawater model of Sillén (1961).

Typically, these models require the computation of equilibrium compositions for systems containing numerous species distributed among an aqueous phase, a gas phase, and several solid phases. For any given model, the temperature and the pressure can generally be taken as constants. Exchange of matter with the surroundings being neglected and ideality being assumed, the thermodynamic treatment of such closed systems is straightforward (Denbigh, 1966), and the equilibrium composition is given by the minimum of the Gibbs free energy function or, equivalently, by the mass action laws, both subject to the constraints of the mole balance conditions.

We have been interested in developing a general purpose computer program especially adapted to solving these types of chemical equilibrium problems. Two main choices have to be made in the development of such a program: First, the choice of a notation that will allow the description of the system in algebraic terms and the setting up of the equations; second, the choice of a method to solve the equilibrium problem.

Every possible kind of notation has been proposed in the literature from the most particular one which identifies every chemical species under a special symbol, to the most general one where elements of multidimensional tensors represent the species and their formulas. Because our prime interest is with coordination processes we have chosen to differentiate between metals (M), ligands (L), and complexes (C). Since acid–base interactions are of special interest to us, the proton has been given a special symbol (H). Gas and solid phases interact with the soluble species in a fairly similar way and they are given a single symbolic representation (S). We feel that

this notation is general enough to allow the treatment of m of the systems we are interested in and that it is particul. enough to facilitate the translation of a particular chemi problem into a general algebraic one. The metals and the li ands are thus logically taken as the components of the syst and this division of the components into two families lows an unusually compact description of the system in a ta leau form. This compactness is important in enabling a lar number of species (up to a few thousand) to be handled.

To solve the chemical equilibrium problem, two princip techniques can be distinguished. First, the so-called equilirium constant approach which consists of solving the set nonlinear equations provided by the mass law and the mo balance equations. This method was pioneered by such wor ers as Brinkley (1947), and its most prominent application aqueous systems is the Haltafall program developed by Sil and his co-workers (Ingri et al., 1967). The second techniq was first proposed by Dantzig and co-workers (White et : 1958) and consists of directly minimizing the Gibbs free enc function subject to the constraints of the mole balance equ tions. This method was applied to large multiphasic syst by Shapiro (1964). A fairly complete review of the two metho has been given by Zeleznik and Gordon (1968).

We have chosen to use the equilibrium constant approa The determining factor in choosing this method was that allows reduction of the number of principal variables. In o case, for example, the concentrations of the complexes can expressed as a function of the free metal and free ligand cone trations by the mass law equations, and the problem is th reduced to finding this set of free metal and free ligand cone trations that will satisfy the mole balance conditions. Thi done by use of the Newton-Raphson method for systems nonlinear equations.

As can be seen, our method is just the application of w known principles to a particular class of problems. Our goal simply to present what we have found to be an efficient and liable tool for solving a fairly general and important class chemical equilibrium problems in order to help others deve similar tools.

By use of examples, the notation and the systematic settin up of the equations, both in the absence and in the presenc solids, will be presented. An iterative procedure to find t equilibrium solid phases will then be shown. An abridged scription of the program will finally be given, followed by . example demonstrating the possibilities of the method.

Description of the System

To derive a general method of computation one has choose some systematic notation that will describe the chen cal system in algebraic terms. The notation that we have d sen differentiates metals and ligands and represents the chea cal system in a tableau form. For example, the iron(III) cium–carbonate–phosphate system in water is represented Figure 1. The values in parentheses are the logarithms of t concentration stability constants for formation of aque

---

[1] To whom correspondence should be addressed.

| | Ligands | | |
	CO_3^{2-}	PO_4^{3-}	OH^-
Ca^{2+}	$CaCO_3$ (1.95) $CaHCO_3^+$ (10.58) $CaCO_3(s)$ (−7.0)	$CaHPO_4$ (12.6) $Ca_5(PO_4)_3OH(s)$ (−51.5)	$CaOH^+$ (0.9) $Ca(OH)_2(s)$ (−4.9)
Fe^{3+}	No important complex or solid known	$FeHPO_4^+$ (18.0) $FePO_4(s)$ (−23.0)	$FeOH^{2+}$ (11.3) $Fe(OH)_2^+$ (22.0) $Fe(OH)_4^-$ (31.0) $Fe(OH)_3(s)$ (−36.0)
H$^+$	HCO_3^- (9.6) H_2CO_3 (15.4) $CO_2(g)$ (−17.0)	HPO_4^{2-} (11.8) $H_2PO_4^-$ (18.5) H_3PO_4 (20.4)	Water

Metals (row label on left)

Figure 1. Tableau representation for the iron(III)·Ca^{2+}–CO_3^{2-}–PO_4^{3-} system in water

librium constant (0.5 M ionic medium) for formation of aqueous species and for dissolution of solids and gases are given in parentheses, as the logarithm

es from their components and for the dissolution of solid seous species. The stability constants used here and in the examples in this paper apply to a constant ionic medium M. They have been selected mainly from the compilations llén and Martell (1964), Ringbom (1963), and Garrels and st (1965). When experimental values for 0.5M ionic me- were not available, approximate values were obtained by ying Ringbom's ionic strength corrections (Ringbom,). Our equilibrium constant values are not intended to be al selections; applications to specific problems will re- critical examination of the appropriate thermodynamic for particular solid phases and aqueous species.

e choice of independent components is, of course, partly rary. For example, either carbonate (CO_3^{2-}) or bicarbon- (HCO_3^-) could be chosen as a component, but both of could not be chosen at the same time if the proton (H^+) o to be a component; (CO_3^{2-}), (HCO_3^-), and (H^+) are ndependent. We have chosen the least-protonated forms e ligands and the unhydrolyzed forms of the metals as the ponents of the system.

e advantage of such a presentation is twofold: It allows a pact writing of large systems, and it has a pedagogic and tical value in pointing out the possible complex formations. main disadvantage of the presentation is that it is not pletely general: Unless special provision is made, no com- involving two different metals or two different ligands can nsidered. Because H^+ and OH^- often react with another l or ligand in complex formation, the general complex ula we use does allow this possibility. A metal M_i and a id L_j can form a complex C_{ijk} of the form

$$C_{ijk} \equiv (M_i)_\alpha (L_j)_\beta (H)_\gamma$$

where i is an index specifying the metal, j is an index specifying the ligand, k is an index specifying the different M_i–L_j complexes in an arbitrary order, α (in fact, α_{ijk}) is the stoichiometric coefficient of the metal in the formula of C_{ijk}, β (in fact, β_{ijk}) is the stoichiometric coefficient of the ligand in the formula of C_{ijk}, and γ (in fact, γ_{ijk}) is the stoichiometric coefficient of the hydrogen ion, H^+, or hydroxide ion, OH^-, in the formula of C_{ijk}. For H^+ in the complex $\gamma > 0$; for OH^- in the complex $\gamma < 0$; so that the formula of C_{ijk} may also be:

$$C_{ijk} \equiv (M_i)_\alpha (L_j)_\beta (OH)_{-\gamma}$$

Then, with the appropriate definition of the stability constant K_{ijk}, one can always write the mass action law:

$$[C_{ijk}] = K_{ijk} \cdot [M_i]^\alpha \cdot [L_j]^\beta \cdot [H]^\gamma \qquad (1)$$

This contains implicitly the result $[OH] = K_w/[H]$ in case $\gamma_{ijk} < 0$.

It should be pointed out that with this notation H^+ is identified at the same time both as H and conventionally as the last metal, M_3, in our example (Figure 2).

In the same way, the solids can be described by

$$S_{ij} \equiv (M_i)_\delta (L_j)_\eta (H)_\lambda$$

or

$$S_{ij} \equiv (M_i)_\delta (L_j)_\eta (OH)_{-\lambda}$$

where δ, η, λ (in fact, δ_{ij}, η_{ij}, λ_{ij}) have definitions similar to those of α, β, γ.

	L_1	L_2	$L_3 (= OH)$
M_1	$C_{111} \equiv (M_1)(L_1)$ $C_{112} \equiv (M_1)(L_1)(H)$ $S_{11} \equiv (M_1)(L_1)$	$C_{121} \equiv (M_1)(L_2)(H)$ $S_{12} \equiv (M_1)_5(L_2)_3(OH)$	$C_{131} \equiv (M_1)(L_3)$ $S_{13} \equiv (M_1)(L_3)_2$
M_2		$C_{221} \equiv (M_2)(L_2)(H)$ $S_{22} \equiv (M_2)(L_2)$	$C_{231} \equiv (M_2)(L_3)$ $C_{232} \equiv (M_2)(L_3)_2$ $C_{233} \equiv (M_2)(L_3)_4$ $S_{23} \equiv (M_2)(L_3)_3$
$M_3 (= H)$	$C_{311} \equiv (M_3)(L_1)$ $C_{312} \equiv (M_3)_2(L_1)$ $S_{31} \equiv (M_3)_2(L_1)$	$C_{321} \equiv (M_3)(L_2)$ $C_{322} \equiv (M_3)_2(L_2)$ $C_{323} \equiv (M_3)_3(L_2)$	

re 2. General representation (aqueous species, solids, and gas) of the system of Figure 1 in terms of metals M_i, ligands L_j, H ions, and OH ions

It should be noted that this notation does not allow the formation of two different solids involving a metal and a ligand (there is no third index). This is being modified in newer versions of the program.

There is no computational reason to differentiate between solids and components of gas phases at constant partial pressure since in both cases we can write the solubility equation in the general form:

$$k = [M_i]^\delta \cdot [L_j]^\eta \cdot [H]^\lambda \qquad (2)$$

where k (in fact, k_{ij}) is corrected by the right power of K_w in case $\lambda < 0$ and contains the partial pressure in case we are dealing with a gas phase. Consequently both solid and gas phase components will be referred to by the letter S.

Now Figure 1 can be rewritten in general terms, as shown in Figure 2.

In this tableau the three-dimensional arrays of numbers K, α, β, γ and the two-dimensional arrays k, δ, η, λ completely describe the general chemical properties of the system. Figure 3 shows these eight arrays of numbers.

To be able to solve a problem we need as many equations as we have unknowns. It is convenient to consider the concentrations of the complexes as secondary unknowns given from the principal unknowns M_i, L_j, and H by Equation 1. We thus need an equation for every metal ($\neq$ H), for every ligand ($\neq$ OH), and for the proton. These equations are given by the particular conditions of the system in different cases.

Case Where No Solid is Present. Let us first suppose that in our example the system has been made by adding 10^{-6} mole of ferric phosphate ($FePO_4$), 10^{-4} mole of calcium hydroxide, $Ca(OH)_2$, and 10^{-3} mole of carbon dioxide (CO_2) in 1 liter of water. Suppose also that we know that no solid phase is present and that we study the equilibrium before the gas phase has had time to form. We can then write down the mole balance equation for each metal ($\neq$ H) and each ligand ($\neq$ OH).

$$M_1: 10^{-4} = [M_1] + [C_{111}] + [C_{112}] + [C_{121}] + [C_{131}] \qquad (3.1)$$

$$M_2: 10^{-6} = [M_2] + [C_{221}] + [C_{231}] + [C_{232}] + [C_{233}] \qquad (3.2)$$

$$L_1: 10^{-3} = [L_1] + [C_{111}] + [C_{112}] + [C_{131}] + [C_{312}] \qquad (3.3)$$

$$L_2: 10^{-6} = [L_2] + [C_{121}] + [C_{221}] + $$
$$[C_{321}] + [C_{322}] + [C_{323}] \qquad (3.4)$$

In general,

$$TOTM_i = [M_i] + \sum_{j,k} \alpha_{ijk} \cdot [C_{ijk}] \quad \text{(sum on line } i \text{ of Figure 2)}$$

$$TOTL_j = [L_j] + \sum_{i,k} \beta_{ijk} [C_{ijk}] \quad \text{(sum on column } j \text{ of}$$

Figure 2)   (3)

where $TOTM_i$ and $TOTL_j$ are the analytical or total concentrations of the metal M_i and the ligand L_j, respectively.

We need one more equation for (H); different cases can be entertained. First, we might know the pH either because we have measured it experimentally or because we have imposed it—practically or conceptually—by adding a buffer which has no interaction (other than through the proton concentration) with the chemicals we are interested in. In this case the problem is trivial: (H) is fixed (pH = 5.21 in our example) and we do not need any other equation. If the pH is not known, we have to compute it by using either the electroneutrality or the proton condition. These two equations are known to be mathematically (not computationally) equivalent and can be deduced from each other by combination with the mole balances (Equations 3). For the electroneutrality condition to be written, we need to include the charges of each metal and each ligand in the data and then to compute the charge of every complex. The electroneutrality equation also has the computational disadvantage that for any salt present in high concentration and essentially free, we will add and subtract the concentrations of the cations and anions, respectively, in such a way as to create a round-off error that might not be negligible.

For these reasons we have judged it preferable to use the proton condition:

$$\sum \text{"acids" put into the system} - \sum \text{"bases" put into the}$$
$$\text{system} = \sum \text{all species containing } H^+ -$$
$$\sum \text{all species containing } OH^-$$

This equation comes from the conservation equations of H^+ and OH^- and from the fact that for any proton produced by the dissociation of water there is a corresponding hydroxide ion produced.

The definitions of "acids" and "bases" are, of course, relative to our choice of metals and ligands—e.g., if $CO_3^{2-} \equiv L_1$ then $HCO_3^- (HL_1)$ and $CO_2 (H_2L_1)$ are acids; if $CO_2 \equiv L_1$ then $HCO_3^- (OHL_1)$ and $CO_3^{2-} [(OH)_2L_1]$ are bases.

With our notation, the proton condition can be written in the general form:

$$TOTH = [H] - [OH] + \sum_{\substack{\text{last row} \\ j,k}} \alpha_{ijk} [C_{ijk}] -$$
$$\sum_{\substack{\text{last column} \\ i,k}} \beta_{ijk} [C_{ijk}] + \sum_{i,j,k} \gamma_{ijk} [C_{ijk}] \qquad (4)$$

$TOTH$ is an input into the problem whose value will correspond to the experimental base-neutralizing capacity (respective acid-neutralizing capacity) of the system if the components are written in their least-protonated (respective most protonated) form. If only neutral components are chosen, the proton condition is strictly identical to the electroneutrality condition. In our example, if $CO_3^{2-} \equiv L_1$ and $Ca(OH)_2 \equiv M_1$ then $TOTH$ = base-neutralizing capacity; if $CO_2 \equiv L_1$ and $Ca^{2+} \equiv M_1$ then $TOTH$ = acid-neutralizing capacity. Since in this case our choice is mixed ($CO_3^{2-} \equiv L_1$ and $Ca^{2+} \equiv M_1$) $TOTH$ has no direct experimental meaning.

In our particular example the proton condition is written:

$$TOTH = [H] - [OH] + [C_{311}] + 2[C_{312}] + [C_{321}] +$$
$$2[C_{322}] + 3[C_{323}] - [C_{131}] - [C_{231}] - 2[C_{232}] - 4[C_{233}] +$$
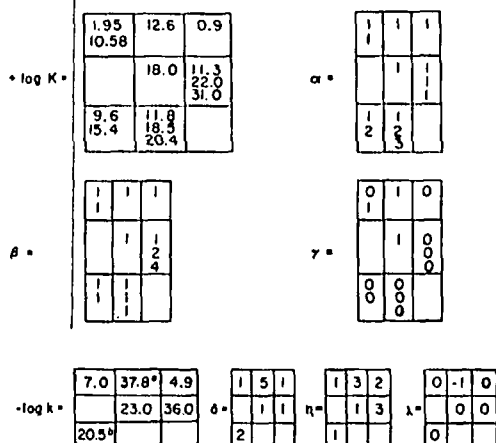$$[C_{112}] + [C_{121}] + [C_{221}] \qquad (4.1)$$

Figure 3. The arrays of stability constants and stoichiometric coefficients required to describe the iron(III)-Ca^{2+}-CO_3^{2-}-PO_4^{3-} system in water

[a] Computed for $K_w = 10^{-13.7}$. [b] Computed for $p_{CO_2} = 10^{-3.5}$ atm

Table I. Successive Computed Solutions for the Equilibrium Values of Free Metals and Ligands for an Iron(III)-Ca^{2+}-CO_3^{2-}-PO_4^{3-} System under Conditions Where No Solid Forms and H_2CO_3 Is Considered a Nonvolatile Species

Components: $[FePO_4]_T = 10^{-6}M$; $[Ca(OH)_2]_T = 10^{-4}M$; $[CO_2]_T = 10^{-3}M$. The equilibrium composition is computed with sufficient accuracy by the tenth iteration

Iteration no.	$[M_1]$	$[M_2]$	$[L_1]$	$[L_2]$	$[H]$
0	1.00×10^{-8}	1.00×10^{-8}	1.00×10^{-8}	1.00×10^{-8}	1.00×10^{-8}
1	1.00×10^{-5}	4.90×10^{-12}	2.43×10^{-5}	2.89×10^{-10}	1.00×10^{-8}
2	9.89×10^{-5}	2.59×10^{-12}	1.80×10^{-5}	7.12×10^{-11}	1.26×10^{-3}
3	9.90×10^{-5}	6.30×10^{-12}	1.80×10^{-6}	2.61×10^{-11}	2.80×10^{-8}
4	9.92×10^{-5}	1.39×10^{-10}	1.80×10^{-7}	2.61×10^{-12}	3.36×10^{-7}
5	9.98×10^{-5}	3.87×10^{-9}	1.80×10^{-8}	2.61×10^{-13}	5.02×10^{-6}
6	9.98×10^{-5}	9.66×10^{-10}	8.06×10^{-9}	2.61×10^{-14}	5.64×10^{-6}
7	9.98×10^{-5}	1.88×10^{-10}	8.42×10^{-9}	4.79×10^{-15}	6.17×10^{-6}
8	9.98×10^{-5}	5.94×10^{-12}	8.46×10^{-9}	8.13×10^{-15}	6.11×10^{-6}
9	9.98×10^{-5}	9.33×10^{-12}	8.46×10^{-9}	8.19×10^{-15}	6.11×10^{-6}
10	9.98×10^{-6}	9.33×10^{-12}	8.46×10^{-9}	8.19×10^{-16}	6.11×10^{-6}

where $TOTH = 2[CO_2]_T - 2[Ca(OH)_2]_T = 2 \times 10^{-3} - 2 \times 10^{-4} = 1.8 \times 10^{-3}$.

Equations 3 and 4 completely define the system once the secondary variables have been replaced by their values (Equation 1). To solve this system of nonlinear equations we have used a slightly modified Newton-Raphson method. This involves writing the general expressions of the derivatives of Equations 3 and 4 with respect to the principal variables (M_i), (L_j), and (H). It is a simple matter; the expressions are given in the Appendix. The Newton-Raphson method starts from an initial guess and improves it by use of the iterative procedure

$$\bar{X}_{n+1} \doteq \bar{X}_n - J_n^{-1} \bar{Y}_n$$

Where $\bar{X}_n$ is the approximation of the solution vector $\bar{X}$ in the system $\bar{Y}(\bar{X}) = 0$ at the nth iteration and $\bar{X}_{n+1}$ is its improvement at the next iteration. J is the Jacobian matrix of the system. $\bar{Y}_n$ is $\bar{Y}(\bar{X}_n)$ and J_n is $J(\bar{X}_n)$. For details see, for example, Isaacson and Keller (1966).

To avoid the convergence toward a negative solution we have slightly modified this iterative procedure and developed the empirical rule to simply divide by 10 any concentration that the Newton-Raphson iteration would make negative—i.e., if $X_{n+1}^i < 0$ take instead $(X_{n+1}^i)' = X_n^i/10$. This "trick" seems to work well. Table I shows how the solution of our particular example [$10^{-6}M$ FePO$_4$; $10^{-4}M$ Ca(OH)$_2$; $10^{-3}M$ CO$_2$] was found, starting with the initial guess that each free metal and each free ligand concentration was $10^{-8}M$ at equilibrium.

At the tenth iteration the values were judged to verify the equations satisfactorily. Specifically: |right-hand side of Eq. 3 − left-hand side of Eq. 3| ≤ 10^{-5} × left-hand side, Eq. 3 and a similar condition for Equation 4. The negative logarithm of the concentrations of every species at equilibrium is shown in Figure 4.

