

THE RECOVERY OF COPPER FROM DILUTE PROCESS STREAMS

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SYNOPSIS

This paper presents a general review of the different methods - in actual use or proposed - of recovering copper from dilute solutions.

The irrigation of low-grade ore bodies and tailings dumps, either by natural mine waters or by enriched lixiviants, offers considerable economic advantages over conventional methods of mining and beneficiation. At the present moment such dilute process liquors are being treated by means of scrap iron to recover cement copper. This practice is costly, especially in isolated localities. Several alternative methods have therefore come under study.

In some cases it is possible to reduce scrap iron consumption by pre-conditioning the weak copper solutions; two such methods are outlined in the paper. Sponge iron containing silver or copper values makes a very effective precipitant for cement copper. Water may be abstracted from dilute effluents so as to pre-concentrate copper ions; quite generally, de-salination techniques used for sweetening sea water may be applicable in the mining industry. A specific case is quoted where a technique based on electro dialysis shows promise.

Chemical precipitation of copper - other than cementation - has often been advocated but not used in practice. Ion exchange systems have been thoroughly studied but so far they are not competitive costwise; the same may be said of solvent extraction and of ion flotation methods.

Certain health hazards are pointed out and a system of automatic analytical control is proposed.

INTRODUCTION

Treating copper ores by heap-leaching and similar hydrometallurgical means is a time-honoured practice, which was well-known even in the 19th century. Later the method lost ground with the advent of better ore dressing processes, particularly selective flotation. More recently there has been a distinct reversion to leaching techniques, particularly for scavenging operations in old mining stopes, in connection with LPF systems, irrigation of tailings dumps and similar situations. One may predict with some degree of confidence that these hydrometallurgical techniques will gain further ground because the processing in essence is simple and it permits better overall extraction of copper, particularly from low-grade or partly oxidized ores.

In a few major operations lixiviation of primary ores is practiced in which case the copper-bearing liquors may undergo recirculation in heap leaching arrangements or the ores may be subjected to systematic percolation treatment. The liquors resulting from this source usually are quite strong (copper content above 10 g/l Cu) and copper would normally be reclaimed by electrowinning or cementation. Such processes when applied to strong electrolytes fall outside the scope of this paper which will concern itself mainly with the recovery of copper from weak liquors which may contain from 0.1 to around 3 g/l Cu.

Total production from such dilute process streams is probably less than 100,000 tons of copper per year and is therefore not a major factor in the overall picture of the world's copper supplies. On the other hand, this source of the red metal is more important to the copper mining industry than mere production statistics would indicate, for the simple reason that we deal here with low-cost copper which shows a high profit margin. Whether we deal

with natural mine waters, with effluents arising from the artificial irrigation of old workings or with run-offs from tailings dumps, all these weak cupriferous streams have certain characteristics in common: they are usually quite acid and contain little copper but plenty of iron; despite such unprepossessing appearances they can be profitable insofar as the copper may be reclaimed at a cost which will normally be well below 10¢ per pound. The reason for such favourable economics is not far to seek: the residual copper in old stopes, tailings, etc., carries no book value and any metal thus available, more or less fortuitously, is to be had cheaply. In consequence the copper mining industry obtains a gross return from such scavenging operations which - on a world-wide basis - must be of the order \$20,000,000 annually. This figure is of course subject to the usual deductions for refining and realization charges, overheads, taxes, etc. Even so, it is not a negligible sum for the mining business, especially in these hard times.

Miners of the old school tend to look with a certain contempt on such activities which fall within the realm of the hydrometallurgist. To them it seems to be less than a man's job to go sloshing around with dirty drainage waters. However, I repeat, such scavenging operations are by no means marginal as regards total dollar contribution and, using this all-important criterion, there is no room for neglect. Approximately, each gallon per minute of an effluent carrying one gram per liter of copper is worth \$1,000 per year.

SUMMARY OF COPPER WINNING METHODS

Broadly speaking there are four basic approaches to the problem of reclaiming copper from very dilute process streams. It is the object of this paper to outline these, to describe the metallurgy involved in each case and to point to those techniques which seem to show most promise of gaining ground during the foreseeable future. In-situ leaching as such, a complex and fascinating subject that deserves the most careful technical study, will not be covered in this particular paper.

The copper winning methods alluded to may be classified into four groups:

- (a) Precipitation of copper by direct reduction to the metallic state which may be by means of cementation on a more electropositive metal or precipitation by a reducing gas or by cathodic deposition.
- (b) Precipitation of a copper compound such a hydroxide, basic carbonate or thiocyanate. This approach may be combined with so-called ion flotation, a technique which is still in the development stage.
- (c) Concentration of cupriferous waste liquors without phase change. Apart from direct segregation of liquors too dilute to be processed this also comprises techniques such as electrodialysis, evaporation and distillation, freeze desalting, etc.
- (d) Absorption of copper compounds with phase change such as ion exchange, solvent extraction, etc.

PRECIPITATION ON SCRAP IRON

This is by far the most common method of treating pregnant mine waters and there are in existence a number of operating plants which have been well described in the literature (1), (2), (3), (4).

The main parameters governing the design of such plants are: contact time, water velocity and launder volume per unit of copper reclaimed. These of course are interdependent with the copper content of the process stream. As will be seen from Table I the design factors vary considerably from plant to plant, as does the copper content of the head and tailings waters. Within certain limits the prime consideration is the volume of launder space in relation to cement copper production, that is to say the size of a given plant is governed less by the water volume to be handled than by the copper content of these waters. From the point of view of turbulence and adequate diffusion a relatively high water velocity is preferable provided that contact time does not suffer.

Centralized precipitation plants located on the surface tend to fall into two groups, the zig-zag launder and the straight line arrangement. Both types have their supporters. The zig-zag arrangement is more compact and somewhat cheaper to operate but it is less flexible if one wishes at a later date to add to the volume of water to be handled. In such a case contact time may be maintained by adding more zig-zag launders to the system, but the velocity will be raised in proportion and this may easily lead to difficulty with suitable falls. Obviously the matter of adequate slopes is extremely difficult to correct in a plant already in existence. The straight line launder arrangement lends itself more easily to the addition of parallel units, if scrap iron is fed by self-propelled mobile cranes with clam shells or electromagnets instead of the overhead gantry arrangements which were formerly in vogue.