Case Where Known Solid Phases or Gas-Phase Components at Fixed Partial Pressure Are Present. In continuing to work on our iron(III)-calcium-carbonate-phosphate system, suppose that the particular conditions are: $p_{CO_2} = 3 \times 10^{-4}$ atm; $[Ca_5(PO_4)_3OH]_T = 2 \times 10^{-3}M$; $[FePO_4]_T = 10^{-3}M$; $[H_3PO_4]_T = 3 \times 10^{-3}M$; and if we know that the solid phases $Ca_5OH(PO_4)_3$, S_{12}, and FePO$_4$, S_{22}, are present at equilibrium, then Equations 1 defining the secondary variables, [C_{ij}], are still the same. Defining $[S_{ij}]$ as the number of moles of solid S_{ij} or gas S_{ij} per liter of solution (a bizarre but convenient definition), we can write the mole balance equations:

$$M_1: \quad TOTM_1 = 5[S_{12}] + \text{(rhs, Equation 3.1)} \tag{5.1}$$

$$M_2: \quad TOTM_2 = [S_{22}] + \text{(rhs, Equation 3.2)} \tag{5.2}$$

$$L_1: \quad TOTL_1 = [S_{31}] + \text{(rhs, Equation 3.3)} \tag{5.3}$$

$$L_2: \quad TOTL_2 = 3[S_{12}] + [S_{22}] + \text{(rhs, Equation 3.4)} \tag{5.4}$$

and the proton condition:

$$H: \quad TOTH = -[S_{12}] + 2[S_{31}] + \text{(rhs, 4.1)} \tag{6.1}$$

The general Equations 5 and 6 are easily written similarly to 3 and 4:

	$pL_1 = 8.07$	$pL_2 = 14.09$	$pL_3 = 8.49$
$pM_1 = 4.00$	$pC_{111} = 10.12$ $pC_{112} = 6.71$	$pC_{121} = 10.70$	$pC_{131} = 11.59$
$pM_2 = 11.03$		$pC_{221} = 12.33$	$pC_{231} = 8.22$ $pC_{232} = 6.01$ $pC_{233} = 13.99$
$pM_3 = 5.21$	$pC_{311} = 3.68$ $pC_{312} = 3.10$	$pC_{321} = 7.50$ $pC_{322} = 6.01$ $pC_{323} = 9.33$	

Figure 4. Results of equilibrium computation for an iron(III)-Ca^{2+}-CO_3^{2-} PO$_4^{3-}$ system in absence of solid or gas phases

The tableau gives the negative logarithm ($p[\ ]$) of each metal ion, ligand, protonated ligand, and complex at equilibrium
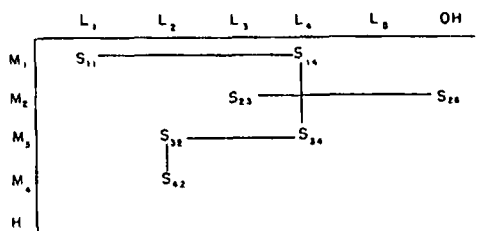
Figure 5. Examples of "connected" solids

S_{23}, S_{26} are connected; S_{32}, S_{42} are connected; S_{11}, S_{42} are also connected
There are two families of connected solids:
$\begin{cases} S_{23}, S_{26} \\ S_{11}, S_{14}, S_{24}, S_{22}, S_{42} \end{cases}$

$$TOTM_i = [M_i] + \sum_j \delta_{ij}[S_{ij}] + \sum_{j,k} \alpha_{ijk}[C_{ijk}]$$

$$TOTL_j = [L_j] + \sum_i \eta_{ij}[S_{ij}] + \sum_{i,k} \beta_{ijk}[C_{ijk}] \quad (5)$$

$$TOTH = [H] - [OH] + \sum_{\substack{\text{last row} \\ j}} \delta_{ij}[S_{ij}] + \sum_{\substack{\text{last row} \\ jk}} \alpha_{ijk}[C_{ijk}] -$$

$$\sum_{\substack{\text{last column} \\ i}} \eta_{ij}[S_{ij}] - \sum_{\substack{\text{last column} \\ i,k}} \beta_{ijk}[C_{ijk}] + \sum_{ij} \lambda_{ij}[S_{ij}] +$$

$$\sum_{ijk} \gamma_{ijk}[C_{ijk}] \quad (6)$$

Let us come back to our example. Not knowing what the value of $[CO_2(g)]_T$ is, we can take it to be some sufficiently large number, say $[CO_2]_T = 0.1M$; then

$TOTM_1 = 5[Ca_5(PO_4)_3OH]_T = 10^{-2}M$

$TOTM_2 = [FePO_4]_T \qquad = 10^{-3}M$

$TOTL_1 = [CO_2]_T \qquad = 10^{-1}M$

$TOTL_2 = 3[Ca_5(PO_4)_3OH]_T + [FePO_4]_T +$

$$[H_3PO_4]_T = 10^{-2}M$$

$TOTH = -[Ca_5(PO_4)_3OH]_T + 2[CO_2]_T +$

$$3[H_2PO_4]_T = 2.07 \times 10^{-1}M$$

We have introduced three new unknowns $[S_{12}]$, $[S_{21}]$, $[S_{31}]$; correspondingly, we can write three new equations of the type 2:

$S_{12}: [M_1]^5[L_2]^3[H]^{-1} = 10^{-37.8} \qquad (2.1)$

$S_{22}: [M_2][L_2] \qquad = 10^{-23.0} \qquad (2.2)$

$S_{31}: [H]^2[L_1] \qquad = 10^{-20.5} \qquad (2.3)$

Rather than to solve this new system with the new unknowns $[S_{ij}]$ (which are, in fact, only formally defined), we have chosen to eliminate systematically those unknowns and thus to reduce the number of equations.

We shall say that solids are connected whenever they share a common metal or a common ligand. We shall also say that solids are connected whenever they are connected to a common solid (Figure 5).

Whenever we have a family of connected solids, we can arbitrarily select a principal variable among the metals and the ligands involved in such a family and, using Equations 2, define the other metals and ligands involved as secondary variables. For example, choosing (H) and (L_2) as principal variables in our system, we get:

from (2.3): $[L_1] = 10^{-20.5} \cdot [H]^{-2} \qquad (7.1)$

from (2.2): $[M_2] = 10^{-23.0} \cdot [L_2]^{-1} \qquad (7.2)$

from (2.1): $[M_1] = 10^{-37.8} \cdot [L_2]^{-3/5}[H]^{+1/5} \qquad (7.3)$

In general:

[secondary variable] $= \mu \cdot$ [principal variable]$^\nu \cdot [H]^{\nu'} \qquad (7)$

For simplicity [H] is always chosen as a principal variable and the coefficients μ, ν, and ν' can be computed on a systematic basis. It can be easily verified that the coefficients ν and ν' so defined for each new secondary variable are those that will eliminate the $[S_{ij}]$ from Equations 5 and 6:

(equation with $[S_{ij}]$ eliminated) =

(equation of principal variable) +

$\sum \nu \cdot$ (equation of connected secondary variable)

$\left[+ \sum \nu' \text{ (equation of any secondary variable) } \atop \text{only for proton condition} \right] \quad (8)$

In our example:

Equation 5.4 $-$ 3/5(5.1) $-$ (5.2) gives:

$TOTL_2 - 3/5 \, TOTM_1 - TOTM_2 = (\text{rhs, 3.4}) -$

$$3/5(\text{rhs, 3.1}) - (\text{rhs, 3.2}) \quad (8.1)$$

and

Equation 6.1 + 1/5(5.1) $-$ 2(5.3) gives:

$TOTH + 1/5\,TOTM_1 - 2\,TOTL_1 = (\text{rhs, 4.1}) +$

$$1/5(\text{rhs, 3.1}) - 2(\text{rhs, 3.3}) \quad (8.2)$$

We then have two equations (8.1 and 8.2) and two principal

	$pL_1 = 9.63$	$pL_2 = 10.01$	$pL_3 = 8.27$
$pM_1 = 2.64$	$pC_{111} = 10.32$ $pC_{112} = 7.12$	$pC_{121} = 5.48$	$pC_{131} = 10.00$
$pM_2 = 12.99$		$pC_{221} = 10.43$	$pC_{231} = 9.96$ $pC_{232} = 7.53$ $pC_{233} = 15.07$
$pM_3 = 5.43$	$pC_{311} = 5.46$ $pC_{312} = 5.09$	$pC_{321} = 3.64$ $pC_{322} = 2.37$ $pC_{333} = 5.90$	

Figure 6. Equilibrium composition of the aqueous phase of the iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} system with $p_{CO_2} = 3 \times 10^{-4}$ atm and with Ca_5OH $(PO_4)_3$(s) and $FePO_4$(s) existing at equilibrium
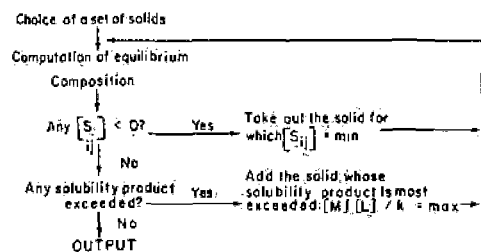
Figure 7. Routine for modifying the existing set of solids in a system at each stage in the computation

Figure 8. Examples of "closed" families of connected solids

S_{11}, S_{12}, S_{42}, S_{43}, S_{23}, S_{21}, S_{11} is a "closed" family of connected solids. S_{36}, S_{56}, S_{54} is also a "closed" family of connected solids since H and OH are not independent. (Water $\rightleftharpoons S_{66}$)

unknowns (H and L_2). The secondary unknowns are given by Equations 1 and 7. The derivatives of those equations with respect to the principal variables are easily computed from the derivatives of Equations 3 and 4 (see Appendix). The Newton-Raphson method can then be used as before and Table II shows how the solution of our example ($p_{CO_2} = 3 \times 10^{-4}$ atm; $2 \times 10^{-3} M$ apatite; $10^{-3} M$ FePO$_4$; $3 \times 10^{-3} M$ H$_3$PO$_4$) was found starting with the initial guess that every free metal and every free ligand were $10^{-8} M$ at equilibrium (in fact, only [H] and [L_2] are important since the others are computed as secondary variables).

At the tenth iteration, the values were judged to verify the equations satisfactorily. The negative logarithms of the concentrations of every species at equilibrium are shown in Figure 6.

Case Where the Solid Phases Present Are Unknown. It is not always possible to know, a priori, which solid phases are actually present at equilibrium; we might guess that a solid is present while it is in fact completely dissolved at equilibrium or, reciprocally, we might not foresee the precipitation of a certain solid. In the first of those cases the system of equations has a solution that corresponds to a negative [S_{ij}]. On the other hand, if we have not foreseen the presence of a solid that does exist at equilibrium, the set of concentrations that solves the problem simply exceeds the corresponding solubility product. In either of those cases a solution can be computed on which the chosen set of solids can be tested. One can then modify this choice and start a new computation. This process is repeated until, hopefully, the right set of solids is found. The following diagram shows how our program modifies the set of solids after each computation. Other ways are, of course, possible; this one seems to work well (Figure 7).

We have chosen to "precipitate" and "dissolve" solids one by one to change the system as little as possible and to use the solution of the preceding computation as a good guess to start the new one. We have also chosen to "dissolve" solids before "precipitating" them to avoid the creation of a "closed" family of connected solids (Figure 8).
Such families are defined by

"number of metals" + "number of ligands" $\leq$
"number of solids"

and they can be shown to be, in general, impossible merely by applying the Gibbs phase rule. In the example of Figure 8 the coefficients λ are all supposed to be zero. If the pH is arbitrarily fixed one needs an additional degree of freedom and the examples are valid even with nonzero λ coefficients.

The scheme of Figure 7 works only for solids and no provision has been made in the program to compute equilibrium of gas phases at constant volume. It is thus important to impose a sufficiently high total concentration of the known gas-phase components to avoid trouble with the "dissolving" routine. Figure 9 shows how the scheme of Figure 7 worked in the example previously treated ($p_{CO_2} = 3 \times 10^{-4}$ atm; $2 \times 10^{-3} M$ apatite; $10^{-3} M$ FePO$_4$; $3 \times 10^{-3} M$ H$_3$PO$_4$) where the solids S_{11}, CaCO$_3$, and S_{23}, Fe(OH)$_3$, were imposed instead of S_{12} and S_{22}.

These numbers at iteration 25 are, of course, identical to those found before (Table II). Cv means that the program converged at that iteration—i.e., the values on that line are the mathematical solution of the system when the corresponding solids are imposed up to that point. For example, at the third iteration, S_{11} and S_{23} are imposed; at the 20th iteration, S_{12}, S_{22}, and S_{23} are imposed.

Iteration no.	[M_1]	[M_2]	[L_1]	[L_2]	[H]
0	3.16×10^{-3}	1.26×10^{-19}	3.16×10^{-6}	1.00×10^{-8}	1.00×10^{-8}
3 (cv)	9.44×10^{-3}	6.50×10^{-19}	1.06×10^{-6}	8.00×10^{-7}	1.73×10^{-3}
			Solid S_{11} "dissolves"		
6 (cv)	9.41×10^{-3}	7.56×10^{-19}	9.57×10^{-6}	7.58×10^{-7}	1.82×10^{-3}
			Solid S_{12} "precipitates"		
14 (cv)	3.01×10^{-3}	1.63×10^{-11}	1.23×10^{-10}	6.88×10^{-11}	5.06×10^{-6}
			Solid S_{22} "precipitates"		
20 (cv)	4.78×10^{-4}	1.48×10^{-14}	1.32×10^{-8}	6.77×10^{-10}	4.89×10^{-7}
			Solid S_{23} "dissolves"		
25 (cv)	2.30×10^{-3}	1.03×10^{-13}	2.33×10^{-10}	9.67×10^{-11}	3.68×10^{-6}

Figure 9. Illustration of successive modifications of solids in an iron(III)–Ca^{2+} CO$_2^{2-}$ PO$_4^{3-}$ system where an initially imposed set of solids was not the equilibrium set [same conditions as in Table II except that the solids CaCO$_3$(s) and Fe(OH)$_3$(s) were imposed at the outset of the computation]

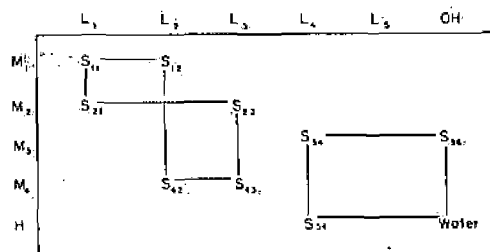At the 25th iteration the correct set of solids has been formed and the equilibrium composition is attained

Table II. Successive Computed Solutions for the Equilibrium Values of Free Metals and Ligands in an Iron(III)–Ca^{2+}–CO_3^{2-}–PO_4^{3-} System Where p_{CO_2} Is Fixed and the Phases $Ca_5OH(PO_4)_3$ (s) and $FePO_4$(s) Are at Equilibrium

Components: $[Ca_5OH(PO_4)_3]_T = 2 \times 10^{-3}M$; $[FePO_4]_T = 10^{-3}M$; $[H_3PO_4]_T = 3 \times 10^{-3}M$; $p_{CO_2} = 3 \times 10^{-4}$ atm. The equilibrium composition is computed with sufficient accuracy by the tenth iteration.

Iteration no.	$[M_1]$	$[M_2]$	$[L_1]$	$[L_2]$	$[H]$
0	4.36×10^{-5}	1.00×10^{-16}	3.16×10^{-5}	1.00×10^{-8}	1.00×10^{-8}
1	1.02×10^{-5}	4.99×10^{-17}	9.90×10^{-7}	2.00×10^{-7}	5.65×10^{-8}
2	5.38×10^{-6}	4.99×10^{-16}	6.01×10^{-8}	2.00×10^{-8}	2.29×10^{-7}
3	2.77×10^{-4}	4.99×10^{-15}	4.61×10^{-9}	2.00×10^{-9}	8.28×10^{-7}
4	1.41×10^{-3}	4.99×10^{-14}	3.97×10^{-10}	2.00×10^{-10}	2.82×10^{-6}
5	5.54×10^{-3}	4.41×10^{-13}	2.15×10^{-10}	2.26×10^{-11}	3.83×10^{-6}
6	3.83×10^{-3}	1.94×10^{-13}	6.29×10^{-11}	5.14×10^{-11}	7.09×10^{-6}
7	2.62×10^{-3}	1.30×10^{-13}	2.47×10^{-10}	7.71×10^{-11}	3.58×10^{-6}
8	2.35×10^{-3}	1.06×10^{-13}	2.22×10^{-10}	9.43×10^{-11}	3.78×10^{-6}
9	2.30×10^{-3}	1.03×10^{-13}	2.33×10^{-10}	9.67×10^{-11}	3.68×10^{-6}
10	2.30×10^{-3}	1.03×10^{-13}	2.33×10^{-10}	9.67×10^{-11}	3.68×10^{-6}

Description of the Program. The program is written in FORTRAN and is usually run on an IBM 360/75 computer. It is made up of 11 principal subroutines organized in the following way (Figure 10):

INMAT is a subroutine that reads the data: general stoichiometric and thermodynamic data; special conditions of the problem; total concentrations of metals and ligands, pH, or TOTH; guesses for the free concentrations of metals and ligands and chosen sets of solids.

SOLIDO finds out if any solid is present; scans the tableau for families of connected solids; defines the principal and secondary variables; and computes the coefficients μ, ν, and ν'.

MLINSO computes the secondary variables M and L (other than C) in function of the principal variables using μ, ν, and ν'.

XCYZ computes the secondary variables, C, the mole balance equations for each metal and ligand ($\neq H$ or OH) and their derivatives with respect to every metal and ligand. By computing a mole balance equation, we mean finding the actual numerical difference between the sum of the concentrations of the soluble species and the imposed analytical (total) concentration of the same component. In the same way the derivatives are the numerical values obtained by replacing the concentrations by their molar values in the formal algebraic formulas of the derivatives.

SUBPH computes the proton condition equation, its derivatives with respect to every metal and ligand, and the derivatives of all the equations with respect to H.
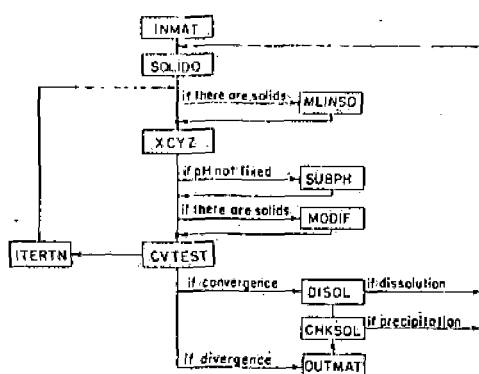
MODIF modifies the equations in accordance with our choice of principal and secondary variables—i.e., eliminates $[S_{ij}]$. It also modifies the derivatives accordingly.

CVTEST verifies that the number of iterations does not exceed any arbitrary number and checks whether or not the equations are satisfied within an arbitrary precision.

ITERTN performs the Newton-Raphson iteration using Gaussian elimination without iterative improvement to solve the system of linear equations: $J_n(\bar{X}_n - \bar{X}_{n+1}) = \bar{Y}_n$.

DISOL computes the amount of every solid precipitated and verifies that none is negative. In case some are negative, the least-probable solid ($[S_{ij}]$ = minimum) is no longer imposed and the computation is restarted.

CHKSOL verifies that no solubility product has been exceeded. In case some are exceeded, the solid for which the driving force is greatest $[([M_i][L_j])/K_{ij}$ = maximum] is imposed and the computation is restarted.

OUTMAT prints the output. Metals, ligands, and complexes are printed in a matrix form.

Example of Computation. The following example shows the application of the program to an equilibrium computation involving 20 metals (+H), 31 ligands (+OH), 738 complexes, 83 possible solids, and one gas-phase component. Pressure, temperature, ionic strength, pH, and oxidation-reduction state are all taken to be constant. Table III gives the list of the metals and the ligands (and their identifying numbers) involved with their imposed analytical (total) concentrations.

Such an example can be seen to have some of the characteristics of certain well-known natural systems. The first guesses for the free metal and the free ligand concentrations were all taken to be $10^{-8}M$. The chosen set of solids at the start of the computation and its subsequent modifications by the program are shown in Figure 11.

The final result was found at the 56th iteration. Figure 12 gives the tableau of the thermodynamic data and has been deposited with the American Chemical Society Microfilm Depository Service. Table IV gives the computed equilibrium concentrations.