At Cerro de Pasco copper reclamation from mine water is still located underground in a channel along a main drift on the 1,400 ft. level. All pregnant waters are pumped from lower levels or gravitate from higher levels to this ditch which is about 1,200 ft. long. By concentrating all activities into one location considerable labour savings have resulted and operations have been streamlined at practically no capital cost whatever. The scrap iron still has to be taken underground but is easily dumped into position from ore cars. Underground segregation of mine waters is practiced and the volume of water undergoing treatment has thereby been cut from 1,800 gallons/minute to 500 gallons/minute. However, segregation is not perfect and the so-called "barren" waters are recombined with the tailings water from the underground launders and pumped to the surface by a single system to undergo further scavenging treatment in launders located on the surface. This arrangement, although quite satisfactory, is not considered to be the final answer and a new surface precipitation plant is now under study.

Another system which we have studied but not put into practice is the use of an old mine shaft into which the scrap iron is dumped. Laboratory testing showed that very adequate stripping of the mine waters can be achieved by a single pass through a packed depth of 65 ft. which we calculate would give a contact time of 45-50 minutes. When percolating mine water through such a column at the rate of 10 gallons/minute per sq. ft. of cross-sectional area the copper content was reduced from 2.4 g/l in the feed liquor to 0.01 g/l in the effluent. In other words, a packed winze 12 ft. dia. would handle 1,000 gallons/minute without flooding. Surprisingly we observed no ill effects from aeration which of course cannot be avoided under these conditions. The vertical column arrangement has much to recommend it in theory but some definite draw-backs could result in practice due to compaction of a long column of scrap iron leading to inadequate liquor distribution.

TABLE I

COMPARISON OF SEVERAL COPPER PRECIPITATION PLANTS

| | <u>Plant A</u> | <u>Plant B</u> | <u>Plant C</u> | <u>Plant D</u> | <u>Plant E</u> | <u>Plant F</u> | <u>Plant G</u> | <u>Plant H</u> |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|-----------------------------|
| Launder system | Zigzag | Straight line | Straight line | Zigzag | Zigzag | Zigzag | Zigzag | Zigzag |
| Mine Water Flow gallons/minute | 2,500 | 840 | 5,000 | 590 | 1,360 | 276 | 2,000 | 1,000 |
| Copper content g/l Cu Head Waters | 0.85 | 2.04 | 0.31 | 2.41 | 3.30 | 1.2 | 1.2- 2.4 | 2.0 |
| Tailings Waters | 0.022 | 0.06 | 0.016 | 0.067 | 0.36 | 0.09 | 0.012(?) | 0.10 |
| Copper recovered in launders - percent | 97.4 | 97.3 | 95 | 97.2 | 89.1 | 92.5 | 99- | 90 (estd) |
| Daily production pounds fine copper | 24,600 | 20,000 | 18,000 | 17,100 | 48,000 | 3,600 | 57,000 | 22,900(calc) |
| Number of launders | 16 double | 200 single | 20 single | 3 6 comp. | 40 single | 8 single | 24 double | 12 double |
| Length per launder ft. | 40 | 16 | 100 | 64 | 40 | 34 | 25 | 12 |
| Cross-section above grid. Width - ft. | 1'8" | 2'8" | 10' | 10' | 5' | 6' | 8' | 8' |
| Depth - ft. | 5' | 2'8" | 3' | 6' | 3' | 4' | 4' | 4' |
| Total effective launder volume - cu. ft. | 64,000 | 21,362 | 54,000 | 69,120 | 16,000 | 6,530 | 28,500 | 9,216 |
| Launder volume to copper produced cu. ft/pounds per day | 2.6 | 1.1 | 3.0 | 4.0 | 0.33 | 1.81 | 0.5 | 0.42 |
| Velocity of mine water ft/min. | 6.7 | 32.0 | 6.5 | 1.3 | 7.3 | 1.5 | 10 | 4.2(8.4 after expansion) |
| Contact time - mins. | 192 | 50 | 78 | 875 | 88 | 181 | 61 | 69 |

Plant A: Inspiration Copper (1)
 Plant B: Ohio Copper
 (Bingham Canyon) (2)
 Plant C: Anaconda, Butte. (3)

Plant D: Andes Copper (1)
 Plant E: Cananea. (4)
 Plant F: Small Instn. in
 South America.

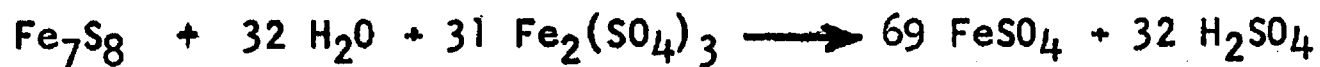
Plant G: Large Instn. in
 North America.
 Plant H: Proposed Surface
 Plant at Cerro
 de Pasco.

SCRAP IRON CONSUMPTION

Although scrap iron is still almost universally used for cementing copper from dilute process streams, it represents a relatively heavy cost item, particularly in isolated localities where the right kind of scrap may be next to unobtainable. Most light sheet metal off-cuts nowadays are lacquered and have to be burned, shredded or otherwise prepared which adds to the expense. In the future light scrap supplies will very likely be contaminated with aluminium cans. While this should be perfectly satisfactory for cementation as such, it may lead to a serious toxic risk as outlined more fully later on. In most mines there is a surplus of heavy scrap such as old castings, rails, and so on. Such materials by reason of their relatively small surface or high carbon content are not very effective precipitants but they can be used up gradually by pushing them into the first few launder sections where the acidity of the waters is high. Obviously the best scrap must go to the final or scavenging sections in order to strip the copper down to the lowest possible figure. Even with those precautions it is doubtful whether any precipitation plant working on scrap iron alone can reduce the copper content of its tailings discharge to less than 60 mg/l Cu. without resorting to artificial agitation.

Scrap iron consumption varies considerably from plant to plant and is very largely dependent on the ferric iron content of the pregnant waters. Obviously all ferric iron must be reduced to the ferrous state and much free acid must be killed before precipitation of copper can take place. In practice a good working figure for effluents containing ferric iron is 2 lbs. scrap per pound of copper precipitated although there are instances where a lower consumption of scrap iron will suffice. We have found that pyrrhotite is a very effective reducing agent for ferric iron and pilot tests have confirmed this fact. By leaving pregnant mine waters in contact with lump pyrrhotite ore for three hours we were able to reduce all iron to the bivalent condition and

effectively cut down scrap iron consumption to 1.25 lbs. scrap/lb. of copper precipitated (5). The reaction may be written stoichiometrically as follows:

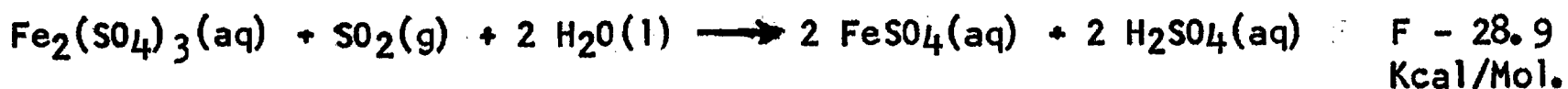


According to the above reaction one pound of pyrrhotite would have the same reducing power as 2.68 pounds of scrap iron. In actual fact we have found that one pound of pyrrhotite will replace from 1.5 to 2.2 pounds of scrap depending on the grade of pyrrhotite used.

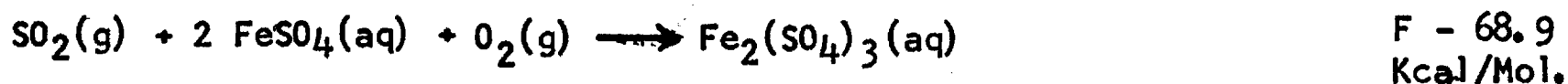
In our experience pyrite does not have the same reducing effect as pyrrhotite even if contact with air is rigidly excluded. Yet from time to time we have come across a curious phenomenon whereby metallic copper seems to have precipitated on truly pyritic mineral in the mine but such occurrences are very rare and we have never been able to reproduce this occurrence under controlled laboratory conditions. Nor is such a reaction very probable in terms of thermodynamics. The coating of pyrite or sphalerite by copper sulphide is of course a very different matter. As every mill man knows, this can and does take place, a contingency that one must always bear in mind when irrigating old stopes with near-neutral waters containing dissolved copper.

Another effective way of conditioning mine waters prior to precipitating copper is to contact them with roaster gases containing sulphur dioxide; this can be done for instance in a normal gas scrubber system. Whenever a roasting operation is carried out in location close to oxidized mine waters this is a possibility that merits careful consideration. A more specific case will be cited below (6). Incidentally the irrigation of roaster gases with oxidized mine waters may help to overcome - at least partially - a nuisance from sulphur dioxide emissions. Small scale experiments which we carried out - contacting actual mine waters and roaster gases containing around 9% SO_2 in stoichiometric proportions - showed that most of the sulphur dioxide can be

absorbed and most of the ferric iron reduced in a simple scrubber system of quite modest proportions. Again the net effect as far as mine waters treatment is concerned is a marked lowering in scrap iron consumption.



A relatively low acidity assists the reaction, while low oxygen concentration is essential; otherwise the "autoxidation" reaction takes over:



The latter reaction can of course be very helpful for leaching but it is quite detrimental in the cementation stage.

A full discussion of the oxidation-reduction reactions that may occur when various sulphide minerals are brought into contact with acidic waters containing ferrous and ferric salts is impossible within the framework of this particular paper. The physical chemistry governing such systems is quite complex and a thorough study is most rewarding, both from the fundamental and from the practical viewpoint. Most publications on the subject seem to limit themselves to empirical observations but there are available a few good dissertations on the thermodynamics involved (7).

SPONGE IRON AND SIMILAR PRECIPITANTS

Indications are that the use of scrap iron will gradually decline in favour of sponge iron. As is well known sponge iron has been coming into use on an increasing scale in connection with leach-precipitation-flotation systems (8), (9), (10), and its use has contributed markedly to the extraction of copper from partly oxidized ores. In LPF plants the sponge is used in the finely divided state, often after magnetic up-grading. There is no fundamental reason why a similar technique should not be applied to mine waters but it is evident that the use of such material would mean contacting in agitation vats

which is relatively costly. Assume an effluent containing 1 g/l Cu at a rate of 2,000 gals/minute. With a contacting time of 30 minutes - which we have found reasonable for this kind of processing - a total agitator volume of 60,000 gallons is called for and this is a fairly big installation. Counter current contacting being impractical, precipitant must be added to each agitator in series ; there should be some excess sponge in the system in the final agitator, to avoid any re-solution of copper.

We have found it possible to make a pelletized sponge by roasting pyrite pellets in a fluidized bed (the roaster gases can be used for pre-conditioning mine waters, see above) after which the pyrite cinders, still in the pelletized form, are converted to sponge iron by gaseous reduction, also in a fluidized bed (11). In this way a particulate product can be obtained which contains 80% metallic iron and has a particle size of around 1/4" diameter. While normal cementation launders are not suitable for this type of precipitant the material can be quite readily handled in jigs. For a prolonged test run we used a converted coal jig of the fixed-bed type and the results we obtained were distinctly encouraging as regards contact time required and copper content in the final tailings discharge. Sponge consumption was similar to that of scrap, based on the content of metallic iron in both materials. Incidentally, we also found jig agitation very useful when practicing cementation on scrap iron. For a scavenging operation involving partly decopperized waters we would recommend a retention time of ten minutes only to strip the water down to less than 30 mg/l Cu (see Table II).