It is worthwhile to note that the whole computation took a little less than 60 sec. Equilibrium solutions at other pH's were also computed with this result as a starting guess; it takes about 35 iterations to go from one pH to the next one, say 8 to 9. The computation was also made without fixing the pH. TOTH = $-0.83M$, found in the first computation, was in-

Figure 10. Chart showing the organization of the principal subroutines of the computer program

Table III. List of Metal Ions and Ligands (Identified by Number) and Their Total Concentrations (Solid, Aqueous, and Gas Phases) in a Hypothetical Model System of 20 Metals and 31 Ligands[a]

Metals					Ligands						
1	Ca^{2+}	$10^{-1.0}$	11	Cd^{2+}	$10^{-6.0}$	1	CO_3^{2-}	$10^{-0.5}$	11	$P_3O_{10}^{-5}$	$10^{-8.0}$	21	DIP	$10^{-7.0}$
2	Mg^{2+}	$10^{-1.2}$	12	Zn^{2+}	$10^{-3.0}$	2	SO_4^{-2}	$10^{-1.5}$	12	$SiO_2(OH)_2^{2-}$	$10^{-0.01}$	22	SUSAL	$10^{-7.0}$
3	Sr^{2+}	$10^{-2.7}$	13	Ni^{2+}	$10^{-6.0}$	3	Cl^-	$10^{-0.2}$	13	$S_2O_3^{2-}$	$10^{-7.0}$	23	GLY	$10^{-6.0}$
4	K^+	$10^{-2.0}$	14	Hg^{2+}	$10^{-6.0}$	4	F^-	$10^{-2.0}$	14	AC	$10^{-6.3}$	24	GLUT	$10^{-6.0}$
5	Na^+	$10^{-0.3}$	15	Pb^{3+}	$10^{-7.0}$	5	Br^-	$10^{-3.0}$	15	ACAC	$10^{-7.0}$	25	PIC	$10^{-6.3}$
6	Fe^{3+}	$10^{-1.0}$	16	Co^{2+}	$10^{-7.0}$	6	I^-	$10^{-6.0}$	16	CIT	$10^{-6.0}$	26	NTA	$10^{-7.0}$
7	Fe^{2+}	$10^{-8.0}$	17	Co^{3+}	$10^{-4.0}$	7	NH_3	$10^{-6.0}$	17	OX	$10^{-5.7}$	27	EDTA	$10^{-7.3}$
8	Mn^{2+}	$10^{-7.0}$	18	Ag^+	$10^{-7.0}$	8	S^{2-}	$10^{-8.0}$	18	SAL	$10^{-6.3}$	28	DCTA	$10^{-7.3}$
9	Cu^{2+}	$10^{-3.5}$	19	Cr^{3+}	$10^{-4.0}$	9	PO_4^{3-}	$10^{-3.0}$	19	TART	$10^{-6.0}$	29	CYST	$10^{-8.0}$
10	Ba^{2+}	$10^{-3.0}$	20	Al^{3+}	$10^{-0.01}$	10	$P_2O_7^{4-}$	$10^{-7.0}$	20	EN	$10^{-7.0}$	30	NOC	$10^{-8.0}$
												31	PHTH	$10^{-7.3}$

[a] The equilibrium computation for this system involves 738 complexes and 83 possible solids. There is one gas-phase component, CO_2. Pressure, temperature, ionic strength, pH, and oxidation–reduction state are all assumed to be constant. Fixed pH = 8; fixed p_{CO_2} = $10^{-3.5}$ atm; ionic strength $\simeq 0.5M$.

AC = acetate	GLY = glycine
ACAC = acetylacetone	GLUT = glutamate
CIT = citrate	PIC = picolinate
OX = oxalate	NTA = nitriloatriacetate
SAL = salicylate	EDTA = ethylenediaminetetraacetate
TART = tartrate	DCTA = 1,2-diaminocyclohexane-tetraacetate
EN = ethylenediamine	CYST = cysteine
DIP = dipyridyl	NOC = nocardamine (desferri-ferrioxamine)
SUSAL = sulfosalicylate	PHTH = phthalate

posed and the result (identical to Table IV) was obtained in 52 iterations ($10^{-8}M$ being the systematic first guess and the correct set of solids having been imposed). The storage space needed for the program itself is about 50,000 bytes while it takes about 90,000 bytes to store the data. In all the examples we have taken a systematic guess of $10^{-8}M$ for every free concentration, not because we could not find a better one, but to show that the domain of convergence is rather large in general.

The program has now been extensively tested on numerous small and large systems and we have been able to converge toward the solution in each case. The program is being currently modified to handle variations in the ionic strength and oxidation–reduction reactions.

To vary the ionic strength, two sets of equilibrium constants are stored, one at $I = 0.0M$, the other one at $I = 0.5M$. An interpolation routine allows computation of the set of constants corresponding to an intermediate ionic strength. An it-

Iteration no.		
0	First guesses: all free concentrations = $10^{-8} M$ Chosen set of solids: $S_{1-1}, S_{1-9}, S_{3-1}, S_{6-32}, S_{10-2}, S_{12-12}, S_{13-1}, S_{14-8}, S_{17-32}, S_{20-12}, S_{20-32}, S_{21-1}$ [CO_2 (g)]	
31	S_{13-1}	dissolves
39	S_{1-4}	precipitates
42	S_{19-32}	precipitates
45	S_{3-2}	precipitates
49	S_{3-1}	dissolves
53	S_{9-1}	precipitates
56	Found set of solid: $S_{1-1}, S_{1-4}, S_{1-9}, S_{3-2}, S_{6-32}, S_{9-1}, S_{10-2}, S_{12-12}, S_{14-8}, S_{17-32}, S_{19-32}, S_{20-12}, S_{20-32}, S_{21-1}$ [CO_2 (g)]. See solution Table IV.	

Figure 11. Successive modifications of sets of solids in a 20-metal, 31-ligand model system

After 56 iterations an equilibrium set of 13 solids [+CO_2 (g)] is found

erative technique looping on the whole program is envisaged to correct the equilibrium constants to the computed ionic strength of the system.

The redox reactions are handled in several ways. One way involves the use of optional complexes ($NO_3^- \equiv NH_3 + 3 H_2O - 9H^+ - 8e^-$), or optional solids ($MnO_2 \equiv Mn^{2+} + 4 OH^- - 2e^- - 2H_2O$) whose equilibrium constants are given as a function of the p_e of the system. Another way is to define new secondary variables ($[Fe^{2+}] = k[e^-][Fe^{3+}]$) much in the same way it has been shown for solids. The existing subroutines MLINSO and MODIF are used to handle these.

Appendix

DERIVATIVES OF THE MOLE BALANCE EQUATIONS

Let $YM_i = [M_i] + \sum_{j,k} \alpha[C_{ijk}] - TOTM_i$ (= 0 from Eq. 3)

$$YL_j = [L_j] + \sum_{i,k} \beta[C_{ijk}] - TOTL_j \ (= 0 \text{ from Eq. 3})$$

$$YH = [H] - [OH] + \sum_{\substack{\text{last row} \\ j,k}} \alpha[C_{ijk}] -$$

$$\sum_{\substack{\text{last column} \\ i,k}} \beta[C_{ijk}] + \sum_{i,j,k} \gamma[C_{ijk}] - TOTH \ (= 0 \text{ from Eq. 4})$$

By use of Equation 1: $[C_{ijk}] = K_{ijk}[M_i]^\alpha[L_j]^\beta[H]^\gamma$ it follows:

$$\frac{\partial YM_i}{\partial[M_k]} = 0 \text{ for } i \neq k$$

$$\frac{\partial YL_j}{\partial[L_k]} = 0 \text{ for } j \neq k$$

$$\frac{\partial YM_i}{\partial[M_i]} = 1 + \sum_{j,k} \alpha^2[C_{ijk}]/[M_i]$$

$$\frac{\partial YL_j}{\partial[L_j]} = 1 + \sum_{i,k} \beta^2[C_{ijk}]/[L_j]$$

$$\frac{\partial YM_i}{\partial[L_j]} = \sum_k \alpha\beta[C_{ijk}]/[L_j]$$

Table III. List of Metal Ions and Ligands (Identified by Number) and Their Total Concentrations (Solid, Aqueous, and Gas Phases) in a Hypothetical Model System of 20 Metals and 31 Ligands[a]

	Metals						Ligands					
1	Ca^{2+}	$10^{-1.0}$	11	Cd^{2+}	$10^{-6.0}$	1	CO_3^{2-}	$10^{-0.5}$	11	$P_3O_{10}^{-5}$	$10^{-8.0}$	21 DIP $10^{-7.0}$
2	Mg^{2+}	$10^{-1.2}$	12	Zn^{2+}	$10^{-3.0}$	2	SO_4^{-2}	$10^{-1.5}$	12	$SiO_2(OH)_2^{2-}$	$10^{-0.01}$	22 SUSAL $10^{-7.0}$
3	Sr^{2+}	$10^{-2.7}$	13	Ni^{2+}	$10^{-6.0}$	3	Cl^-	$10^{-0.3}$	13	$S_2O_3^{2-}$	$10^{-7.0}$	23 GLY $10^{-5.0}$
4	K^+	$10^{-2.0}$	14	Hg^{2+}	$10^{-6.0}$	4	F^-	$10^{-2.0}$	14	AC·	$10^{-6.3}$	24 GLUT $10^{-6.0}$
5	Na^+	$10^{-0.3}$	15	Pb^{3+}	$10^{-7.0}$	5	Br^-	$10^{-3.0}$	15	ACAC	$10^{-7.0}$	25 PIC $10^{-6.5}$
6	Fe^{3+}	$10^{-1.0}$	16	Co^{2+}	$10^{-7.0}$	6	I^-	$10^{-6.0}$	16	CIT	$10^{-6.0}$	26 NTA $10^{-7.0}$
7	Fe^{2+}	$10^{-8.0}$	17	Co^{3+}	$10^{-4.0}$	7	NH_3	$10^{-6.0}$	17	OX	$10^{-5.7}$	27 EDTA $10^{-7.3}$
8	Mn^{2+}	$10^{-7.0}$	18	Ag^+	$10^{-7.0}$	8	S^{2-}	$10^{-8.0}$	18	SAL	$10^{-6.3}$	28 DCTA $10^{-7.3}$
9	Cu^{2+}	$10^{-3.5}$	19	Cr^{3+}	$10^{-4.0}$	9	PO_4^{3-}	$10^{-3.6}$	19	TART	$10^{-6.0}$	29 CYST $10^{-8.0}$
10	Ba^{2+}	$10^{-3.0}$	20	Al^{3+}	$10^{-0.01}$	10	$P_2O_7^{4-}$	$10^{-7.0}$	20	EN	$10^{-7.0}$	30 NOC $10^{-8.6}$
												31 PHTH $10^{-7.3}$

[a] The equilibrium computation for this system involves 738 complexes and 83 possible solids. There is one gas-phase component, CO_2. Pressure, temperature, ionic strength, pH, and oxidation–reduction state are all assumed to be constant. Fixed pH = 8; fixed p_{CO_2} = $10^{-3.5}$ atm; ionic strength $\simeq 0.5M$.

AC = acetate	GLY = glycine
ACAC = acetylacetone	GLUT = glutamate
CIT = citrate	PIC = picolinate
OX = oxalate	NTA = nitriloatriacetate
SAL = salicylate	EDTA = ethylenediaminetetraacetate
TART = tartrate	DCTA = 1,2-diaminocyclohexane-tetraacetate
EN = ethylenediamine	CYST = cysteine
DIP = dipyridyl	NOC = nocardamine (desferri-ferrioxamine)
SUSAL = sulfosalicylate	PHTH = phthalate

posed and the result (identical to Table IV) was obtained in 52 iterations ($10^{-8}M$ being the systematic first guess and the correct set of solids having been imposed). The storage space needed for the program itself is about 50,000 bytes while it takes about 90,000 bytes to store the data. In all the examples we have taken a systematic guess of $10^{-8}M$ for every free concentration, not because we could not find a better one, but to show that the domain of convergence is rather large in general.

The program has now been extensively tested on numerous small and large systems and we have been able to converge toward the solution in each case. The program is being currently modified to handle variations in the ionic strength and oxidation–reduction reactions.

To vary the ionic strength, two sets of equilibrium constants are stored, one at $I = 0.0M$, the other one at $I = 0.5M$. An interpolation routine allows computation of the set of constants corresponding to an intermediate ionic strength. An it-

Iteration no.		
0	First guesses: all free concentrations = $10^{-8} M$ Chosen set of solids: S_{1-1}, S_{1-9}, S_{3-1}, S_{6-32}, S_{10-2}, S_{12-12}, S_{13-1}, S_{14-8}, S_{17-32}, S_{20-12}, S_{20-32}, S_{21-1} [CO_2 (g)]	
31	S_{13-1}	dissolves
39	S_{1-4}	precipitates
42	S_{19-32}	precipitates
45	S_{3-2}	precipitates
49	S_{3-1}	dissolves
53	S_{9-1}	precipitates
56	Found set of solid: S_{1-1}, S_{1-4}, S_{1-9}, S_{3-2}, S_{6-32}, S_{9-1}, S_{10-2}, S_{12-12}, S_{14-8}, S_{17-32}, S_{19-32}, S_{20-12}, S_{20-32}, S_{21-1} [CO_2 (g)]. See solution Table IV	

Figure 11. Successive modifications of sets of solids in a 20-metal, 31-ligand model system

After 56 iterations an equilibrium set of 13 solids [+CO_2 (g)] is found

erative technique looping on the whole program is envisaged to correct the equilibrium constants to the computed ionic strength of the system.

The redox reactions are handled in several ways. One way involves the use of optional complexes ($NO_3^- \rightleftharpoons NH_4 + 3 H_2O - 9H^+ - 8e^-$), or optional solids ($MnO_2 \rightleftharpoons Mn^{2+} + 4 OH^- - 2e - 2H_2O$) whose equilibrium constants are given as a function of the p_e of the system. Another way is to define new secondary variables ($[Fe^{2+}] = k[e^-][Fe^{3+}]$) much in the same way it has been shown for solids. The existing subroutines MLINSO and MODIF are used to handle these.

Appendix

DERIVATIVES OF THE MOLE BALANCE EQUATIONS

Let $YM_i = [M_i] + \sum_{j,k} \alpha[C_{ijk}] - TOTM_i$ ($= 0$ from Eq. 3)

$$YL_j = [L_j] + \sum_{i,k} \beta[C_{ijk}] - TOTL_j \ (= 0 \text{ from Eq. 3})$$

$$YH = [H] - [OH] + \sum_{\substack{last\ row \\ j,k}} \alpha[C_{ijk}] -$$

$$\sum_{\substack{last\ column \\ i,k}} \beta[C_{ijk}] + \sum_{i,j,k} \gamma[C_{ijk}] - TOTH \ (= 0 \text{ from Eq. 4})$$

By use of Equation 1: $[C_{ijk}] = K_{ijk}[M_i]^\alpha[L_j]^\beta[H]^\gamma$ it follows:

$$\frac{\partial YM_i}{\partial[M_k]} = 0 \text{ for } i \neq k$$

$$\frac{\partial YL_j}{\partial[L_k]} = 0 \text{ for } j \neq k$$

$$\frac{\partial YM_i}{\partial[M_i]} = 1 + \sum_{j,k} \alpha^2[C_{ijk}]/[M_i]$$

$$\frac{\partial YL_j}{\partial[L_j]} = 1 + \sum_{i,k} \beta^2[C_{ijk}]/[L_j]$$

$$\frac{\partial YM_i}{\partial[L_j]} = \sum_k \alpha\beta[C_{ijk}]/[L_j]$$

Table IV. Equilibrium Composition of th[e] ...

Concentrations of metals, ligands, and complexes are given as negative logarithms. The values for the complexes are the sums of the co...

Metals	Total concn	Free concn	CO_3^{2-}	SO_4^{2-}	Cl^-	F^-	Br^-	I^-	NH_3	S^{2-}	PO_4^{3-}	$P_2O_7^{4-}$	$P_3O_{10}^{5-}$	$SiO_3(OH)_2^{2-}$	$S_2O_3^{2-}$	A...
Ligands Total concn			0.5	1.5	0.3	2.0	3.0	6.0	6.0	8.0	3.0	7.0	8.0	0.01	7.0	6.?
Ligands Free concn			4.50	2.00	0.30	3.65	3.00	6.05	7.23	32.55	11.10	10.43	12.43	10.60	15.75	6.?
Ca^{2+}	1.0	2.50	4.33(s)	3.30		5.65(s)			9.93		9.00(s)	7.93	9.53		17.45	8.?
Mg^{2+}	1.2	1.28	3.17	1.99		3.63			8.31			7.98	7.12	8.02	16.33	7.?
Sr^{2+}	2.7	4.20		(s)							10.88	11.33	12.58		19.04	10.?
K^+	2.0	2.01			3.52							10.15	11.65		17.35	
Na^+	0.3	0.31	4.11		2.11							8.04	9.94		15.95	
Fe^{3+}	1.0	18.90		18.48	18.39	16.83	22.20	23.65			20.00	23.13		15.50	32.65	21.?
Fe^{2+}	8.0	8.95		9.75	8.85				14.78							12.?
Mn^{2+}	7.0	7.57	9.07	8.37		7.17			14.00		12.47	14.41			22.52	13.?
Cu^{2+}	3.5	7.90	7.59(s)	8.70	8.50	10.75	10.40		9.23		13.40	11.63	13.03			12.?
Ba^{2+}	3.0	8.00		(s)								13.83	14.13		22.54	13.?
Cd^{2+}	6.0	8.28	10.78	9.09	6.00	11.43	9.68	11.93	12.91		17.38	11.52	12.52		21.23	13.?
Zn^{2+}	3.0	6.80		7.60	6.27	9.65	10.40		11.73			8.51	12.34	(s)	21.35	11.?
Ni^{2+}	6.0	6.34		7.15	6.84	9.39	9.44		10.77			10.98			21.09	12.?
Hg^{2+}	6.0	20.05		20.71	6.06	22.70	8.65	8.35	17.00	32.15(s)		18.79			7.00	
Pb^{2+}	7.0	9.19		9.69	7.01		11.09	13.97				24.76			19.83	13.?
Co^{2+}	7.0	7.25		7.85	7.75		10.35		12.48				13.08		22.10	12.?
Co^{3+}	4.0	26.70				25.78			26.51							
Ag^+	7.0	14.75		16.25	9.87		13.35	7.00	18.58	30.50					22.20	20.?
Cr^{3+}	4.0	13.20		12.20		12.29										
Al^{3+}	0.01	15.30		15.86	10.84									(s)		
H^+		8.00	2.90(g)	8.20		8.75			6.03	27.92	7.28	9.93	12.53	4.48	22.45	9.?

ᵃ —log (moles solid per liter of solution): $CaCO_3$, 1.05; CaF_2, 2.32; $Ca_5(PO_4)_3OH$, 3.48; $SrSO_4$, 2.72; $Fe(OH)_3$, 1.00; $Cu_2CO_3(OH)_2$, 3.80; $BaSO_4$, 3.0...

$$\frac{\partial YL_j}{\partial [M_i]} = \sum_k \alpha\beta[C_{ijk}]/[M_i]$$

$$\frac{\partial YM_i}{\partial [H]} = \sum_{j,k} \alpha\gamma[C_{ijk}]/[H] - \sum_{\substack{last\ column \\ k}} \alpha\beta[C_{ijk}]/[H]$$

$$\frac{\partial YH}{\partial [M_i]} = \sum_{j,k} \alpha\gamma[C_{ijk}]/[M_i] - \sum_{\substack{last\ column \\ k}} \alpha\beta[C_{ijk}]/[M_i]$$

$$\frac{\partial YL_j}{\partial [H]} = \sum_{i,k} \beta\gamma[C_{ijk}]/[H] + \sum_{\substack{last\ row \\ k}} \alpha\beta[C_{ijk}]/[H]$$

$$\frac{\partial YH}{\partial [L_j]} = \sum_{i,k} \beta\gamma[C_{ijk}]/[L_j] + \sum_{\substack{last\ row \\ k}} \alpha\beta[C_{ijk}]/[L_j]$$

$$\frac{\partial YH}{\partial [H]} = 1 + [OH]/[H] + \sum_{i,j,k} \gamma^2[C_{ijk}]/[H] + \sum_{\substack{last\ row \\ j,k}} \alpha^2[C_{ijk}]/[H] + \sum_{\substack{last\ column \\ i,k}} \beta^2[C_{ijk}]/[H]$$

Whenever a solid S_{ij} precipitates, a new secondary variable is defined according to Equation 7; say

$$[M_i] = \mu[L_j]^p[H]^{p'}$$

Then the derivatives are modified in the following way:

$$new\ \frac{\partial YM\ or\ \partial YL}{\partial [L_j]} = old\ \frac{\partial YM\ or\ \partial YL}{\partial [L_j]} + \nu\ \frac{[M_i]}{[L_j]}\ \frac{\partial YM\ or\ \partial YL}{\partial [M_i]}$$

$$new\ \frac{\partial YM\ or\ \partial YL}{\partial [H]} = old\ \frac{\partial YM\ or\ \partial YL}{\partial [H]} + \nu'\ \frac{[M_i]}{[H]}\ \frac{\partial YM\ or\ \partial YL}{\partial [M_i]}$$

Furthermore, since the equations are modified according to Equation 8; say

$$new\ YL_j = old\ YL_j + \nu \cdot YM_i$$

$$new\ YH = old\ YH + \nu' \cdot YM_i$$

(YM_i will be discarded in the rest of the computation.) We have to modify the derivatives further:

$$new\ \frac{\partial YL_j}{\partial [M]\ or\ \partial [L]} = old\ \frac{\partial YL_j}{\partial [M]\ or\ \partial [L]} + \nu\ \frac{\partial YM_i}{\partial [M]\ or\ \partial [L]}$$

$$new\ \frac{\partial YH}{\partial [M]\ or\ \partial [L]} = old\ \frac{\partial YH}{\partial [M]\ or\ \partial [L]} + \nu'\ \frac{\partial YM_i}{\partial [M]\ or\ \partial [L]}$$