TABLE II

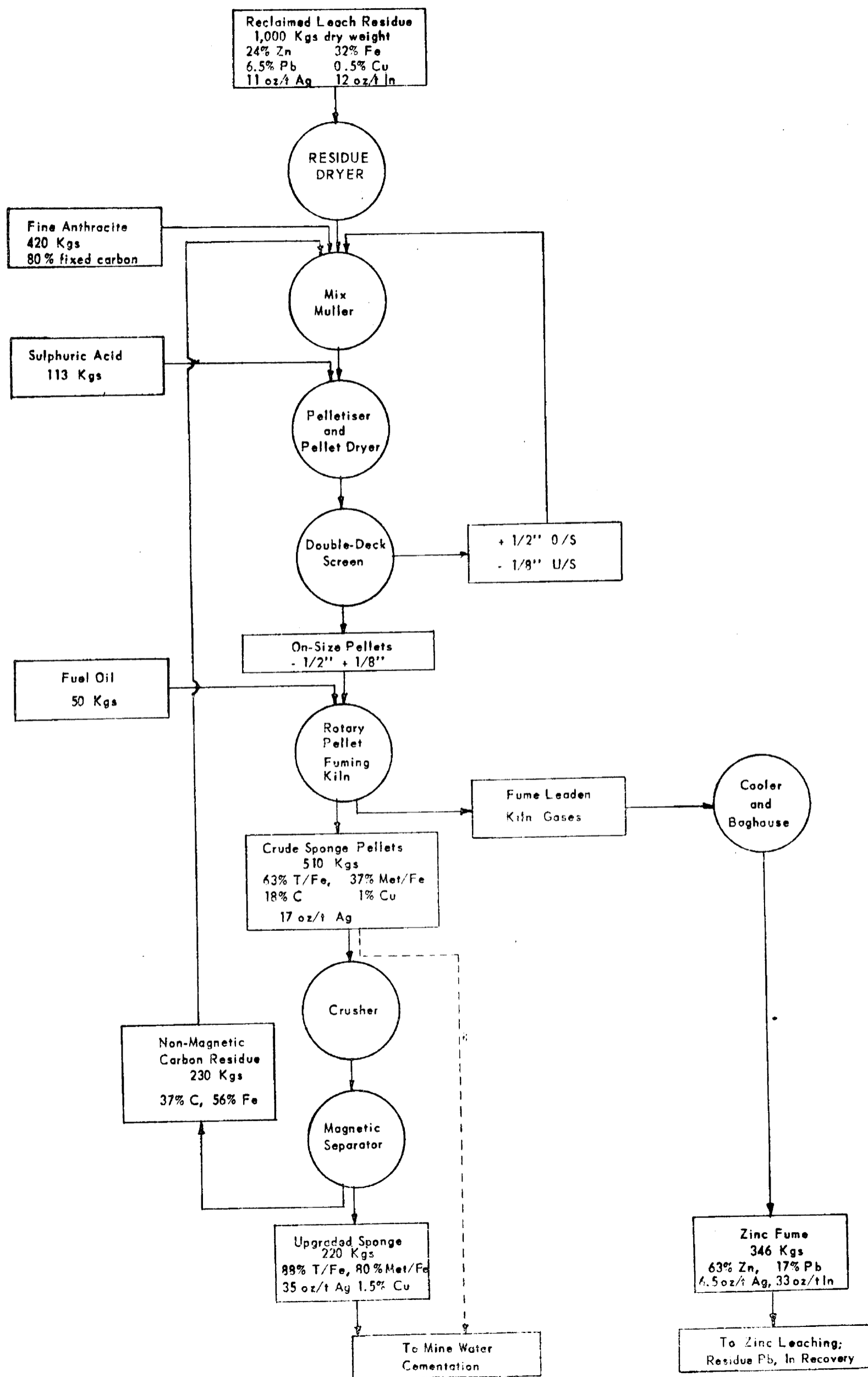
COPPER RECOVERY IN PILOT JIG
WITH DIFFERENT TYPES OF SCRAP IRON

| | Feed Water Strength - mg/l Cu | | | |
|---|-------------------------------|---------------|---------------|---------------|
| | <u>352</u> | <u>230</u> | <u>212</u> | <u>120</u> |
| Lacquered Offcuts - burned | 92.9% (25) | 90.9% (21) | 87.5% (27) | 79.1% (25) |
| Galvanized Iron and Clean Tinned Scrap | 90% (35) | 86.5% (31) | 85.3% (31) | 79.1% (25) |
| Old Tin Cans (used) | 91.8% (29) | 85.6% (33) | 84.1% (34) | 72.7% (33) |
| Black Steel | 86.1% (49) | 82.2% (41) | 87.5% (27) | 75.9% (29) |
| Lacquered Offcuts - unburned | 87.4% (44) | 67.5% (75) | 67.5% (69) | |

Figures in () denote copper content of jig discharge in mg/l Cu;
Contact time 10 minutes in all tests.

The economics of preparing sponge iron pellets depend very largely on the raw material at hand. In our particular case we have available pyrite containing silver to the tune of 10 oz/ton Ag, plus a small amount of copper. Under such conditions we estimate that the cost of making the sponge is fully defrayed by the value of the silver which enters the cement copper to be reclaimed through the normal copper refining circuit. An interesting scheme which we have studied and piloted rather extensively is the preparation of sponge iron from zinc leach residues (12). These zinc leach residues arise from the treatment of marmatitic (high-iron) zinc concentrates in our electrolytic zinc refinery. They are in essence a crude zinc ferrite carrying all the silver and lead present in the original concentrates. The processing scheme in simplified form is indicated in Table III. The leach residue slurry

TABLE III
SPONGE IRON FROM LEACH RESIDUE
PROPOSED FLOWSHEET - SIMPLIFIED



is thickened and filtered; after partial drying the filter cake is pelletized with anthracite or similar low volatile fuel. A rotary kiln treatment volatilizes all the zinc, lead, indium and cadmium plus a minor portion of the silver. This zinc fume is re-cycled to the zinc refining circuit and all the metals are recovered by a system which is outside the scope of this paper. The kiln residue consists of a crude sponge carrying the iron, copper and most of the silver. As withdrawn from the kiln it has a metallic iron content of around 40% Met/Fe. It remains in the pelletized state throughout and thus effectively prevents accretions in the kiln. (The formation of accretions has been a major drawback in rotary kiln processes heretofore).

This crude sponge can be used for the cementation of copper from mine waters, etc., directly; (alternatively it may be up-graded by retorting or by crushing and magnetic separation.) In the former case the resulting cement copper will be of relatively low grade, particularly if the original zinc concentrates carry more than one percent or so of insoluble gangue all of which will report in the kiln product. Although contaminated by various inert fillers, the sponge is an active precipitant for copper. While outside the scope of this paper it may be added that unlike scrap iron the sponge also will precipitate metallic lead from chloride solutions (13).

Although cement copper obtained with this kind of sponge iron will have a lower copper content than the cement deposited on scrap, this is of secondary importance in cases where the crude cement copper can be smelted locally without undergoing long distance transport or being sold outside. Cement copper is normally charged to the converter and the smelting cost is not very seriously affected provided the grade is above 30% Cu. In fact a small smelting credit accrues to any silica contained in the cement copper which is beneficial in the converter. The important point is that the silver and copper originally in the zinc concentrates report in the leach residue,

from there they migrate via sponge iron to the cement copper and are eventually thrown into the converter charge.

Table IV illustrates the point that in this kind of operation copper recovery is far more significant than cement grade. In a typical case it would be in order to raise copper recovery from 90% to 91% even if such action resulted in a drop in the grade of the cement copper from 75% Cu to 55% Cu.