It should be noted that the order in which those modifications are made is not indifferent for $\frac{\partial YL_j}{\partial [L_j]}$ or $\frac{\partial YH}{\partial [H]}$; the order shown here is the correct one.

exes of a particular metal and ligand. (s) indicates that a solid exists at equilibrium,ᵃ and (g) indicates the gas phase component (CO)₂

	AC	CIT	OX	SAL	TART	EN	DIP	SUSAL	GLY	GLUT	PIC	NTA	EDTA	DCTA	CYST	NOC	PHTH	OH
0	6.0	5.7	6.3	6.0	7.0	7.0	7.0	6.0	6.0	6.3	7.0	7.3	7.3	8.0	8.0	7.3		
96	16.32	6.94	11.80	6.30	9.83	7.97	10.60	7.83	7.75	7.45	12.28	19.59	20.88	16.13	21.65	7.35	5.70	
		7.32	6.44		7.10				9.73	8.85	8.15	8.38	11.39	10.88		12.85	8.25	7.30
04	6.81	5.82		6.38	10.71	8.76		8.12	7.13	6.54	8.16	14.18	11.86		8.94		4.88	
	9.72	9.73						11.43	10.54	9.95	11.47	15.19	15.07		13.95		9.30	
											10.98	18.20						
40	10.22	17.75	13.95			14.69	16.73	14.55		10.60	12.51	10.44	19.95	8.05		8.30(s)		
21	9.77		14.15		14.48	12.52	13.65	12.88	12.60	11.51	12.42	14.24	11.63	14.07			8.15	
72	12.49	11.80	13.47		14.70	13.04	12.97	13.40	12.52	11.44	12.45	13.16	11.65	20.09	17.31		10.07	
06	6.22	10.33	9.10	11.00	7.15	7.77	9.00	7.47	8.22	7.24	7.43	8.69	7.48		14.90	12.15	8.20	
	29.92	13.72	19.49	12.79				15.43	14.44	13.76	15.57	19.79	20.85			13.85	13.30	
84	12.08	12.32	14.49	11.78	12.61	11.76	14.19	11.72	11.63	11.15	10.46	11.38	9.97		21.06	13.14	9.68	
16	11.72	10.04	11.70	10.70	10.93	9.37	11.30	9.37	9.55	8.96	8.58	9.89	8.98	13.02	16.25	11.95	8.69	
80	8.35	9.18	11.14		8.47	7.18	10.55	8.37	8.59	7.00	7.32	7.33	7.82	19.79	15.79	11.59	7.44	
				16.32				16.19			19.25	16.73	17.78	16.63	8.30			
95	12.26			11.69		14.16		11.92		12.05	9.67	10.78	10.37	13.01			13.14	8.68
21	26.77	10.69	12.25	11.45	11.17	9.52	11.85	10.38	10.40	9.01	9.03	10.54	9.23	14.27	17.09	17.95	8.05	
				9.29								10.29					(s)	
	30.72	19.29			19.88	23.89		19.28		18.82		27.04					18.55	
		14.64					14.20					8.84					6.30(s)	
14	6.72	18.17	13.10			12.91				12.78	16.39	17.80					7.50(s)	
16	8.32	10.94	6.30	10.20	7.86		7.00	6.03	6.05	10.06	10.48	17.29	18.07	13.08	17.65	10.25		

nO₄, 3.00; HgS, 8.00; Co(OH)₃, 4.00; Cr(OH)₃, 4.00; Al₂Si₂O₅(OH)₄, 0.31; Al(OH)₃, 2.99

Nomenclature

C_{ijk}	= complex k formed by reaction of M_i with L_j
H	= hydrogen ion
J	= Jacobian matrix of the system
k_{ij}	= dissociation constant for the solid S_{ij} (corrected for ionic strength)
K_w	= ion product of water
L_j	= ligand j
M_i	= metal i
OH	= hydroxide ion
p[ ]	= negative logarithms of the concentrations
S_{ij}	= solid formed by reaction of M_i with L_j
TOTM, TOTL	= analytical (total) concentrations of metals and ligands in all phases of the system, respectively
$[\bar{F}(\bar{X}) = 0]$	= general system of equations to be solved

GREEK LETTERS

α_{ijk}	= stoichiometric coefficient of M_i in C_{ijk}
β_{ijk}	= stoichiometric coefficient of L_j in C_{ijk}
γ_{ijk}	= stoichiometric coefficient of H or OH in C_{ijk}
δ_{ij}	= stoichiometric coefficient of M_i in S_{ij}
η_{ij}	= stoichiometric coefficient of L_i in S_{ij}
λ_{ij}	= stoichiometric coefficient of H or OH in S_{ij}
u,v,v'	= constants defined in text

SYMBOLS

[ ]	= concentrations
[ ]ᵣ	= number of moles of a substance used to make up the system, per liter of solution
≡	= defines the formulas (distinct from =)

Literature Cited

Brinkley, S. R., J. Chem. Phys., 15, 107 (1947).
Denbigh, K. G., "The Principles of Chemical Equilibrium," Cambridge Univ. Press, Cambridge, England, 1966.
Garrels, R. M., Christ, C. L., "Solutions, Minerals, and Equilibria," Harper, New York, N.Y., 1965.
Ingri, N., Kakolowicz, W., Sillén, L. G., Warnqvist, B., Talanta, 14, 1261 (1967).
Isaacson, E., Keller, H. B., "Analysis of Numerical Methods," Wiley, New York, N.Y., 1966.
Ringbom, A., "Complexation in Analytical Chemistry," Wiley-Interscience, New York, N.Y., 1963.
Shapiro, N. Z., "A Generalized Technique for Eliminating Species in Complex Chemical Equilibrium Calculations," Rand Corp. Memo 4205-PR, AD-605 316 (1964).
Sillén, L. G., "Oceanography," in "Physical Chemistry of Sea Water," M. Sears, Ed., American Association for the Advancement of Science, Washington, D.C., 1961.
Sillén, L. G., Martell, A. E., Chem. Soc. Spec. Publ. 17 (1964).
Stumm, W., Morgan, J. J., "Aquatic Chemistry," Wiley-Interscience, New York, N.Y., 1970.
White, W. B., Johnson, S. M., Dantzig, G. B., J. Chem. Phys., 28, 751 (1958).
Zeleznik, F. J., Gordon, S., Ind. Eng. Chem., 60, 27 (1968).

UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

New method suggested for leaching

SOLUTION MINING of underground uranium ore in formations below the water table using a cluster of injection, recovery and monitor wells was the subject of a patent* recently issued to John Gardner and Malcolm I. Ritchie, and assigned to Utah Construction & Mining Co.

The method involves introduction of a cold acid solution containing an oxidant and flocculant into the ore zone through the injection wells, then maintaining a controlled pressure gradient between the injection wells and a recovery well. Utah Construction & Mining has tested solution mining in Wyoming's Shirley Basin on an on-and-off basis for at least three years but has said little about commercial or economic success.

The patent states that following exploration, cores are drilled and studies are made to determine the permeability, porosity and water bearing characteristics of the formation. In this manner, the area and configuration of the underground deposit, the pattern of injection and recovery wells and the anticipated solution flow rates in the leach area can be determined.

The accompanying diagrams illustrate the method and placement of the bore holes. The more permeable and porous the deposit, the greater the spacing permitted between the wells. The pattern will generally consist of a centrally located recovery well with a group of injection and monitor wells placed around it. In the pattern indicated by the diagram, the injecting wells are approximately 50 ft apart and placed about 35 ft from the recovery well. Casing is set in the well bore down to a point adjacent to the upper ore horizon and terminates in a slotted screen with a length determined by the thickness of the orebody.

The screen terminates in the area of the impermeable bottom and the space between the well bore and the screen is packed with sized gravel. The annular opening between the casing, above the screen and upper ore horizon, is then sealed off with a chemical gel which has a triggering catalyst for control of gel time and position of the seal. All materials used in the holes must be resistant to the corrosive properties of the reagents involved.

No formation fracture

On completion of the wells, a volume of leach solution, sufficient to displace the reservoir water within the planned pattern, is introduced through the injection wells at a pressure below formation fracture strengths. When released below the water table, the injected leach solution forms a more or less circular pool having positive pressure at each injection point. As inflow continues, the pool will expand until merging with similar pools at other injection wells, at which time, the reservoir water will have been replaced with leach solution.

Tracking and eventual control of this expanding front is accomplished by observing the variation in the static water level in the monitor wells located at the planned perimeter of the leach pattern. A rise in water level in monitor wells indicates that the contained area has been filled and is at a pressure above that of the surrounding reservoir. At this time, pumping from the recovery well can be started at a rate equal to the combined inflow volume of the injection wells. From here on, the pattern is operated on this single pass solution flow system until satisfactory mineral recovery has been attained.

Close control of solution is said to be possible throughout the operation by regulation of water level in the monitor wells and by recovery of tracer, which is introduced in the injection wells along with the leach solution. Uranium can be recovered from the pregnant solution pumped to the surface by direct precipitation or by selective ion exchange into an organic solvent with subsequent removal from the organic phase of the stripping agent.

Results from one test

The patent states that the method was used on a particular orebody in the following manner:

Radiometric probes located the exact position of the ore and contact was made at 331 ft below the surface. Initial exploration had proved the existence of a mineral area and study showed that the static water was found at 300 ft below the surface. Formation permeability indicated that a four spot pattern would be more suitable with injection wells spaced 25 ft from the recovery well. The formation would support flow rates of 20 gpm at each injection well and 60 gpm from the recovery well.

Solvent concentration was set at 10 gm per liter nitric acid, 1 gm per liter sodium chlorate and 10 ppm flocculant (Separan).

Nitric acid was selected in preference to less costly sulphuric acid because of a high calcium content of the orebody to be leached which would result in formation of insoluble calcium sulphate. The latter could cause blockage of the leach zone and loss of permeability. Calcium nitrate, on the other hand, is soluble in water and does not present this problem. Hydrochloric acid could be used as well but it is more expensive than nitric and does not have the same oxidizing power as nitric.

500 lb of U_3O_8 a day

Average daily production on the particular orebody described was approximately 500 lb U_3O_8 over a period of approximately 30 days, and tracer recovery was 90% proving the close control of the leach solution, the report says. At the end of the operation, samples taken from the monitor wells had a neutral pH showing that solution control was as planned.

The patent holders say that contacting uranium bearing ore with any mineral acid causes the liberation of H_2S, probably due to the reaction with soluble sulphides such as pyrrhotite and, because of the pressure involved, also creates a highly reducing atmosphere. Under these conditions optimum extraction of uranium is impossible. To counteract the reducing atmosphere, an oxidant, such as sodium chlorate, is added to the leach solution. Its function is to convert ferrous iron into ferric iron which, in turn, promotes the conversion of tetravalent uranium to hexavalent ura-

uranium ore in place

nium. In the hexavalent form, uranium is soluble in dilute acid but the tetravalent form is relatively insoluble. Other oxidants can be used.

To prevent blinding . . .

The flocculant is added into the leach solution to assist in maintaining permeability of the orebody. During the process of leaching, clays contained in the orebody are dislodged and carried away with the solution flow. This material can accumulate and pack together resulting in an impermeable film which blocks the passage of the solution. The flocculating action holds the fine clay particles in a sponge-like mass allowing the solution to filter through to the recovery well.

The pregnant solution recovered from the system contains uranium and other cations such as hydrogen, iron, aluminum, magnesium, calcium, etc., and has as associated anions, nitrate, and some chloride and sulphate. The concentration of uranium in the pregnant solution will vary from zero to 5 gm per liter U_3O_8 depending upon the stage of leaching.

Gardner and Ritchie point out that the method permits use of cold leach solutions without the use of excessive pressure and without the necessity of using a flow and counterflow form of circulation of the solution through the orebody. They say that an appropriate pattern of recovery, injection and monitor wells, which is determined by the permeability, porosity and water bearing characteristics of the deposit, can produce an island of leach solution about the injection wells and recovery well, which is substantially confined by the reservoir of fluid.

All this assumes that the wells are properly sealed, that injection takes place at a pressure insufficient to fracture the formation, and that solution introduction and withdrawal rates are equalized so that the island of leach solution is maintained. The method is said to provide means of minimizing solution loss and dilution of the island of leach solution by an influx of environmental water.

*U.S. Patent 3,309,140 Leaching of Uranium Ore In-Situ, John Gardner, Los Altos, Calif., and Malcolm I. Ritchie, Riverton, Wyo., assignors to Utah Construction & Mining Co., San Francisco, Calif.

Group of wells on predetermined pattern taps U_3O_8 orebody allowing solution flow at pressures below formation fracturing level
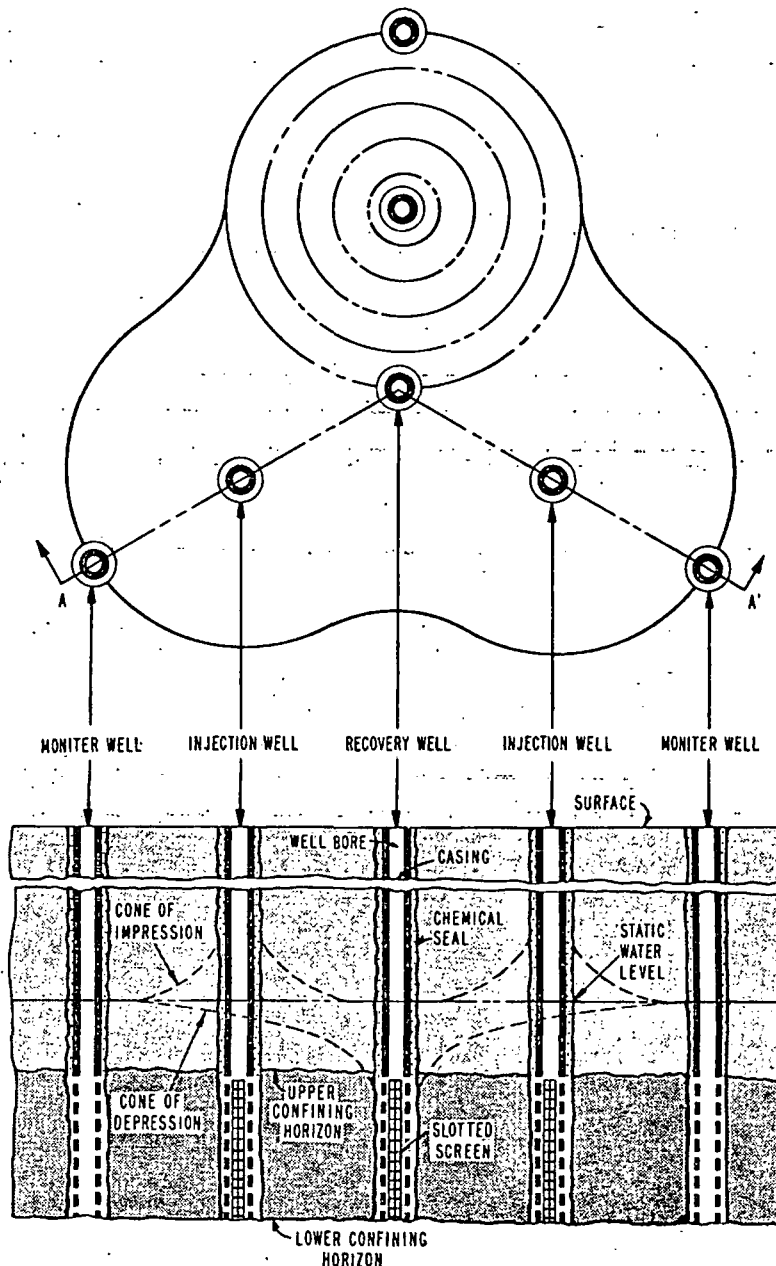
WELL PATTERN is shown in plan (upper drawing) and vertical section. Acid solution is injected at a rate that balances the withdrawal of pregnant solution from the recovery well. The operation is tracked by observing static water level of monitor wells and by recovery of tracer.

NICKEL PRECIPITATION FROM SPENT PICKLING SOLUTIONS

UDC 669.243

I. A. Vainshtein, L. D. Klenysheva, and L. N. Kononenko

At present the spent solutions from pickling alloy steels at ferrous metallurgy enterprises, which contain considerable amounts of salts of Ni, Co, and other metals, are neutralized with lime and dumped; this leads to irrecoverable losses of valuable constituents. Every year 600-800 tons of nickel (converted to NiO) are lost in the effluents from a metallurgical combine of average capacity.

The All-Union Research and Design Institute for Gas and Effluent Purification and Secondary Energy Utilization in Ferrous Metallurgy has developed a method for two-stage treatment of spent pickling solutions which involves the precipitation of Fe, Cr, and other metal cations and the conversion of nickel to an ammonium complex. After separating out the solid phase, the filtrate contains a mixture of nickel and ammonium sulfates.

Reagent methods of nickel precipitation have been widely used to separate the nickel from these solutions [1]. However, there are no data on the conditions for the process of nickel precipitation from $NiSO_4 - (NH_4)_2SO_4 - H_2O$ systems.

A study was therefore made in the present work of the effect of ammonium ion concentration, temperature, and the type and excess of reagent upon the completeness of nickel precipitation and residue separation. The experimental data were expressed as relative magnitudes: the degree of nickel precipitation α and the degree of reagent conversion K [2].

The investigations showed that better results were obtained in precipitation with ammonium sulfide than with sodium sulfide (Fig. 1). Irrespective of the type of reagent used, raising the temperature to 100°C causes the nickel precipitation results to deteriorate; however, it helps to coagulate the finely dispersed sulfide residues and to produce pure ammonium sulfate mother liquors. In addition, heating lowers the specific resistance by one order of magnitude and reduces the residue moisture content somewhat (see Table). Optimum utilization of sulfide reagents occurs at a relative consumption rate of 100-110%. The presence of ammonium sulfate in the nickel solution in this case does not affect the precipitation process or the physical properties of the sulfide residues.

Precipitation of nickel by alkaline reagents occurs only at elevated temperatures. In solutions containing ammonium sulfate, the addition of alkali causes a decomposition reaction with formation of free ammonia, which reacts with the nickel ions to form relatively stable ammonia-nickel complexes. The precipitation process begins only after complete decomposition of ammonium sulfate, breakdown of the ammonia-nickel complexes, and elimination of ammonia from the solution (Fig. 2).

When solutions which do not contain ammonium ions are treated with alkali, basic nickel salts of variable composition are formed, not hydroxides [3]:

$$(x+y)NiSO_4 + 2xNaOH \rightarrow xNi(OH)_2 \cdot yNiSO_4 + xNa_2SO_4.$$
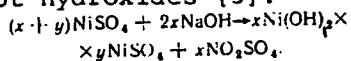
Losses of nickel during washing of the residue are high, due to their relatively high solubility. The residues are colloidal and in practice do not settle.

Increasing the precipitation temperature has practically no effect upon the degree of precipitation or the quality of the residues.

Results of Nickel Precipitation with Sulfide and Alkaline Reagents

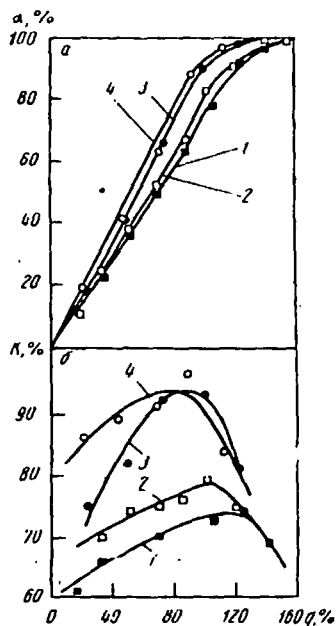| HI Reagent	Initial solution	t, °C	Moisture content of residues, %	Specific resistance of residues, $r \cdot 10^{-10}$ cm/g	Nickel extraction, %
17% $(NH_4)_2S$	$NiSO_4+(NH_4)_2SO_4$	20/100	77.7/69.7	5.5/0.4	90
	$NiSO_4$	20/100	77.4/74.4	4.8/0.9	
17% Na_2S	$NiSO_4+(NH_4)_2SO_4$	20/100	67.6/67.7	11.7/4.6	80
	$NiSO_4$	20/100	78/73.6	83/1.2	
13% Na_2CO_3	$NiSO_4+(NH_4)_2SO_4$	20/100	No precipitation 60	2	98
	$NiSO_4$	20/100	79/80	2.4/1.1	
24% NaOH	$NiSO_4+NH_4OH$	20/100	No precipitation 70	1.9	82
	$NiSO_4+(NH_4)_2SO_4$	20/100	No precipitation 62	1.4	
	$NiSO_4$	20/100	80/77	75/73	

Fig. 1. Relationship of nickel precipitation (a) and reagent conversion (b) to type of sulfide reagent and its consumption q at room temperature. The solution and reagent are respectively:
1- $NiSO_4 + (NH_4)_2SO_4$, Na_2S; 2- $NiSO_4$, Na_2S; 3- $NiSO_4 + (NH_4)_2CO_4$, $(NH_4)_2S$; 4- $NiSO_4$, $(NH_4)_2S$.