TABLE IV

RECOVERY -v- GRADE OF CEMENT COPPER

| | | | | | | |
|---|----------|----------|----------|----------|----------|----------|
| When raising copper recovery from- | 70% | 75% | 80% | 85% | 90% | 95% |
| to- | 71% | 76% | 81% | 86% | 91% | 96% |
| Grade of cement copper may be lowered from- | 75% Cu | 75% Cu | 75% Cu | 75% Cu | 75% Cu | 75% Cu |
| to a minimum a of- | 50.7% Cu | 51.8% Cu | 52.8% Cu | 53.7% Cu | 54.6% Cu | 55.4% Cu |

Assumptions:

| | |
|--------------------------------------|----------------------|
| Cement Copper contains | 25% water |
| Dry Cement Copper contains | 75% Cu |
| Production cost Cement Copper | \$75 per DST |
| Transport and Converter Smelting | \$9 per DST |
| EMJ price | £30 per pound copper |
| Refining, Shipping and Sales Charges | £4 per pound copper |

While we have found that pelletized crude sponge acts extremely well when contacted with mine waters in a jig of the plunger type, for industrial operation we would prefer a moving bed type of jig for this duty. The mechanics of the process are then quite akin to those which apply to the resin-in-pulp technique of ion exchange. Jig agitation promotes a continual cleaning of the active iron surfaces and achieves close contact of fresh sponge with copper-bearing liquors, hence the favourable retention time. This very fact entails a certain disadvantage: while much of the cement copper collects in the jig hatches, some is carried over into the effluent stream whence it has to be separated either by thickeners of the conventional

type or by hydroclones. Inasmuch as some of the cement copper is of fairly fine particle size (5μ or less) we have found cyclone separation at modest pressures not too effective; sedimentation however is rapid when assisted by the addition of some proprietary coagulant. We would have no hesitation in basing a clarification system for a dilute slurry containing cement copper in suspension on a settling rate of 1 ft/hr. (see Table V)

TABLE V
SEDIMENTATION OF CEMENT COPPER

| <u>Overflow Rate</u> <u>ft/hour</u> | <u>Separation</u> <u>Size - μ</u> | <u>Copper Recovered</u> <u>in Underflow</u> |
|--|---|--|
| 0.41 | 3.0 | 99.5 |
| 0.45 | 3.5 | 99.0 |
| 0.64 | 4.0 | 98.0 |
| 0.83 | 4.5 | 97.0 |
| 1.63 | 6.0 | 92.0 |
| 3.75 | 9.0 | 78.5 |

- - - - -

NOTES: Copper precipitated in a jig at pH 2.5, from a pregnant solution containing 0.78 g/l Cu; 0.1 g/l Separan added; Recovery based on suspended copper only.

Nevertheless it must be stressed that re-solution of some copper during thickening can and does occur, particularly when the jig overflow has been stripped to a point where it carries less than 50 mg/l dissolved copper. Speed is of the essence in this clarification step and final tailings losses should always be calculated on dissolved plus suspended copper. In some cases it may be advantageous to add a little ground sponge iron to the thickener for added protection; this may be separated later by a magnet, for re-use. In other situations where the final tailings waters are re-cycled over leach dumps etc, the problem may not be significant. One thing is certain; a mechanically agitated cementation device will produce a cement copper of finer grain than a more or less stagnant launder system filled with scrap

iron. The grain size of the cement copper is also very much affected by the strength of the mine water and by the final acidity; at a high pH a much coarser cement product results.

Underflow from the thickeners or hydroclones can conveniently be handled in vacuum filter pans or in pressure filters. From a pulp containing 34% solids we were able to build up a 1" filter cake in less than 2 minutes under 40 psig pressure, final moisture of the cement copper cake being 13%. No doubt de-watering by means of a centrifuge would be equally satisfactory (14).

Other forms of iron may become available for purposes of copper cementation: recently there appeared on the market a granulated pig iron (15) which would be handled equally well in launders or in jigs but, being a chilled iron, the carbide content makes it rather unreactive. By contrast our sponge iron contains much carbon but very little carbide, having been produced in a kiln at relatively low temperatures. An interesting type of iron intended for cementation of copper is under development by one of the big copper producers (16, (17). It is made from a special copper converter slag exceptionally low in silica; this is subsequently granulated and reduced to the metallic state. This material may contain up to 5% Cu which of course would be recoverable when the product is used for cementation purposes.

CEMENTATION OF COPPER BY REDUCING GASES

Cementation of copper powder by hydrogen, particularly from ammoniacal solutions, has received much publicity recently but as far as is known there have been no attempts to apply these relatively costly pressure processes to very dilute effluents such as mine waters.

CATHODIC PRECIPITATION OF METALLIC COPPER

In the present state of the art there would appear to be little scope for reclaiming copper by direct electrowinning from solutions containing the metal in concentrations below 5 g/l. Low current efficiencies, polarisation and consequently high cell potentials severely militate against such an approach. It is true that some copper refineries strip their discard electrolyte down to 0.5 g/l Cu by means of cells with insoluble anodes, but the main objective in such cases is to remove impurities from the circuit, to reclaim nickel sulphate, etc, etc.

Yet some intriguing ideas appear on the horizon of copper hydrometallurgy; these may well affect our thinking and direct it towards electrowinning of copper from dilute discard solutions; some metallurgists (18) have reported copper refining at very high current densities using a system of so-called channel electrolysis, whereby the copper electrolyte is swept past the cathodes at high velocity, while research workers at the U. S. Bureau of Mines have gone even further (19) in effecting electrodeposition at extremely high current densities with the aid of ultrasonic vibrations. In neither case have there been reports of applying such methods to very dilute electrolytes, but it is easy to extend the principle in this direction. The only impediment in the way of such techniques is the limiting factor of diffusion rates which in turn leads to polarisation and excessive hydrogen evolution at the cathode. If the thickness of the diffusion layer can be reduced sufficiently through violent agitation of the electrolyte (it matters little what means are employed to this end) electrowinning of copper from mine waters may become quite commonplace, with residual copper in the discard stream in the milligram-per-liter range. Such a system would yield notable advantages in other ways: the copper would be in the form of a fairly pure metallic sponge, to be refined without further

smelting treatment or even - to follow a more recent development - to be compacted directly into commercial shapes. Depending on the composition of the electrolyte, acid and/or ferric sulphate would be regenerated at the anode; this could be very useful in cases where the de-copperised waters are to be re-cycled over leach dumps etc.

Indirect electrowinning of copper from mine waters is of course perfectly feasible, i.e. after pre-concentration by one of the methods to be described later on. Assuming a normal electrolyte circuit, the copper content of the eluate or concentrated secondary liquor should be not less than 10 g/l Cu, and preferably twice this strength.