Complete nickel precipitation is achieved in the presence of ammonium sulfate by adding a 10% excess of alkali. The residue formed is crystalline, settles rapidly, and is easily filtered.

When the nickel solutions are treated with soda ash, basic nickel carbonate residues are formed with properties and composition which are closely dependent upon the conditions of formation: the solution composition, reagent consumption, pH, temperature, and precipitation time. Thus a milky green fine crystalline residue is formed when pure nickel solutions are treated with soda at room temperature; on heating, emerald green residues are formed and the residue basic phase accordingly consists of the following compounds:

$$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O \text{ или } NiCO_3 \times$$
$$\times 2Ni(OH)_2 \cdot 4H_2O.$$
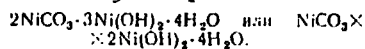
The residues readily settle, and the nickel content of the dried residue is ~ 50%. Complete precipitation of nickel is achieved at a relative soda consumption of about 110%, but most of the nickel is precipitated when 60% soda is added (Fig. 3).

A fine crystalline yellow-green residue is formed in solutions containing ammonium sulfate. The reduction in residue moisture content can be explained by the fact that the gradual breakdown of the ammonia-nickel complexes formed by the reaction of evolving ammonia and nickel ions leads to a reduction in the speed of nickel evolution from the homogeneous solution and so helps to form a more perfect residue structure.

Thus soda should be used to precipitate nickel from solutions formed by ammonia treatment of spent pickling solutions. Subsequent calcining of the basic nickel carbonates will produce a highly concentrated nickel product, nickel tetroxide.
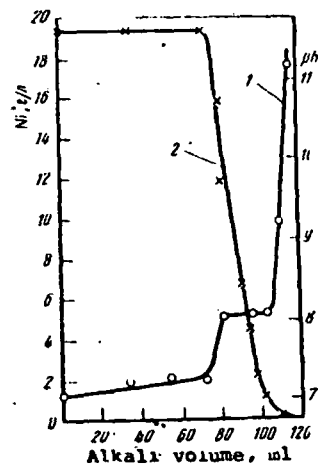
Fig. 2. Relationship of pH (1) and nickel concentration (2) to alkali consumption in precipitation from the $NiSO_4 \stackrel{.}{-} (NH_4)_2SO_4$ - H_2O system.
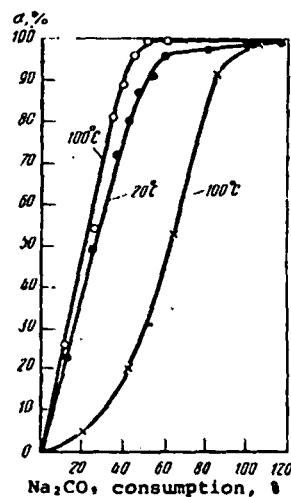
Fig. 3. Relationship of nickel precipitation to sodium consumption and temperature in solution of: $O,O - NiSO_4$; $x - NiSO_4 + (NH_4)_2SO_4$.

REFERENCES

1. V. I. Beregovskii and B. B. Kistyakovskii, Copper and Nickel Metallurgy, Moscow, Metallurgiya, 1972, 455 pages, illustrated.
2. I. A. Vainshtein, L. D. Klenysheva, L. N. Kononenko, and Yu. I. Jl'ichev, Air and Water Purification at Ferrous Metallurgy Enterprises, Issue 4, Moscow, Metallurgiya, 1975 (MChM SSSR, VNIPIChermetenergoochistka), pp. 182-188.
3. K. L. Yushkovskaya, Purification of Effluents and Natural Waters, Minsk, Nauka i Tekhnika, 1970 (USSR Ministry of Irrigation, Drainage and Water Resources, Water
4. I. M. Vasserman and E. A. Fomina, Zh. Prikl. Khim., 1961, 34, No. 1, 34-36.

New Returns from Old Reliable

*Du Pont explosives know-how helps launch a mining venture aimed
at retrieving valuable copper from a long-abandoned deposit*

By JACK MURPHY

Tunnels and crosscuts in Old Reliable ore body
were loaded with 4 million pounds of explosives.

It seems an unlikely locale for an event of world record-setting proportion. Situated 40 miles northeast of Tucson, Ariz., in the Copper Creek area of the Galiuro Mountains, it's a parched, hilly terrain, sparse of vegetation and only tentatively brushed by civilization. That is, until the technological hand of civilization created a stir of historic note here a little less than two years ago.

Just before noon on March 9, 1972, some 75 observers gathered near here. From an elevated vantage point—the dusty, sun-baked mezzanine of a mountaintop roadway—all eyes were trained on a hillside nearly three miles away. That hillside, an outcrop of andesite (lava) rock some 4,000 feet above sea level, was to be center stage for an imminent drama. Through a loudspeaker, a countdown sounded. At zero, the ground shifted perceptibly underfoot. Geysers of rock and earth began to spout from the hillside. As a muffled roar swept past the vigilant audience, it seemed that the entire hillside now was airborne, climbing skyward in a vast, boiling chaos of dust.

Minutes later, the dust cleared. The hillside, except for a slight change in coloration and texture, appeared unscathed. It surrendered scant evidence of its part in a brief but surpassing event—the world's largest non-nuclear explosion to date, and the biggest pre-production blast in mining history. So began, with the detonation of four million pounds of Du Pont explosives, an unconventional effort to recover copper from a mineral deposit popularly known as Old Reliable.

It's a name that smacks of irony when you consider the 90-year life of Old Reliable as a recognized copper deposit. For two-thirds of that time, it's been anything but reliable. Located on ground first claimed
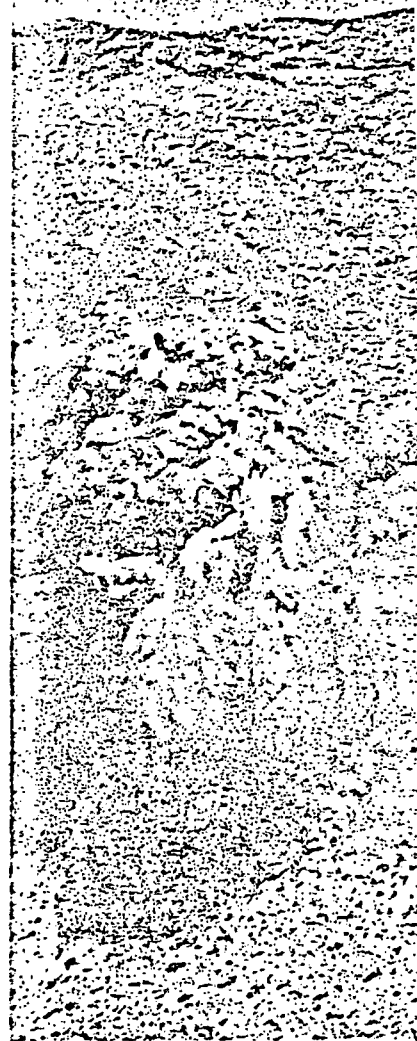
Four million tons of rock and earth are ripped by largest pre-production blast in mining history to that time. When the dust had cleared, entire ore body had slumped back in place and appeared unscathed.
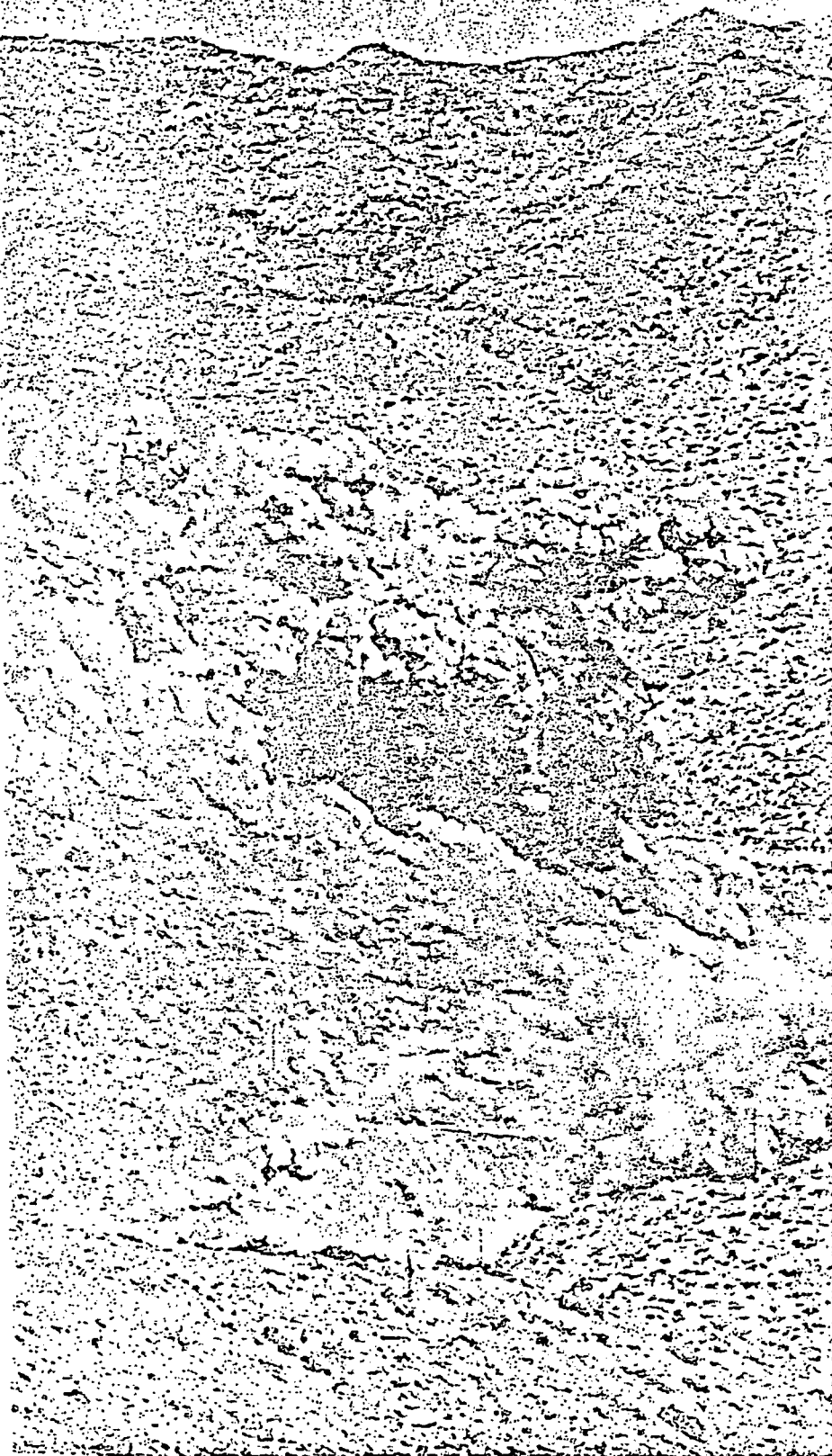
for mineral value during the Civil War, Old Reliable was mined sporadically from 1890 to 1919. During that period, it yielded about 30,000 tons of ore. Except for one other abbreviated turn at working it in 1953 and 1954, the deposit had gone unmined for half a century. Reason: The amount of ore contained in the deposit made conventional mining techniques economically unfeasible.

Then in 1970, the deposit came under the scrutiny of Ranchers Exploration and Development Corporation. With general offices in Albuquerque, N. M., Ranchers is a young, imaginative organization formed in 1954 during the uranium boom. Presently, the company is a developer of diverse mineral properties, notably uranium, copper and tungsten. Upon examining the inactive Old Reliable deposit, Ranchers discovered an ore body of enough promise to warrant serious venture consideration, reports Maxie Anderson, president of the 20-year-old firm.

"As we figure it," Anderson explains, "molten granite intruded on the area of the deposit perhaps 68 million years ago. It cracked the volcanic rock, and copper-bearing solutions flowed into these cracks and voids in the brecciated lava. Then later, ground water dissolved and redeposited

(continued)
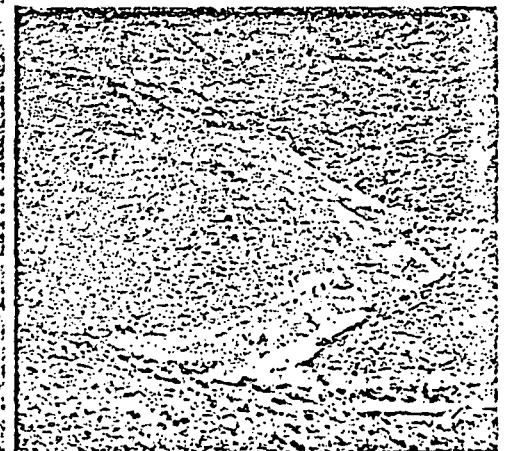
Precision shot produced excellent ore fragmentation. Pieces averaged nine inches in diameter.
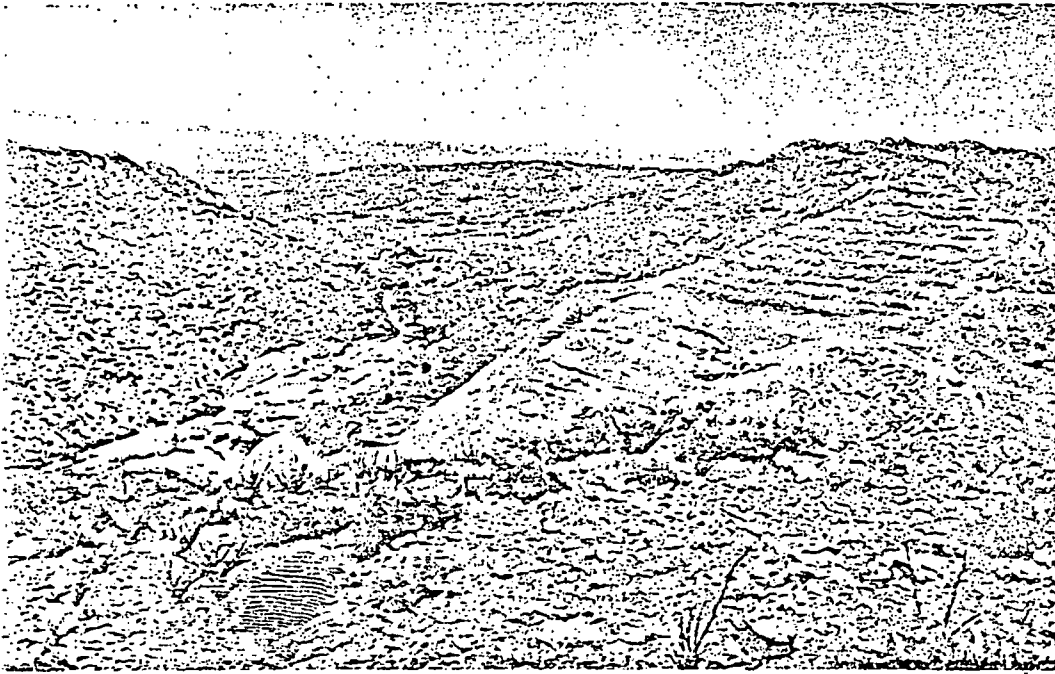
In preparation for in-situ leaching with acid/water solution, fragmented ore deposit was terraced.

the copper deeper in the ore body in concentrated form. The most abundant copper minerals that we've identified here are chalcoite, malachite, chalcanthite, and chrysocolla."

Following study and evaluation, Ranchers felt confident that valuable mineral returns could be coaxed out of Old Reliable's low grade ore deposits (average copper content: 0.8 percent). But to do it economically, they recognized, would require a unique approach—combined blasting and leaching. "Individually, each is a common mining technique," says Anderson. "But to combine the techniques, as we conceived of it, was most uncommon. In fact, this project represents the first attempt in the industry to fragment an entire ore body with explosives, and then leach the ore in place with a solution of acid and water."

It was an approach that promised real advantages. For one, it would be a low-cost method of mining the deposit. If the ore could be blast-fragmented into small pieces, it would be possible to terrace the deposit and percolate a solution of sulfuric acid and water through the matrix. By gravity flow, the leaching solution—now enriched with about 10-20 pounds of copper per 1,000 gallons of solution—could be collected at the bottom of the deposit, and then

pumped to a precipitation plant to be transformed into cement copper.

That transformation involves an electrochemical exchange. The copper-bearing solution is run through launderers (tanks) filled with scrap iron. In effect, the iron trades places with the copper content of the solution, iron migrating into solution and copper migrating out. The resulting cement copper is about 80 percent copper in mineral content. Subsequent smelting or refining of the material raises it to an almost 100 percent copper product. While this refining step introduces an added cost, in-situ leaching as a mineral recovery technique offers significant economies.

Says Anderson: "Since the ore itself is never removed from the deposit, this method reduces the cost of producing copper by 30 to 50 percent over conventional mining operations. In addition, it minimizes environmental damage. At Old Reliable, this approach affects an area 400 to 500 feet in diameter around the deposit. By contrast, open pit mining there would affect an area as much as 15 times greater in size. Also, it would require a large area in which to stack the waste material removed from the pit."

The task of planning and executing the blast required to effectively fragment the Old Reliable ore body fell upon explosives

technicians for the Du Pont Comp. The Minerals Section of the Du Pont ymer Intermediates Department alre was involved in the project. They were in gating the deposit with Ranchers witl eye to a possible joint venture. "It's pa an interest we began pursuing in 1969, ports James Todd, development man for the Minerals Section. "Our approac to look for investments in mineral o ations where Du Pont can offer a techn contribution. We've also undertaken ; search program aimed at defining ch ical opportunities in the recovery of (per, nickel and silver, and chemical p lems in high-value minerals that migh solved by our expertise.

"As a first step in learning more ab the business, we contacted Ranchers ploration & Development to discuss ; sible joint participation arrangements. Tl discussions led us to Old Reliable. Prio the blast, we acquired slightly less tha 20 percent interest in the project."

After a thorough investigation of the body, the Explosives Products Divisioi Du Pont, under the direction of Hai Carlevato, national sales manager, rec(mended a "coyote" shot. In contrast to conventional technique of drilling ver blastholes for explosives, a "coyote" s involves using a hivelike system of tunr and crosscuts driven into the deposii contain explosives: "As an aftermath earlier mining operations," Carlevato plains, "Old Reliable already was pe trated by 4,000 feet of tunnels and cr cuts. Based on our shooting plan, we ured another 4,000 feet of tunneling ha(be driven. We calculated, moreover, the shot would require a pound of ex sives for each ton of ore in the deposit.

That made for some neat mathemat The Old Reliable ore body measured ou four million tons. Thus, the shot would quire the detonation of four million pound explosives—at that time, a blast of rec(size for conventional explosives. A ! Francisco engineering firm, John A. Blu & Associates, was engaged to conduct tensive tests to assess blast effects and response of structures in the area. Fr

Leaching solution is piped, sprayed on deposit gravity flow, it carries copper to collection b; for later retrieval by electrochemical exchar

these tests, it was concluded that damage from the blast would be virtually nil.

When additional tunneling was completed, Du Pont began rolling its convoy of 100 truckloads of explosives—ammonium nitrate in 50-pound bags—to the site. A total of 80,000 bags were placed in the tunnels and crosscuts. A wired system of blasting caps, detonating cord, and high explosive primers was connected to the detonation station in a bunker about a mile from the blast site. The explosive charges were confined by blowing sand into the tunnels and crosscuts and by placing bags of sand for stemming in these areas.

On March 9, 1972, all was ready. The countdown proceeded without a hitch. At 11:45 a.m., Old Reliable was fractured by 2,000 tons of explosives. In the town of Mammoth, just ten miles away, citizens scarcely felt the mild tremor created by the shot. "There wasn't a single report of damage following the shot," notes Jim Todd. "And the breakage of the ore was excellent; pieces averaged approximately nine inches in diameter."

Ranchers' Maxie Anderson waxes even more enthusiastic: "The professionalism with which the shot was planned and executed really impressed me. The precision of the operation was incredible. Prior to the shot, the Du Pont explosives engineers drew a hyperboloid line on a topographic map to indicate the area of expected breakage. Actual breakage varied from that predicted line by a maximum of only 12 feet and in most areas, by less than three feet."

Terracing of the fragmented deposit began almost immediately, and was completed by May 30. A six-mile-long pipeline to provide water for leaching solutions was constructed in July. By September, solutions were being added to the fragmented ore, and production of copper began in January 1973. Design production capacity of the operation, according to Maxie Anderson, is about 20,000 pounds of cement copper a day.

"We figure the production life of this deposit at roughly five years," Anderson adds. "In that time, we ought to produce close to 30 million pounds of cement copper. But equally important, the success of this in-situ blasting and leaching venture will confirm the efficacy of the technique. So, it can be applied in the future to other mining undertakings." ■

2

*Research towards finding an improved
process for separating copper values
from dump leach liquors has brought in a ...*

A New Reagent for Liquid Ion Exchange Recovery of Copper

D. W. AGERS, J. E. HOUSE, R. R. SWANSON, and J. L. DROBNICK

Since the commercial acceptance of the liquid ion exchange process in the mineral processing industry, it has been predicted that eventually the hydrometallurgist would have a wide selection of commercially available chemical reagents to make separations efficiently and economically of virtually all metals in solution under a wide range of conditions. Several years ago, General Mills began a research and development program to determine if it were possible to develop a reagent to extract a specific metallic ion from solution at a cost that would allow large scale commercial application.

A giant step toward reaching this objective was announced in late 1963, when development quantities of LIX®-63 reagent, a highly selective reagent for the extraction of copper, were first offered to industry. The properties of this reagent were described in a previous paper.[1]

The development work with this reagent indicated that perhaps the largest potential application for a copper extractant, the treatment of acidic dump leach liquors, would not be economically possible with LIX-63 because of limitations of the reagent below pH 3.0. The relatively small pH adjustment necessary with LIX-63 would result in both a significant processing cost and the undesirable precipitation of ferric hydroxide from the liquor. A reagent was needed which would extract copper from dump leach liquors without pH adjustment.

A second reagent for the extraction of copper, LIX-64 reagent, broadens the pH range in which copper can be effectively extracted to include typical dump leach solutions. Of special significance to

---

® Registered Trademark, General Mills, Inc.

DONNELL W. AGERS is Product Mgr., Mining Industry Chem. Div.; J. E. HOUSE, Mgr. Market Development Dept.; R. R. SWANSON, Research Chemist, Central Res. Labs., all at General Mills, Inc. J. L DROBNICK is Mgr. of Research, Chemical Div., Colorado School of Mines Research Found. The authors are members of AIME. The paper was presented at the SME Fall Meeting, 1965, Phoenix, Ariz.

Fig. 1.—(A) Flowsheet of the liquid ion exchange process; (B) Flowsheet for recovery of copper from dump leach solutions.

the hydrometallurgist is the fact that LIX-64 was developed by combining the technical requirements of a specific problem in hydrometallurgy with theoretical organic and physical chemical principles.

THE LIQUID ION EXCHANGE PROCESS

Fig. 1-A shows a typical counter-current mixer-settler liquid ion exchange unit. In the extraction section, a water-immiscible organic solvent (normally kerosene) containing an organic extractant is contacted with an aqueous solution containing the metal to be extracted, and the two phases are allowed to separate. A variable number of mixer-settler stages and flow rates may be used to achieve the desired recovery and concentration of the metal from the feed solution. After removal of the metal

·values,· the aqueous solution leaving the extraction section is referred to as the *raffinate*.

The organic phase containing the metal values (referred to as the *loaded organic*) is then transferred to the stripping section where the metal values are transferred from the organic phase to an aqueous solution for subsequent treatment, and the stripped organic recycled to the extraction section. Occasionally, specific problems make it desirable to add a "wash" stage or section between the extraction and stripping sections, or following the stripping section before organic recycle to the extraction section.

The major objectives of the liquid ion exchange process can be defined as:

1) Purification of a metal from unwanted contaminants.
2) Concentration of metal values to the point where further processing is economical.
3) Conversion of the metal values to a form which simplifies eventual recovery.

Fig. 1-B shows a flow sheet using liquid ion exchange for the recovery of copper from dump leach solutions.

Chemistry of LIX-64

While the exact chemical structure of LIX-64 cannot be disclosed at this time, the reagent can be considered as operating on a hydrogen ion cycle:

Extraction:

$$[2HR]_{ORG} + [Cu^{++} + SO_4^=]_{AQ} \rightleftharpoons [R_2Cu]_{ORG} + [2H^+SO_4^=]_{AQ}$$

Stripping:

$$[R_2Cu]_{ORG} + [2H^+ + SO_4^=]_{AQ} \rightleftharpoons [2RH]_{ORG} + [Cu^{++} + SO_4^=]_{AQ}$$
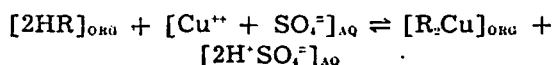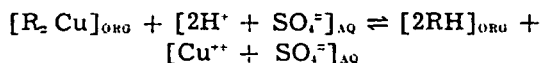
As would be expected from the above equations, both extraction and stripping are pH dependent. The major advantage of LIX-64 is its selectivity for extracting copper over other elements, especially ferric iron.

LABORATORY EVALUATION PROGRAM

A typical laboratory evaluation program for LIX-64 begins with a series of separatory funnel "shake out" tests to determine the maximum loading capacity of the organic solution for copper, and equilibrium isotherms for extraction and stripping. Equilibrium isotherms can be used to predict the number of stages necessary to obtain the desired efficiency or recovery.

The maximum capacity of the LIX-64 solvent for copper is primarily dependent on the concentration of LIX-64 used in kerosene, and is determined by contacting a portion of the organic solution with fresh portions of copper containing feed solution until the raffinate analyzes the same in copper concentration as the feed liquor, then analyzing the organic solution for copper.

It was determined that when an organic solution consisting of ten volume per cent LIX-64 in kerosene is contacted with a typical dump leach liquor, it can be loaded in the extraction section to slightly

in excess of 2.5 gm per liter of copper. This figure is important, since it determines the flow rate of organic required to treat the dump leach liquor and to some extent the size of the mixer-settler units required to treat a given feed solution at a prescribed flow rate.

A typical extraction equilibrium isotherm is shown as Fig. 2. An equilibrium isotherm may be prepared in the laboratory by contacting the same volume of feed solution with varying amounts of solvent, or by setting up a batch counter-current system of locked stages. The equilibrium isotherm was plotted from a circuit profile of a laboratory continuous mixer-settler unit operating on an actual dump leach liquor. The operating line is a straight line with a slope equal to the ratio of the aqueous to organic feed rate, corrected from the origin by the amount of copper returned on the stripped organic.

As could be predicted from the equilibrium isotherm, the ten volume percent LIX-64 solution, when fed at an $\dfrac{A}{O} = 1.95$ counter current to a feed liquor containing 1.11 gm per liter of copper, pH 2.22 can be loaded to 2.42 gm per liter copper and in four stages will produce a raffinate of 0.03 gm per liter of copper.

Within reasonable limits, the effects of varying the aqueous to organic feed rates on recovery can be determined by adjusting the operating line and replotting the individual stages.
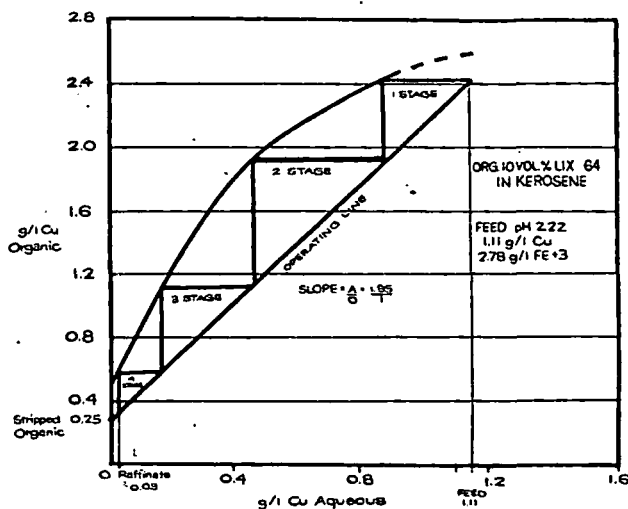

Fig. 2:—*Extraction equilibrium isotherm was derived from work on an actual dump leach liquor.*

From the extraction equation, it can be seen that as copper is extracted from the feed liquor, it is replaced by hydrogen ion and the pH drops. In general, it may be stated that the lower the pH, the poorer the extraction efficiency. Fig. 3 shows the effect of the feed pH and copper concentration on the equilibrium isotherms for three actual dump leach liquors representing the expected variation in liquor composition.

Liquor C probably represents the lower limit of feed pH that could be processed in a four-stage extraction circuit without a pH control system to prevent the pH drop during extraction, at least without an appreciable drop in recovery. With a pH
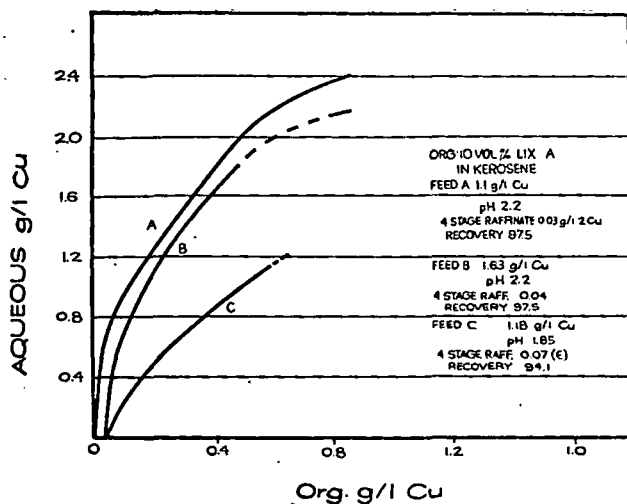
Fig. 3:—*Effect of feed pH and copper concentration on extraction efficiency.*

control system, it would probably be possible to eliminate one extraction stage from the system, but the increased processing cost does not appear to be justified for the normal dump leach operation.

SELECTIVITY OF THE REAGENT

Table 1 shows the relative extraction power of LIX-64 for a number of other metals.

Of these metals, only the extraction of ferric iron appears to present any potential problem. Separation factors for copper over ferric iron range from 25/1 to about 100/1 on actual dump liquors which have been tested to date. No definitive data are available on the variation of ferric ion extraction with the ferric iron content of the feed liquor.

The extraction of ferric iron at this low level would appear to be a problem only in a closed cycle stripping system. Several ways to control the build-up of ferric iron in the strip solution without a bleed from the closed system are being investigated. One method which appears promising is to install a "scrub" stage between the extraction and stripping sections. It was found that a dilute solution of ammonium bifluoride will remove essentially all of the extracted ferric iron without stripping any copper from the loaded organic.

STRIPPING THE COPPER FROM LIX-64

While there are probably many stripping techniques possible to provide a variety of copper end products, study has been mainly with the simplest

TABLE I: Relative Extraction Power of LIX-64 for Metals at pH 2.0

Metal	Relative Extraction Power
Cu^{+2}	Very strongly extracted
Fe^{+3}	Slightly extracted
Mo^{+6}	Very slightly extracted
V^{+4}	Very slightly extracted
Zn^{+2}	Nil
Sn^{+3}	Nil
Ca^{+}	Nil
Mg^{+}	Nil
As^{+3}	Nil
Al^{+3}	Nil
Fe^{+2}	Nil
Si^{+4}	Nil
Co^{+2}	Nil
Ni^{+3}	Nil

and most economic system apparently available. This system is the use of a sulfuric acid strip solution, followed by electrowinning of copper metal.

Fig. 4 shows an equilibrium stripping isotherm for LIX-64 using 200 gm per liter H_2SO_4 with 8.0 gm per liter copper. This isotherm was also plotted from circuit profile data from a continuous laboratory unit operating on an actual dump leach liquor (Feed A). The objective of this run was to determine the maximum concentration of copper that could be obtained with the 200 gm per liter H_2SO_4 strip solution. About 90 gm per liter copper appears maximum with three strip stages, without excessive recycle of copper on the stripped organic.

Much of the stripping work has been designed to produce a feed to electrolysis of about 30 gm per liter copper, with 10 gm per liter stripped during electrolysis and the spent electrolyte recycled to the stripping section for build-up to strong electrolyte. Excellent quality electrolytic copper has been produced with a voltage of about 1.8 and a current density of 25-30 amps per sq ft. From the stripping isotherm, when about 200 gm per liter H_2SO_4 spent electrolyte are used for stripping, one stripping stage is adequate to produce the desired copper build-up during stripping. While this has also proven true from the continuous runs, two stripping stages have been operated for safety and to provide flexibility to increase the copper concentration in the strong electrolyte if desired.

Because of the small scale of the continuous unit, approximately 50 cc of feed per min, the electrolytic section, with a flow rate of about 5 cc per min, is too small to allow optimization of conditions. However, to give at least a preliminary indication of the quality of electrolytic copper that has been produced from an actual dump liquor, the analyses are presented in Table II.

SCALE-UP

An important part of a liquid ion exchange laboratory evaluation program is the development of design data for scaling up the process to commercial equipment.

The required mixing time to obtain good extraction efficiency, and the settler area required for the mixed phases to separate, are the essential requirements for scale-up. While power input to provide adequate mixing can also be a critical factor, laboratory work indicates that the scale-up based on geometric similarity will hold true for this system. Power input scale-up based on geometric similarity has been used quite successfully in the uranium and vanadium industries.

The effect was studied of increased aqueous flow on the dispersion band between the aqueous and organic phases for various O/A phase ratios. For an organic continuous system, maximum aqueous throughput is obtained with an O/A ratio of 1:1. For the systems discussed previously, the organic is loaded with more copper than the aqueous feed liquor. To maintain the desired 1:1 phase ratio, some organic is recycled from the settler back to the mixer.
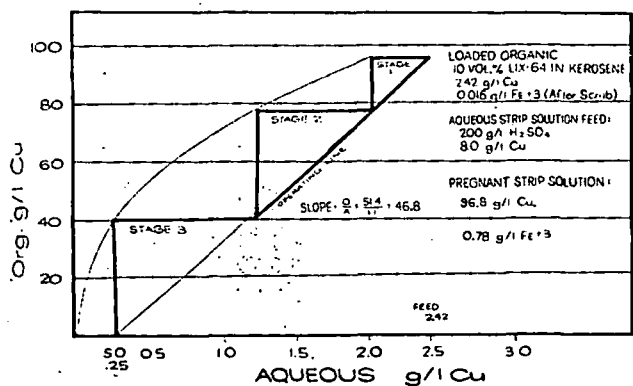
Fig. 4:—*Equilibrium stripping isotherm. (Feed A after scrub.)*

The LIX-64 system appears to "flood" more quickly than other systems. Therefore, it was decided, at least for pilot plants, to design on the aqueous flow rate that produces a 2-in. dispersion band. On this basis, one sq ft of settler area is required for each 0.8 gpm of aqueous flow.

Organic continuous means that the aqueous feed is dispersed in the organic phase during mixing. It has been exclusively proven that operating organic continuous, especially in the last extraction stage, will give the lowest organic losses, since most of the organic loss is through physical entrainment of the organic solution in the raffinate. It appears that operating aqueous continuous could increase plant capacity by a factor of 4 or 5.

Due to the flexibility possible in stripping the copper from LIX-64 at a wide range of concentrations, strip design data was obtained for 200 gm per liter H_2SO_4 strip solution at organic to aqueous ratios of from 5:1 up to 50:1. In all cases, better than 99% stripping efficiency was obtained with 2-min retention time in the mixer, using the stripping at a 4-min retention time as 100% efficient.

PILOT PLANT

The above design data were applied to a commercial unit available from the Denver Equipment Co. to determine the estimated aqueous throughput and the limiting design factor. This unit has the following critical dimensions:

Extraction Section (Four Stages)
Mixer Volume
3 x 3 x 4 ft (effective) — 35 cu ft
Settler Area
6 x 13 ft = 78 sq ft

Stripping Section (Four Stages)
Mixer Volume
2.75 x 2.75 x 3.50 ft = 26.50 cu ft
Settler Area
4.50 x 13.00 ft = 58.50 sq ft

Allowing a 6-in. freeboard in the mixer and organic recycle to give a 1:1 organic to aqueous phase ratio, the extraction units will give a 2-min retention time in the mixer when operated at the designed aqueous throughout of 78 x 0.8 = 62.4 gpm. If operated at the estimated maximum aqueous throughput of 78 x 1.0 = 78 gpm, the mixer retention time would drop to 1.6 min, still well above the critical retention time limit.

The stripping units shown above would provide a designed organic flow of 1.2 x 58.5 = 70.2 gpm, well above the anticipated 38 gpm organic flow with an O/A in the extraction circuit of 0.62 and an aqueous throughput of 62.5 gpm. This apparent overdesign of the strip circuit appears to be justified at least for a pilot unit, since stripping capacity should be available to test the maximum estimated aqueous throughput through the extraction section. The estimated maximum aqueous throughput of the extraction circuit at 78 gpm would give an organic flow rate to the strip circuit of 78 x 0.62 = 58 gpm compared to the 70.2 gpm design capacity. Also, it may prove desirable to reduce the extractant concentration from ten volume per cent LIX-64 to approximately five volume per cent, which would provide the desired O/A of 1:1 in the extraction circuit. This would increase the organic flow rate to about 62.4 gpm at the designed extraction unit capacity, and to 78 gpm at the estimated maximum capacity. It is felt that the strip circuit could handle his 7.8 gpm increase over strip unit design capacity without any serious problems.

COST ESTIMATE

This unit, properly protected for acid service with a fiberglass reinforced polyester lining, would sell for the approximate price of $48,500 f. o. b. Colorado Springs, Colo. Since the unit is prefabricated before shipment, an installation cost of 50% over equipment cost is estimated, or roughly $75,000 total cost installed. Both smaller and larger pilot units are also available commercially.

Assuming a direct scale-up from currently available data and no major changes in equipment, we estimate full plant installed cost for solvent extraction equipment at $200-$300 per gpm of aqueous feed for dump leach operations at a flowrate of 1000 gpm or more.

REAGENT COST

The economics of the LIX-64 reagent system are quite difficult to compare with cementation, since both processes are intermediate unit operations in producing a marketable copper product, and both the production cost and intermediate value of cement copper varies considerable from plant to plant. For a "typical" dump leach operation containing 10 lb of copper per 1000 gal, an iron consumption of 1.5 lb Fe per lb Cu is assumed, with an

TABLE II: Typical Analyses* of Electrolytic Copper Produced from Dump Leach Copper Liquor

% Cu	99 +
% Fe**	0.0038
% Mn	ND**
% Ni	0.0004
% Zn	0.0007
% Ca	0.004
% Mg	0.00001
% Sn	ND***

* All analysis by atomic absorption spectrophotometry.
** Ferric iron build-up at the time this copper metal was deposited was approximately 7.9 gm per liter, due to recycle of strip solution. No scrub stage was included in the circuit at this time.
*** Not detected (<0.0002%).

iron cost of $50 per ton, or an iron consumption cost of 3.75¢ per lb of cement copper produced.

The LIX-64 system, when operated in conjunction with an electrowinning plant, might have the following chemical and power consumption cost to produce cathode copper:

Solvent Loss* Cost	approx.	1.0-2.5¢ per lb Cu
Stripping Acid[b] Cost		0.1
Scrubbing Cost[c] (Optional)		0.0-0.2
Power Cost[d]	approx.	1.0
Total Chemicals and Power		
Consumed	approx.	2.1-3.8¢ per lb Cu

*Assuming ten volume per cent LIX-64 at the current developmental price of $2.50 per lb, with solvent losses in the range of 0.05-0.12 gal mixed solvent per 1000 gal aqueous treated. Steady state solvent losses have been measured on the laboratory continuous unit at approximately 0.087 gal mixed solvent per 1000 gal aqueous treated.

[b]Slight excess of acid required over stoichiometric amount produced during electrolysis due to slight iron loading.

[c]Based on estimated regeneration cost of the ammonium bifluoride scrub solution.

[d]Assuming power can be purchased or generated at a cost of 1¢ per kw-hr, and greater than 90% current efficiency as demonstrated in the continuous laboratory unit.

Certainly there are many other factors which will affect the final cost analysis comparing these systems, but it appears that cathode copper might be produced at a cost equal to or below the processing cost of cement copper for a typical operation. The over-all economics can only be determined by the operating company.

OTHER CONSIDERATIONS

A number of factors that cannot be properly evaluated by the authors, but which appear to offer additional economic incentive for a thorough evaluation of the LIX-64 process are listed below:

1) No attempt has been made to define the additional value of cathode copper compared to cement copper.

2) The ferric iron in the dump leach liquor is recycled to the dump in the ferric state with no build-up of the iron concentration. The present tendency for the dumps to "plug" by the conversion of ferrous to ferric iron and precipitation of basic ferric sulfate until equilibrium is established; should be eliminated.

3) No credit has been assigned for the acid return to the dump with the recycled raffinate. The combination of acid and ferric sulfate entering the top of the dump should materially increase leaching efficiency, especially in the top portion of the dump.

4) The pregnant strip liquor feed to electrolysis can be adjusted in copper concentration up to over 90 gm per liter if desired. This allows

optimization of the subsequent electrolysis from both operating cost and electrolytic plant capital cost.

5) The use of this process would materially reduce the time required to produce a marketable product, thus reducing in-process inventory.

6) The process has the flexibility to produce a feed liquor suitable for producing an end product other than electrolytic copper, for example, hydrogen reduction to copper powder, or copper sulfate crystals.

There are also several factors remaining to be defined in more detail before this process can be recommended for large scale commercial use. These factors include:

The actual effect of the recycled raffinate on the dump leach operation. One question that has been raised is the possible effect of the small organic entrainment on the bacterial activity of the dump. No problem is expected in this area, since the LIX-64 is relatively non-toxic, and any organic entrainment would be quickly filtered in the top few feet of the dump.