PRECIPITATION OF COPPER COMPOUNDS

The use of ground limestone or burnt lime has often been advocated and occasionally practiced as a "simple" way to precipitate copper from low-grade effluents. Also it has been claimed that iron can be separated from dissolved copper by neutralising the liquors with ground limestone. This approach may be quite suitable where the ratio of iron to copper in solution is low (a rare case indeed) or where the principal object of the treatment is to prevent an effluent nuisance from acid or from soluble sulphates. Such I understand was the situation which confronted a major copper mining operation in Chile and neutralising the noxious discharge waters with limestone proved to be the answer. On the other hand if it is desired to reclaim the most copper at the lowest cost, then this kind of procedure has little to recommend it. The precipitate will consist mainly of basic iron salts and calcium sulphate and will be very awkward to handle; the copper content of the precipitate being quite low the amount to be treated will be prohibitive. Anyone who has encountered mine water propositions which suffer from co-precipitation of "ochre" slimes will know what I mean. Parenthetically, the chances of in-situ leaching

of old mine stopes will be severely curtailed if the active lixiviant waters pass through adjacent limerock formations. Next to seepage losses uncontrolled precipitation underground is the greatest bug in this kind of irrigation scheme.

As far as preferential precipitation of basic iron carbonates is concerned, leaving copper in solution, we have never had much luck with it: during an extended pilot run on ion exchange separation - to be described more fully later on - we had first to condition our mine waters at pH 3.5; this was done with crushed limestone. Even under such relatively acid conditions we always had to accept a copper loss amounting to around 15% of intake; admittedly in this case the iron:copper ratio in the liquor was high at 16:1.

Precipitation of copper sulphide has been mentioned in the literature; it may have its place in certain special situations, e.g. if crude natural gas happens to be on hand. Another proposal of interest is the precipitation of cuprous thiocyanate, which is decomposed to cuprous oxide with simultaneous regeneration of the expensive thiocyanate radicle (20). The scheme which calls for the addition of sulphur dioxide gas to the mine waters is quite ingenious and must have tickled the fancy of several hydrometallurgists, but I have never heard of an actual installation based on the method. We carried out some half-hearted pilot tests, but found that the cuprous compound was not nearly as readily filtrable as the inventors claimed. Also the consumption of caustic soda - which is used to regenerate an alkali thiocyanate - seemed to us a little costly. Lime may be used in place of caustic soda but this entails a secondary flotation step to separate the insoluble salt from cuprous oxide. I repeat, our own work on the process was rather cursory and I would not care to pronounce definitely for or against it.

PRE-CONCENTRATION OF DILUTE PROCESS STREAMS CONTAINING COPPER

The most obvious approach to pre-concentration and one that naturally appeals to practical mining men and extraction metallurgists is to make a clean separation of copper-rich streams and of "barren" water, before processing. However, along this seemingly straightforward route there lie many pitfalls. In some cases where segregation appears to be called for at first sight, it actually may lead to loss of copper and of monetary contribution. This arises from two causes: firstly in the case of mine waters collected underground it is quite difficult to separate water streams which are absolutely barren. Secondly it must be emphasised again that cement copper is low-cost copper and the aim must always be to get maximum metal recovery even though it may mean processing larger volumes of liquor. Even labour productivity may have to be sacrificed to some extent to the prime objective of maximum metallurgical efficiency. In a typical case labour cost for a cementation operation would be of the order of one tenth of the value of the recoverable copper. It follows that a rationalisation measure which reduces labour cost by a third must not lead to a lowering of metal recovery in excess of 3% otherwise a loss in contribution results.

Also the capital cost and operating expense of most precipitation plants tends to be governed by the amount of copper produced, not by the water volume handled. A typical cost pattern would be expressed by a formula such as :

$$\text{Operating cost per pound of copper} = A + \frac{B}{q}$$

where A and B are constants while q denotes the concentration of copper in the mine water. A numerical example is given in Table VI from which it will be seen that - for the particular case quoted - it would be unsound to reject weak liquors unless they contain less than 79 mg/l Cu, while the actual cut-off

TABLE VI

EFFECT OF SPLITTING MINE WATER INTO PROCESSING AND DISCARD STREAMS

Assumptions: Original Water contains 0.25 g/l Cu

Cost of Cement Copper = $3.0 \pm \frac{1.25}{q}$ cents per pound fine copper
 where q = copper content of water in grams/liter.

| | | | | | | | |
|---|---------|--------|------|------|-------|--------|-------|
| Mine water strength - g/l Cu | (0.057) | (0.10) | 0.25 | 0.50 | 1.00 | 2.00 | 5.00 |
| Cost - ¢/lb. fine copper recovered | (25.0) | (15.5) | 8.0 | 5.5 | 4.25 | 3.625 | 3.25 |
| Gross return - ¢/lb. fine copper recovered | (0) | (9.5) | 17.0 | 19.5 | 20.75 | 21.375 | 21.75 |
| Recovery - percent (based on constant tailings value of 0.030 g/l Cu) | | (70) | 88 | 94 | 97 | 98.5 | 99.4 |

Gross return - ¢/lb. copper in mine water at different ratings of discard stream:

| | | | | | |
|---|-------|-------------------------|-------|-------|-------|
| Discard stream: 0.00 g/l Cu 0.03 " " 0.05 " " 0.08 " " 0.10 " " 0.15 " " | 14.96 | → Segregation sound ← | | | |
| | | 18.33 | 20.13 | 21.05 | 21.62 |
| | | 17.16 | 18.26 | 18.81 | 19.14 |
| | | 16.29 | 16.95 | 17.27 | 17.47 |
| | | 14.84 | 14.88 | 14.91 | 14.94 |
| | | 13.75 | 13.42 | 13.30 | 13.24 |
| | | 10.47 | 9.47 | 9.10 | 8.92 |
| | | → Segregation unsound ← | | | |

Example: Mine water containing 0.25 g/l Cu will give a gross return of £14.96 per pound of copper contained. If this is split into a processing stream (2.00 g/l Cu) and a discard stream (0.10 g/l Cu) the monetary return is reduced by £14.96 - 13.30 or £1.66, equivalent to a loss of 11.1%

point for waters without separation is a little lower still at 57 mg/l Cu.