Certainly the exact organic losses need to be pinned down in more detail before the process can be more accurately costed. This information might be best obtained in a pilot operation approximately the size discussed above.

Further work to optimize operating conditions for subsequent electrowinning is needed, including estimates of the capital cost of an electrowinning plant at optimum conditions, and, if necessary, power generation.

New stripping techniques—both chemical and combination of chemical and physical techniques need further definition.

SUMMARY

From the data currently available, there appear to be no technical problems with the application of this liquid ion exchange process using extractant LIX-64 for the recovery of copper from dump leach solutions. While the economics of using it can only be estimated in a rather wide range at this time, they appear very favorable and warrant further intensive investigation of the process on a larger scale as a replacement for cementation.

Looking to the future, it is not difficult to envision the economic feasibility of the hydrometallurgical treatment of copper sulfide flotation concentrates, followed by liquid ion exchange and electrowinning at the mill site, especially for operations a considerable distance from smelting and refining facilities and for those operations without internally owned smelting and refining facilities. ●

REFERENCES

[1] D. W. Agers and R. R. Swanson, "A New Reagent for the Extraction of Copper." Presented at the February, 1964, Annual Meeting of AIME.
W. C. Hazen, "Solvent Extraction Techniques." Deco Trefoil, August-September-October, 1963.
A. D. Ryon and R. S. Lowrie, "Experimental Basis for the Design of Mixer-Settlers for the Amex Solvent Extraction Process." Oak Ridge National Laboratory Report ORNL-3381.
D. W. Bridges and J. B. Rosenbaum, "Metallurgical Application of Solvent Extraction." Bureau of Mines Information Circular IC-8139.
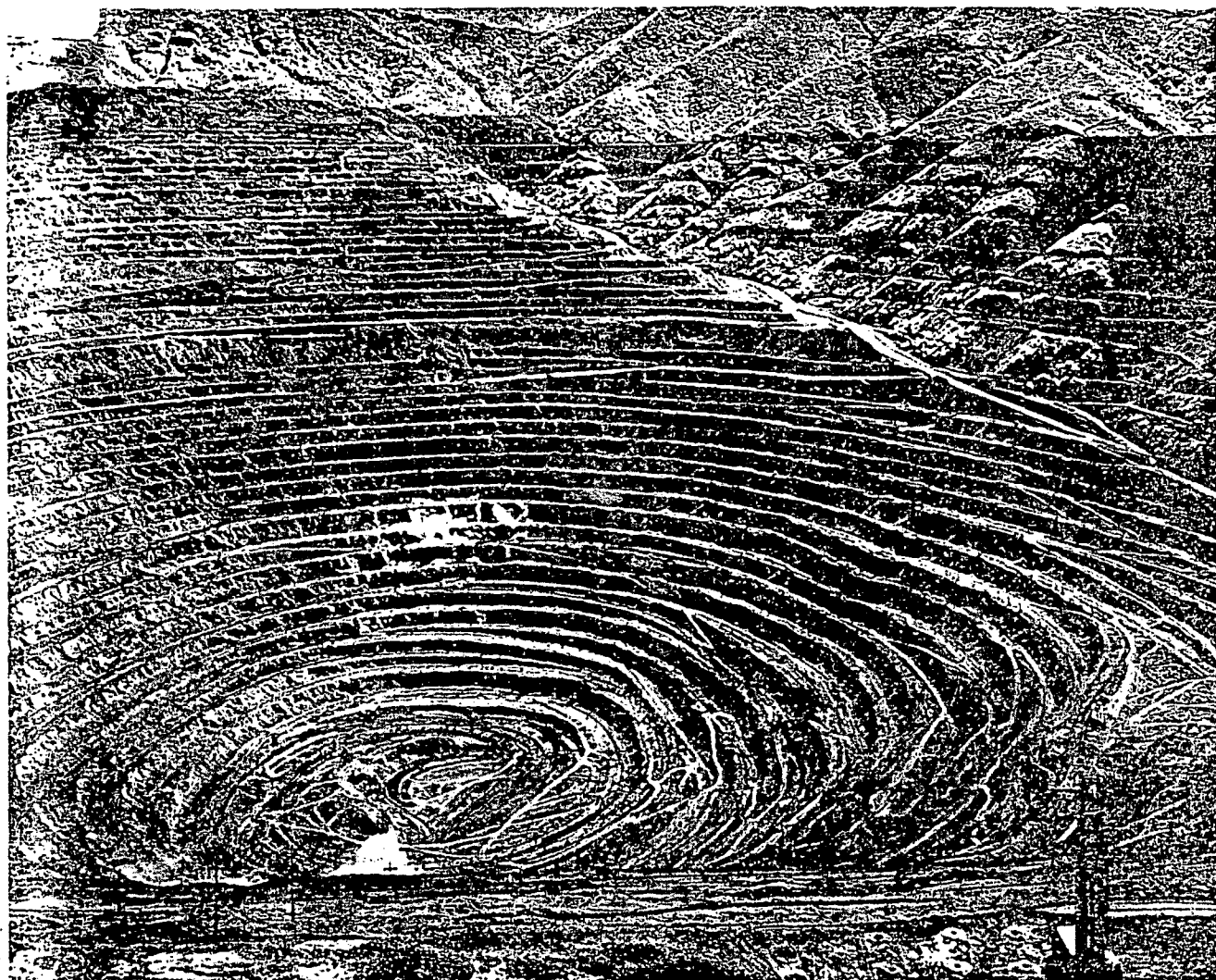
Kennecott **Copper Corp.'s** Bingham Canyon mine, is truly a miracle of modern mining. Within the last 14 years, ore grade has dropped from 19 to 15 lb per ton of ore, but a $100-million plant expansion maintains metal productivity.

Process Control series — Part 3

New servo-systems bolster Kennecott output

Heinz R. Seck
Robertshaw Controls Co.

LIKE MANY OTHER MINING OPERATIONS, Kennecott Copper Corp's. Utah Copper Div. found it had to "run just to stay even."

Kennecott is completing a $100-million expansion of its mining-processing complex near Salt Lake City, which will boost its copper production to 25,000 tons monthly, but this monthly production is about the same as it was in the mid-1950's.

The reason: The grade of ore available for mining has steadily declined, and the average ton of ore mined in 1966 at the Utah operations contained about 15 lb of copper, compared to 19 lb in 1952.

The expansion program can be divided into two major segments: (1) A 20% increase in mining, concentrating and smelting capacity for handling from 90,000 to 108,000 tpd of ore; (2) a program to increase recovery of precipitate copper from leaching of overburden dumps, from 150,000 to 400,000 lb daily.

The huge effort to restore production to past levels in spite of continued decline in quality of ore included installation of very sophisticated instrumentation and control systems, probably the most advanced in the copper mining-processing industry.

Robertshaw Controls Co. was a major supplier of these systems under contracts with Bechtel Corp. and Western Knapp Engineering.

Modern automatic controls are especially adaptable to the expanded leaching operation, which involves massive movement of water.

During its more than 60 years of operation, 1½-billion tons of overburden have been accumulated at the Bingham Canyon mine, claimed to be more than two miles across and almost half a mile deep.
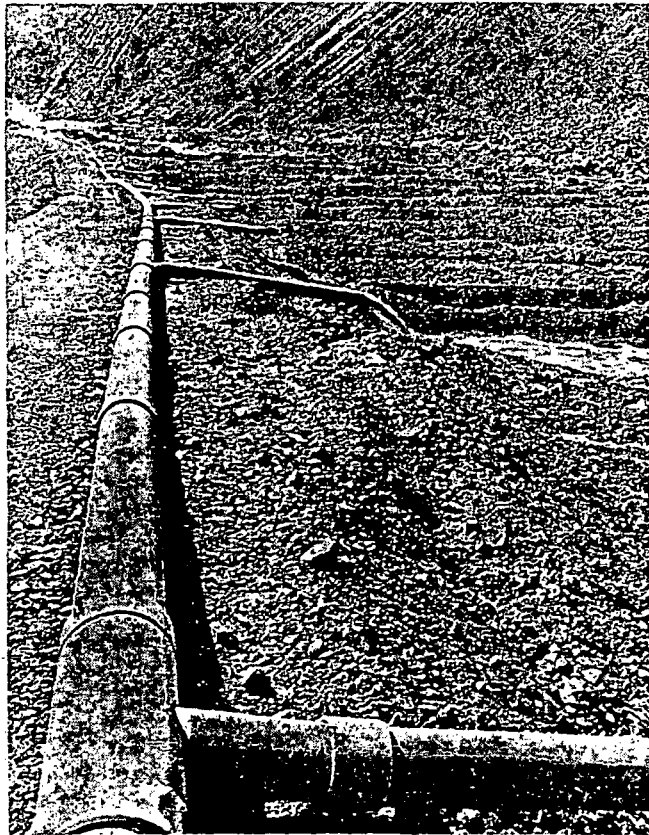
Leach pits atop the low-grade dumps receive acid solution which percolates downward leaching Cu on its way. Pregnant solution is collected and sent to the precipitating plant.

Transite asbestos-cement pipe (36-in.) carries pregnant solution from the dumps to the precipitating plant. Workmen lay a section with Ring-tite couplings which permit deflection.

For decades trains of railroad dump cars—replaced now by giant diesel haulage trucks—have circled around the pit's levels carrying ton after ton of overburden to dump areas outside.

These overburden dumps—growing at the rate of over 200,000 tpd—rise almost 2,000 ft on either side of the canyon. The expanded program to leach copper from these man-made mountains of waste rock requires piping systems which stagger the imagination.

The leaching system includes more than 45 miles of pipe above and below ground, comprising make-up water and primary water supply, collection and distribution systems on each side of the canyon, and other specialized lines.

At the top of the overburden dumps gigantic ponds are dug in the relatively flat tops, each 30 to 40 ft wide and as long as 200 ft. Acid solution pumped to the ponds percolates down through the dumps, leaching out the soluble copper.

The copper-bearing solution flows from the bottom of the dumps and runs down natural ravines to collect behind check dams. The pregnant liquor then gravity-flows through asbestos-cement pipelines to two central collection tanks, and thence to the precipitation plant.

Fresh water for primary supply and make-up is pumped from the North Jordan and Utah Salt Lake Canals, 7 and 9 miles away respectively. It is delivered by pipeline to a new 500-million-gal reservoir, which also receives a portion of the effluent from the precipitation plant, and overflow from the solution collection system for the settling out of solids and reintroduction of water into the system.

A pumping station at the reservoir boosts the water through a pipeline and a distribution box into the sump of the central pumping station, where chemicals are added to form the leaching solution. The solution then is pumped through the east-side and west-side distribution systems to the ponds atop the dumps.

The east-side piping system extends 2½ miles and climbs 1,720 ft. The west-side system is 6½ miles long and rises 2,000 ft. The complex includes an auxiliary make-up water system, used primarily for providing process, fire and drinking water to the plant, and also to a truck maintenance shop 2,200 ft above the water source.

## Operation-by-exception creates economies

Designers of the system incorporated modern instrumentation and control techniques to provide significant operating efficiencies and economies. These permit location of line breaks in any part of the system, so that a repair crew can be dispatched to the scene or adjustment of flows made to prevent extensive damage.

The control system not only detects and locates such problems but, because it is automatic, it eliminates the need for manual control at the various pumping stations.

Operational information is obtained through the use of recorders and a supervisory control system which telemeters status information and abnormal operating conditions to a control center located in the operations building, at the precipitate plant. Here, visual readout devices provide the operator with immediate information on the entire solution distribution system and a limited amount of overriding control capability.

For total control of the distribution system, solution level in the surge tanks and the pumping station's sump must be closely watched—this, too, is handled by the automatic control system. Variation in leaching solution demand causes the control system to start and stop pumps at the various stations and regulate bypass valves for efficient
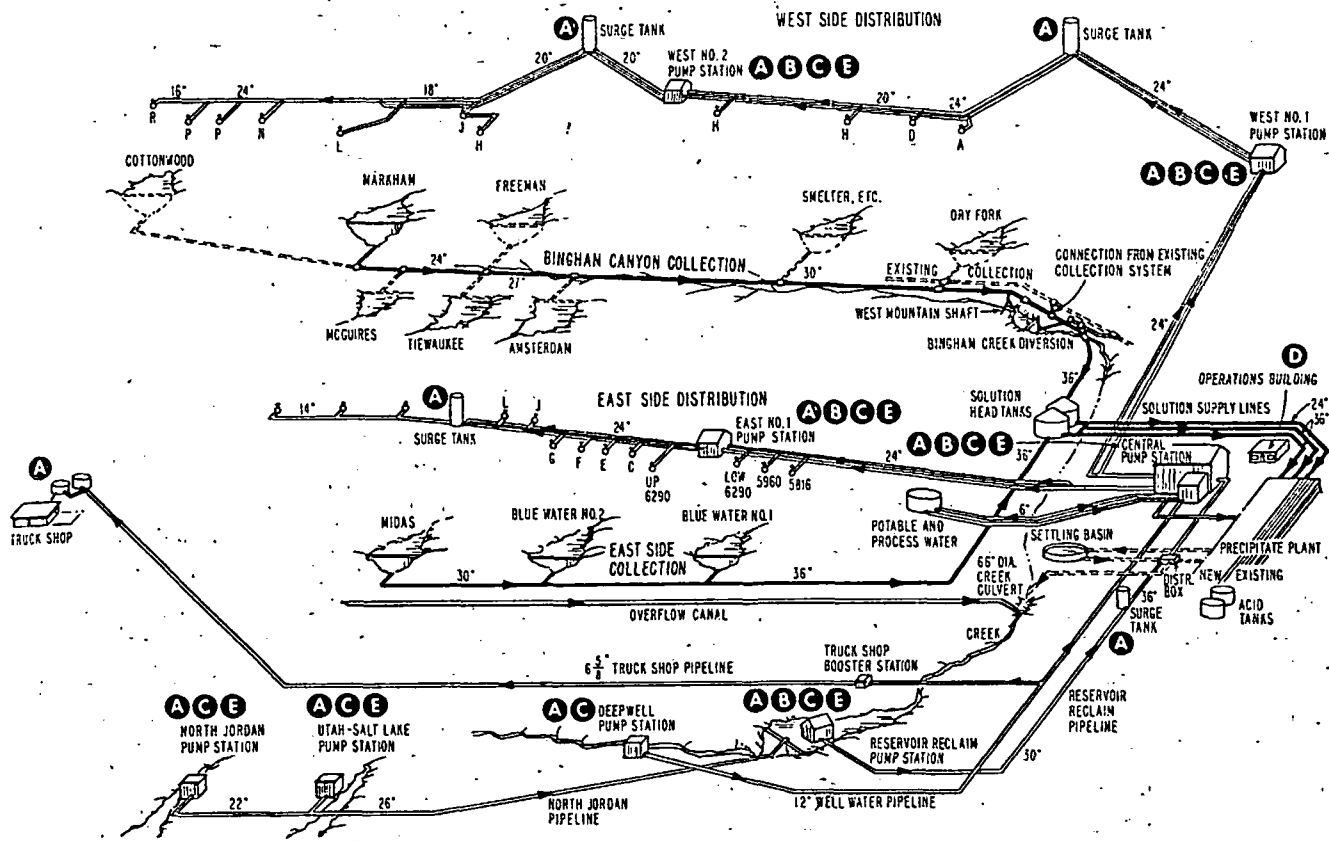
Instrumentation and control hardware for leaching system is indicated with letters as follows: A—Level controls, B—Automatic control system, C—Supervisory control system, D—Master operations console, and E—Local alarm and status annunciators. Robertshaw Controls Co.'s vibration detecting devices shutdown motors when excessive shaking develops.

Special materials of construction are dictated by corrosive conditions

When Kennecott engineers were considering the new leach system, careful selection of the materials of construction was necessary because of the corrosive conditions under which the facilities would operate. Pressure and pH varies widely from one location to another and these factors dictate to a large extent the type of material to be used.

Thus some is stainless steel pipe, plastic-lined steel pipe, epoxy-lined and unlined asbestos-cement pipe. The large part of the pipeline systems is asbestos-cement pipe, and Johns-Manville "Transite" pipe was selected. Transite pipe is already in use in the existing leaching system, and its record of performance contributed to the decision to select it again.

Make-up water is carried from the reservoir to the plant through 1½ miles of 36-in. asbestos-cement pipe. The distribution system carrying the leaching solution to the top of the dumps uses some 63,000 ft (12 miles) of epoxy-lined asbestos-cement pipe. It ranges from 24 in. down to 10 in.

in diameter in Class 100, 150, and 200. The larger diameters are in the lower pressure sections of the main distribution lines, which go up the sides of Bingham Canyon some 2,000 ft to the top of the west-side dumps, and 1,720 ft up to the top of the east-side dumps. There are hundreds of feet of smaller diameter lateral pipes that carry the leaching solutions to the ponding areas atop the dumps.

Twenty-four stainless steel pumps in the central pumping station and booster stations, rated at 4,000 gpm each, are used to pump the leaching solution through the distribution system pipelines.

The distribution pipelines have a total capacity of 52,000 gpm, with 28,000 gpm capacity for the east side, and 24,000 gpm for the west side.

Trenching was the most difficult part of laying the distribution system. The majority of the trench for the west-side system was blasted, and some of the east-side trench was blasted because of the rocky material along the asbestos-cement pipeline route.

A backhoe was used to clean the trenches working up from the bottom of the slope and, because of the steepness of the terrain, most of the time two crawler tractors were also needed. One tractor would tow the backhoe up the slope, the other would be at the top of the grade serving as an anchor to the towing tractor and backhoe. Grades ranged to 65%.

Wherever possible, the Transite pipe was strung along the pipeline right-of-way and lowered in place by a sideboom tractor. Where terrain was too steep, the pipe was stockpiled at the bottom and "walked-up" by sideboom.

Installation crews laid the pipe uphill whenever possible, with the belled end (end of the pipe with collar on it) being the uphill end of each section of pipe. This method permitted the workers to easily assemble the section of pipe into the collar about 95% of the time.

Much easier to install was the collection system that carries the pregnant solution from the collection dams below the bases of the dumps to the precipitate plant.
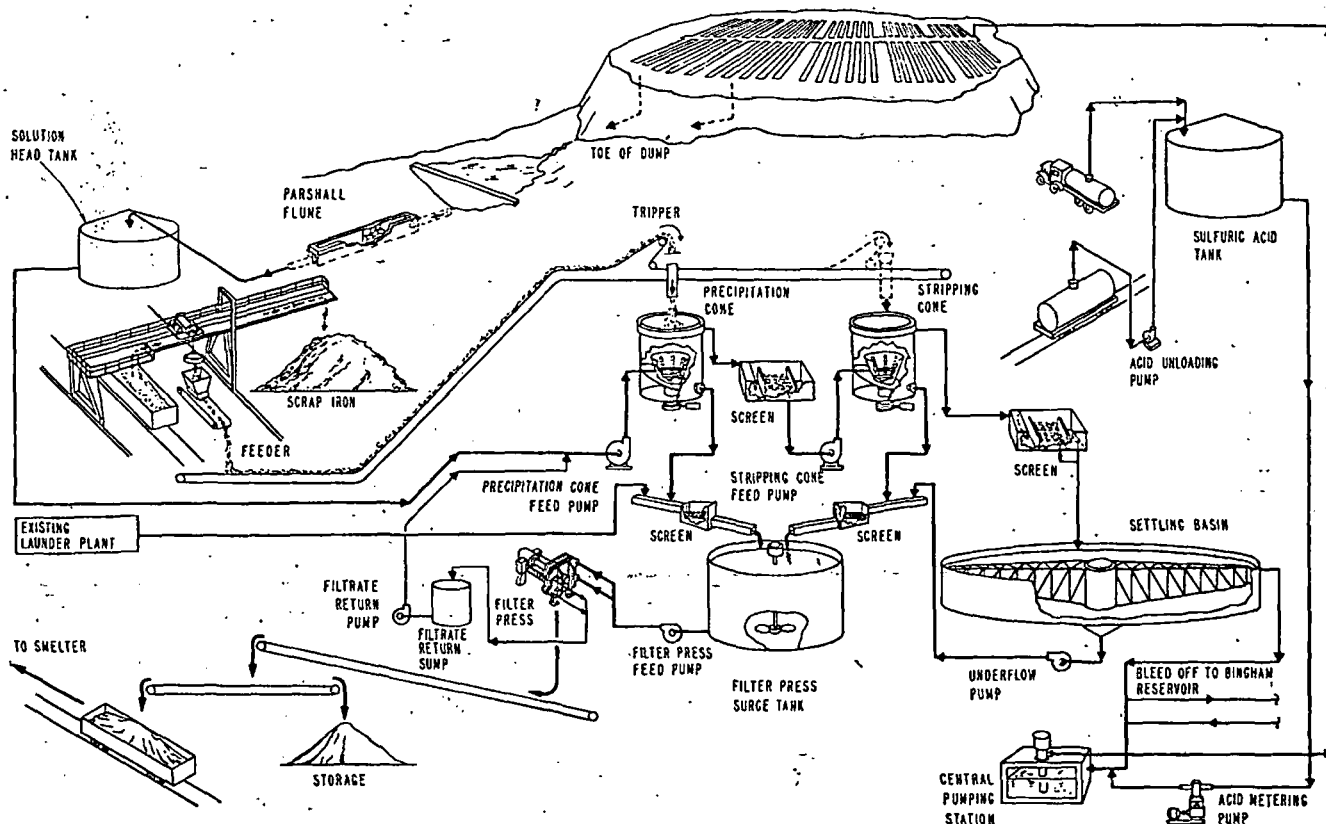
Flow scheme for new precipitating plant is coordinated with output from existing launder-type cement copper plant. New installation boosts cement copper production from 2,250 to 6,000 tons monthly, which represents 25% of total capacity.