Even if thorough test work proves that a near-barren water flow can be successfully rejected, due allowance must be made for the possibility of human error. By an accidental situation underground it may happen that for a limited period barren and pregnant streams intermingle and are carried to waste. If this should occur for only a few days every year any advantage of segregation may well be nullified. Where segregation is practiced, separate launder and pumping systems underground are mandatory. To use the same equipment alternatively for pumping pregnant and barren solutions would be courting disaster, to say nothing of the considerable surge storage capacity which would be needed, both ahead of the pumps and ahead of the precipitation plant.

It is often thought that by splitting off water streams which carry next to no copper a strong but barren lixiviant may be obtained for surface heap leaching etc. This surmise seems reasonable if one deals with water percolating through a pyritic ore body where it should pick up no copper but plenty of ferric iron. As far as the Cerro de Pasco mine is concerned we were disappointed in this respect; Extensive sampling has proved beyond doubt that the iron:copper ratio in all the water streams from various parts of the mine remains more or less constant. One possible explanation may be that the presence of a little copper catalyses the oxidation of pyrite by a reversible shift from the cupric to cuprous iron. Incidentally, this is a good reason why mine waters intended for recirculation should not be stripped of their copper content entirely: a little residual copper will assist quite markedly in promoting re-oxidation of ferrous iron for subsequent heap leaching etc. It is well known that the mechanism of regenerating ferric sulphate has been quite extensively studied in recent years and that bacteria have been called in to redress the balance (21).

From our own observations we are inclined to think that it is quite easy to re-oxidise spent mine waters; in fact we cannot keep them in the reduced condition. Perhaps we have some very potent bugs in our tailings waters, without knowing it.

Subject to the limitations outlined above it is agreed then that the mining engineer should avoid indiscriminate mixing of effluents which Nature has kept apart. More often the problem confronting us is the reverse, namely that of splitting up a dilute and truly homogeneous solution into a concentrated electrolyte and into fresh water. In this field there are distinct opportunities for technical development. The idea of sweetening saline waters has aroused keen interest of late and money is being put into some extensive piloting ventures. In our minds we do not normally connect such activities with mining in any form, but a moment's reflection will show that the principle of separating sea water into potable water and residual brine is exactly analogous to that of enriching dilute sulphate liquors by abstracting fresh water from the system. Even the technology could be similar if for the moment we restrict the discussion to processes not involving phase change of the solutes. Provided the solvent (water) is abstracted by freezing, by evaporation, distillation or through the separation of solid hydrates, in principle it matters little whether the residuum is salt brine or a concentrated solution of heavy metal sulphates, except for secondary engineering problems such as corrosion or scale formation.

A full discussion of these de-salting processes would be impossible within the framework of this paper; in any case there is available an abundance of technical literature on the subject. A recent paper by B. F. Dodge (22) presents an excellent outline of the thermodynamics

and energy requirements of the different separation methods, while an ACS monograph published in 1960 (23) gives very full details of the different techniques under study. For a brief summary the reader may be referred to an article by E. D. Howe (24) which appeared three months ago. A very elegant technique is that of removing the water, not by simple freezing, but by precipitation as a solid hydrate; such hydrates are formed under conditions of moderate pressure and temperature by the higher hydrocarbons.

The object of all these processes is to provide fresh water suitable, if not for human consumption, at least for irrigation purposes, at a cost of around \$0.50 per 1,000 gallons. (I have found no mention of recovering metals from the residual brine, but such an approach would not be beyond the realm of possibility). When dealing with mine drainage waters our first consideration would be to recover the heavy metals, particularly copper, but there may be many situations where the co-produced fresh water would be a distinct asset for use in concentrators etc. The problem of cost may not be insuperable. Assume fresh water can be separated at the figure mentioned; for a mine effluent containing 1 g/l Cu this would be equivalent to 6¢ per pound of copper. It could be worth that much to obtain the copper in a concentrated electrolyte from which the metal can be obtained by electrowinning. Free acid and zinc - our mine waters normally contain around 1 g/l Zn - would also be recoverable and, last but not least, on the credit side there would be fresh water.

One technique of this kind which deserves special mention is that of electrodialysis. It is heartening to report that this was pioneered by one of the big mining groups, not so much for recovery of metal values but to combat a fresh water shortage (26). Many dissertations on

the possibilities of using this method - both for generating fresh water and for chemical processing - continue to appear in the technical press and are worth following up (27), (28), (29), (30). I am not quite clear whether electrodialysis should strictly be classed amongst the processes that involve no phase change of the solute because in some respects the principle involved is related to that of ion exchange, but in actual practice a concentrated aqueous "transfer stream" is obtained directly and on a continuous basis.

We are carrying out some bench scale tests on the concentration of mine waters by electrodialysis. Our objective is a limited one which fits into the local picture at the Cerro de Pasco mine: a lead-zinc mill is situated close to the minehead which uses copper sulphate for zinc activation. It would save some money if instead of shipping cement copper to the smelter at La Oroya and returning copper sulphate to the concentrator - the salt being obtained from the copper refinery discard electrolyte - we were to branch off a fairly concentrated copper sulphate liquor directly from the mine and pipe it to the mill. This would also make available a corresponding quantity of copper sulphate for outside sale. In this case we are aiming at an enriched mine water containing at least 10 g/l Cu. Only about one tenth of the copper arising in our total mine water flow would be needed for this particular scheme. Therefore we are in the fortunate position of not having to make a good copper recovery in the electrodialytic system; the tailings stream would simply be added to the cementation launders or jigs. So far we have been able to upgrade the copper from 2 g/l in the feed stream to around 8 g/l in the transfer stream. Ferric iron in the feed gives rise to various difficulties with the membranes and electrodes, but after reducing most of the iron to the bivalent condition we are experiencing little trouble. Up to now we have not obtained much selectivity; cupric, ferrous, hydrogen and sulphate ions all migrate to the product stream.

RECOVERY OF COPPER BY ION EXCHANGE AND RELATED PROCESSES

The application of ion exchange techniques has been extensively studied in our research laboratories (31), (32). A pilot plant was installed in 1956 and was in active and continuous use for almost two years. Laboratory work had established that cationic resins of the carboxylic type were the most promising, with regard both to selectivity and absorption capacity, for the particular mine waters we had to treat. The raw waters - partly de-copperised in cementation launders underground - were passed through tanks filled with limestone to raise the pH to 3.5 which we found was the highest permissible acidity consistent with good performance of the resins in the calcium form. During this pre-conditioning some ferric hydroxide was removed from the feed liquors. After clarification in sand filters the mine waters were passed through a three-column resin bed system as follows: two columns were connected in series, the resin in the first being loaded to capacity and that in the second column to the breakthrough point for copper. Meanwhile the third column was eluted, treated with saturated lime water for resin regeneration and flushed out with fresh water to remove minor amounts of calcium sulphate formed during regeneration. This cycle permitted continuous operation and was quite satisfactory. The eluate contained about 10 g/l Cu and was subjected to cathodic stripping of copper, the acid electrolyte being returned to the system for resin elution.