Kennecott cone-type precipitators are self-cleaning and operate continuously


Cone-type precipitators produce cement Cu having a typical analysis: 90%-95% Cu, 0.1%-0.2% silica, and 0.1% to 0.2% Al_2O_3.

Kennecott Copper Corp.'s newly developed copper precipitation vessel consists of a 14-ft dia tank, 24 ft tall, in which is mounted an inverted cone 10 ft in diameter by 10 ft high. The outer 14-ft-dia tank contains a 45° sloped false-bottom floor from one side of the tank to a bottom side discharge at the opposite side. The annular space between the inner cone and the tank is covered by a heavy-gage stainless steel screen. The screen is mounted as a continuation of the cone and is anchored to the cone and tank. The cone supports a pressure manifold that consists of six vertical legs, with each leg containing a series of nozzles directed inward from the tangent to the cone, and upward from the angle of the legs of the manifold. The nozzles are arranged in such a manner as to create a vortex when the copper-bearing solutions are pumped through the manifold into the cone. In operation, the inner cone and the area of the tank above the stainless steel screens are filled with shredded detinned iron scrap.

Copper-bearing solutions are pumped through the manifold with the nozzles injecting the copper-bearing solutions into the mass of iron. Injection of the solutions has the effect not only of rapidly precipitating copper, but also removing the metallic copper from the iron surface, thereby exposing clean, fresh iron.

The precipitation cone is a continuously operated unit that is self-cleaning. The pressure and velocity of the solutions in the lower conical section tend to move the copper precipitates upward and out of the cone into the reduced velocity zone created by the larger diameter of the holding tank. The copper precipitate settles down through the stainless steel screen and accumulates on the sloped false bottom of the tank. The copper can then be discharged intermittently with the use of a pneumatically operated valve on a time cycle or bled continuously through a small diameter pipe into a thickener or holding basin. The copper precipitates produced in this manner are of substantially higher grade than conventional cement copper produced in a launder-type plant. They will typically contain 90 to 95% Cu.
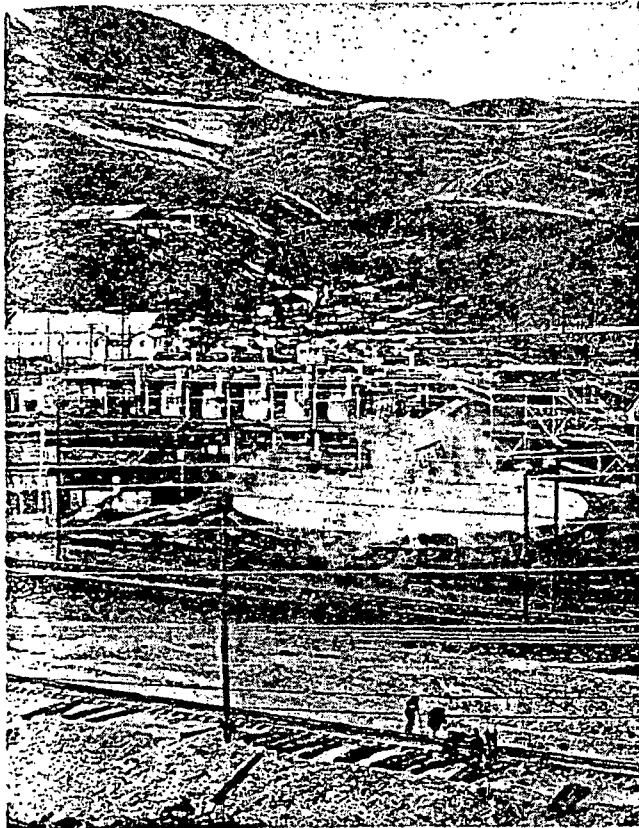
The new precipitating plant showing some of the 26 cones in the center ground behind the steaming thickener.

The control center for the leach-solution distribution in the precipitating plant operations building.

flow control. Extensive electrical and logic interlocks are are employed to safeguard operation of the system.

The control system also monitors levels in the new main reservoir for the make-up water system.

The leach flow system is expected to be efficient enough so that 80% of the solution pumped onto the dumps will be recovered and reused.

The copper-enriched solution is supplied to the new precipitation plant from two wooden solution head tanks of 200,000-gal capacity, which feed the plant through two buried pipelines. The precipitation process is the only one of its kind in the copper industry.

Precipitation of pregnant liquor takes place in semi-automated cone-type units using cones developed by Kennecott Research Center personnel. Shredded, detinned scrap iron is used to precipitate soluble copper as metallic copper, based on the chemical replacement of soluble copper with metallic iron.

The plant consists of two modules of 13 cones each; storage, and handling facilities for the detinned scrap precipitant used in the cones; acid storage tanks; de-watering equipment; loading facilities for precipitate copper; and an operations building.

Earth moving on a gigantic scale

Increasing ore and precipitate tonnages meant increasing sequential facilities to handle this material. The 16-mile ore haulage railroad linking the mine and processing plants has been improved, and 160 new ore cars were constructed at the division to handle increased mine output.

In addition, 34-million cubic yards of material were moved to construct 9 miles of additional track to serve the new Bonneville "concentrator." This plant crushes and grinds 27,000 tpd of ore. The uniform, finely crushed ore is delivered to older Arthur and Magna concentrators for processing by flotation into copper concentrate.

The Bonneville complex consists of a twin rotary car dumper, a 54-in. gyratory crusher, coarse ore storage with 12,000 tons live storage and 40,000 tons dead storage capacity, secondary and tertiary crushers, a fine ore storage building with 39,000 tons live storage and 37,000 tons dead storage capacity, and a conventional grinding circuit of four rod and eight ball mills.

Instrumentation and control devices are installed throughout the Bonneville concentrator to provide for ultimate operation. Central control rooms are located at the primary crushing, fine crushing, and grinding buildings.

Digital hardware supervises operations

Equipment malfunction and miscellaneous material handling difficulties are indicated on annunciation alarm panels, and the installed instrumentation and controls will provide shutdown of certain critical equipment. Sonic devices are used to sense level in the tertiary crusher surge bin and fine ore storage area. A complex digital system controls operation of two trippers, providing proper ore distribution.

An automatic "splitter position control" releases the rod mill product to the proper ball mill, and an ore-to-water ratioing device maintains the proper product density. The control system also keeps the slurry at the proper pH level by regulating the amount of lime added.

Another facet of the expansion is modification of the smelter. Its modernization is taking place while normal production is maintained. Smelter expansion includes: elimination of the roasting phase of the smelting process, along with all related handling systems; construction of three large, direct-charge, green-feed reverberatory furnaces; and installation of 9 new or modified converters. The reverberatory furnaces are equipped with recuperators to supply preheated air at 800°F for furnace combustion. Support
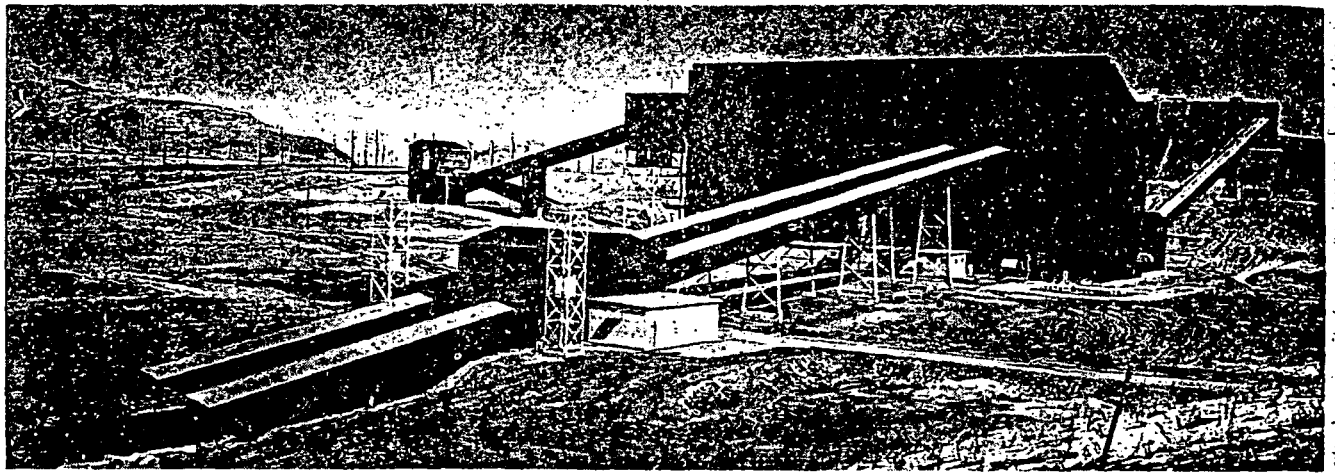
The Bonneville plant has four sections for size preparation of the feed to both the Magna and Arthur concentrators. Ore flow is controlled from individual central control rooms, one in the grinding and one each in the two crushing buildings.
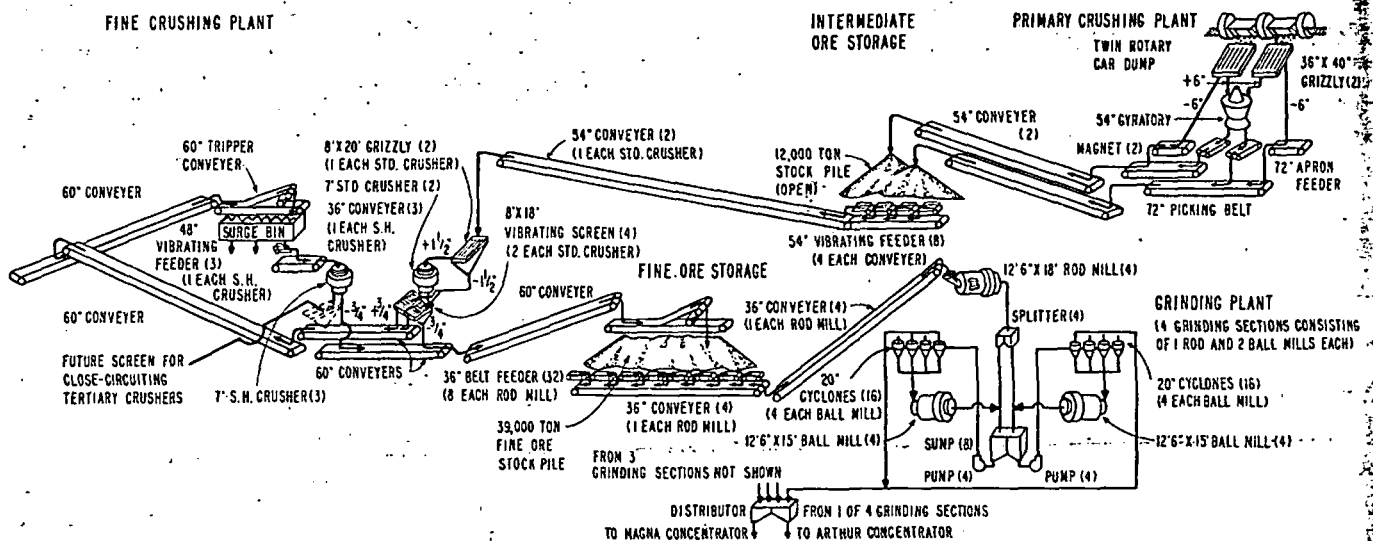
Bonneville plant instrumentation includes: Feeder control panel in primary crushing; feed rate and ratio control systems in fine crushing; sonic and capacitance level devices for measuring bin levels in the fine ore storage section plus fully automated digital tripper logic for ore profiling and distribution; a 38-ft control panel in the grinding plant for controlling feed rate and ratio of H_2O-to-ore in slurries. The entire operation has extensive electrical interlock control.
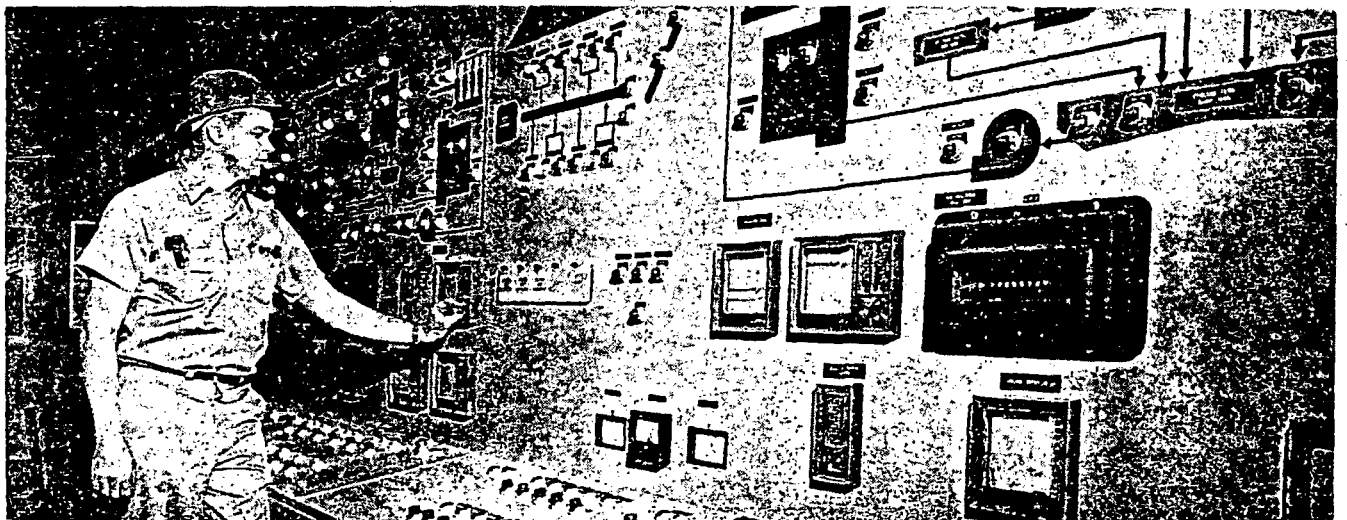
Grinding building control panel from which ore reclaiming, wet grinding and distribution of plant product is controlled. Control units also exist in the other major areas of the concentrator. They supervise reclaiming, secondary and tertiary crushing, distribution of ore to storage, plant air compressors, levels of process and potable water supply.

facilities include power plant equipment to provide additional converter air at higher pressure and to accommodate additional waste heat steam.

Some excess steam for high-pressure boilers is used to drive forced and induced draft fans and converter blowers, with the remainder developing electrical energy required for other plant auxiliaries.

In addition, and apart from the expansion program, a new molybdic-oxide plant has been constructed at the smelter, with an annual capacity of 18-million lb of molybdenum as technical grade and high-purity molybdic oxide. The plant also produces a chemical compound of rhenium (ammonium perrhenate).

Also, construction has been completed on a 500-tpd acid plant. Eventual smelter acid production will be about 1,440 tpd, with the combined capacities of the new and previously existing acid plants.

The final step at Kennecott-Utah is refining. Anodes produced by the smelter are processed at the refinery, emerging as 99.96% Cu. In forms of ingots, ingot bars, wirebars, slabs, cakes, cut cathodes and billets, the metal is shipped to fabricating plants and to other customers.

Bingham's history — a crown of superlatives

The Utah copper mining story began in 1863, when Bingham Canyon was first prospected actively by soldiers of the Third California Infantry stationed at Ft. Douglas, just east of Salt Lake City. Many of them had explored the California gold fields before joining the army.

Their commanding officer, Colonel Patrick E. Conner, called the "father of Utah mining," encouraged his men to spend their leisure time searching for metals.

Fragments of lead ore were found, and the first mining district in Utah was organized. Gold was discovered the following year. Some promising mineral deposits were located, but many difficulties, including lack of a railroad, slowed development.

Ironically, the first copper deposits were largely neglected because they were low grade and not as easily smelted as lead ores. Bingham Canyon, until after the turn of the century, was essentially a lead-silver-gold camp.

As the years passed others became interested, and in 1903, the Utah Copper Co., predecessor of Kennecott's Utah Copper Div. was organized.

Today, the Bingham Canyon mine, and its associated facilities, are believed to have these distinctions:

- It is the first open-pit mine in the copper industry.
- It is the largest single mining project man has ever undertaken.
- It is the world's largest man-made excavation, the result of removing more than 2.46-billion tons of material.
- From this huge tonnage of ore and overburden, there has been produced over 15-billion lb of copper, a record for any single copper mine. Normally, the facilities produce about 17% of the nation's newly mined copper each year.
- The 16-mile standard gage railroad, operated by Kennecott between Bingham Canyon and the ore concentrating plants, sets another record—the highest traffic density of any railroad in the world.

The mine is also the Western Hemisphere's second largest producer of gold, and the nation's second largest producer of molybdenite concentrate, important in making alloy steel. Other byproducts are silver and metals including platinum, palladium and selenium, present in the ore in minute quantities.

Kennecott is confident that its four-year expansion program in Utah, incorporating the latest technological advancements, will put Utah's copper production on an even sounder footing.
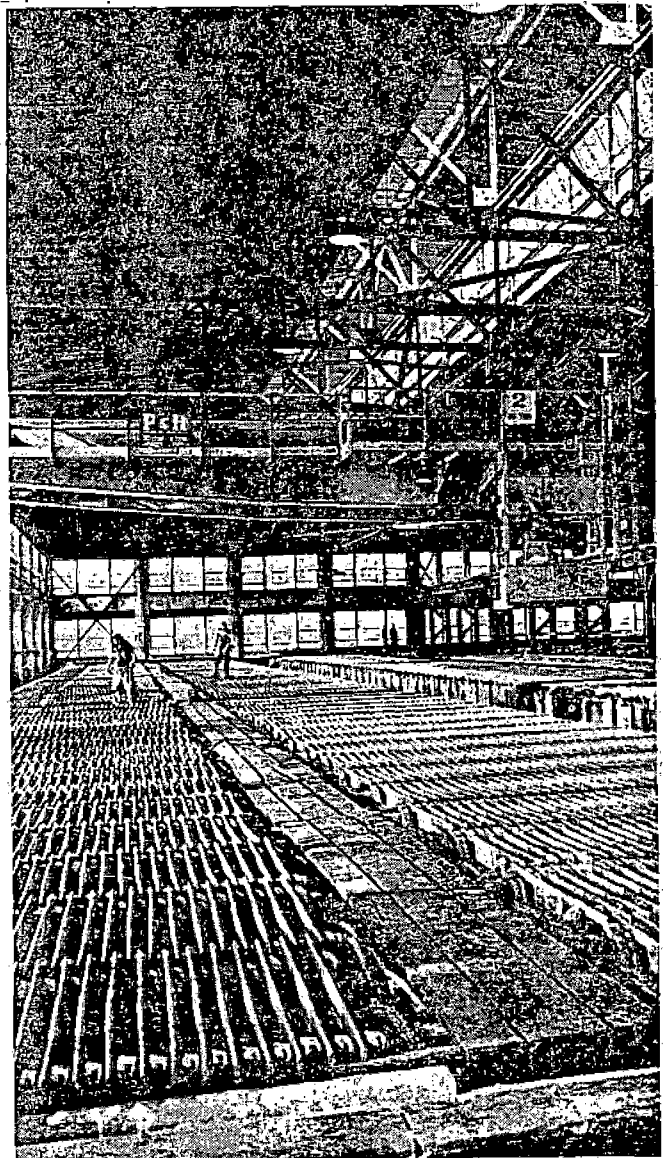
Kennecott's Utah electrolytic refinery showing plant in operation with copper cathodes being formed.

H. R. Seck

Heinz R. Seck, now project engineer for the Aeronautical & Instrument Div., Robertshaw Controls Co., holds a B.S. in electrical engineering and an M.S. in systems engineering from the West Coast University of Los Angeles, Calif. Seck has an extensive background covering instrument design and development plus systems engineering. He is an associate member of IEEE, and before working for Robertshaw he was employed by Minnesota Mining & Mfg. Co. as senior development engineer at Hawthorne, Calif. While with 3-M, Seck was responsible for data acquisition systems, computer feasibility studies, and digital and special counter systems. Prior to coming to the U. S. he worked in Canada and Germany in related electro-mechanical fields.