Metallurgical results for this system are summarised in Table VII. It will be appreciated that many process variables came in for testing during the 21 months of operation. The data quoted are not the optimum conditions established during this work but are the mean values covering the whole test period. In the light of the experience gained we could certainly improve further on the metallurgy in a full scale production plant.

We encountered a fair amount of resin degradation (for details please see Table VIII) which was mechanical rather than chemical; this undesirable feature would put a distinct limitation on the ion exchange method as applied to a relatively low-value process stream. Our work on this project was terminated in 1958 and it may well be that better and cheaper resins are now available.

Our findings from this extended test programme may be summed up as follows:

- The ion exchange process for the recovery of copper from mine waters high in iron is technically perfectly sound.
- Given adequate equipment for pre-conditioning the feed water copper recoveries of well over 90% can be maintained.
- Concentration ratio for copper (eluate to feed) under our conditions was 38 to 1, while over 95% of the iron was rejected.
- The recovery of high grade metallic copper or copper sulphate from the eluate presents no particular problem.
- If good quality burnt lime is available reagent consumption is not unreasonable.
- Resin life is distinctly limited. We would estimate 15% resin replacement per year.
- Plant investment would be at least \$400,000 per daily ton of fine copper produced, starting with mine water containing 0.45 g/l Cu. For more concentrated effluents the investment cost (per pound of copper) would not be much lower.
- Net operating costs, while not entirely prohibitive, would be higher than for a conventional scrap iron cementation plant.
- Capital charges make such a proposition unattractive under the particular conditions studied.

TABLE VII

ION EXCHANGE PILOT PLANT
Summary of Operating Results

| | | <u>Single Column</u> | <u>Two Columns</u> <u>In Series</u> |
|---|------------------|----------------------|--|
| Overall testing period | months | 11 | 7 |
| Net operating time | hours | 6,363 | 3,492 |
| Operating time | percent of total | 80.3 | 89.8 |
| Total mine water treated | gallons | 3,099,100 | 1,819,200 |
| Mine water fed per hour | gallons | 487 | 521 |
| Copper in raw mine water | g/l | 0.277 | 0.264 |
| Copper in feed to I. E. columns | g/l | 0.243 | 0.220 |
| Copper in discharge from I. E. columns | g/l | 0.006 | 0.012 |
| Copper intake to plant | lbs | 7,163 | 4,013 |
| Copper recovery (columns only) | % | 95.9 | 91 |
| Copper recovery (whole plant) | % | 83.5 | 74.3 |
| Copper lost during conditioning | % | 12.4 | 16.7 |
| Copper lost in column discharge | % | 2.0 | 4.4 |
| Copper lost in spent electrolyte | % | 2.1 | 4.6 |
| | | <u>100.0</u> | <u>100.0</u> |
| Copper in eluate | g/l | 9.80 | 10.49 |
| Concentration ratio eluate : feed | | 38:1 | 36.8:1 |
| Iron in raw mine water | g/l | 4.38 | 5.12 |
| Iron in feed to I. E. columns | g/l | 3.43 | 4.27 |
| Iron in eluate | g/l | 8.62 | 14.37 |
| Copper : iron ratio in column feed | | 1:14.1 | 1:19.4 |
| Copper : iron ratio in eluate | | 1:0.88 | 1:1.37 |
| Iron rejection | % | 92.4 | 95.3 |
| Reagent Consumption per pound copper | | | |
| Limestone (74.5% CaCO ₃) | | 21.54 lbs | 16.26 lbs |
| Burnt lime (61.9% av. CaO) | | 10.89 lbs | 10.70 lbs |
| Sulphuric acid (66°Bé) | | 11.74 lbs | 7.45 lbs |
| Resin | | 0.0010 cu. ft. | 0.0021 cu. ft. |
| Power consumption DC - kwh per pound copper | | 3.80 | 2.79 |
| Current efficiency | % | 33.2 | 50.8 |

TABLE VIII

ION EXCHANGE PILOT PLANT
Resin Deterioration

a) Single column downflow operation (Resin IRC-50)

| <u>Mesh Size</u> | <u>Original</u> | | <u>After 6 months</u> | | <u>After 10 months</u> | |
|------------------|-----------------|-----------------|-----------------------|----------------|------------------------|----------------|
| | <u>% wt.</u> | <u>% cumul.</u> | <u>% wt.</u> | <u>% cumul</u> | <u>% wt</u> | <u>% cumul</u> |
| + 28 | 47.8 | 47.8 | 22.0 | 22.0 | 4.7 | 4.7 |
| + 35 | 31.0 | 78.8 | 29.2 | 51.2 | 29.8 | 34.5 |
| + 48 | 16.9 | 95.7 | 34.9 | 86.1 | 41.8 | 76.3 |
| - 48 | 4.3 | 100.0 | 13.9 | 100.0 | 23.7 | 100.0 |

b) Two columns in series upflow operation (Resin IRC-50)

| <u>Mesh Size</u> | <u>Original</u> | | <u>After 2 months</u> | | <u>After 4 months</u> | | <u>After 6 months</u> | |
|------------------|-----------------|-----------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------|
| | <u>% wt.</u> | <u>% cumul.</u> | <u>% wt</u> | <u>% cumul</u> | <u>% wt</u> | <u>% cumul</u> | <u>% wt</u> | <u>% cumul</u> |
| + 28 | 10.8 | 10.8 | 6.3 | 6.3 | 4.7 | 4.7 | 4.6 | 4.6 |
| + 35 | 50.0 | 60.8 | 27.8 | 34.1 | 26.0 | 30.7 | 25.0 | 29.5 |
| + 48 | 30.4 | 91.2 | 56.3 | 90.4 | 53.6 | 84.3 | 35.1 | 64.6 |
| - 48 | 8.8 | 100.0 | 9.6 | 100.0 | 15.7 | 100.0 | 35.4 | 100.0 |

c) Two columns in series upflow operation (Resin H-70)

| <u>Mesh Size</u> | <u>Original</u> | | <u>After 2 months</u> | | <u>After 4 months</u> | | <u>After 6 months</u> | |
|------------------|-----------------|----------------|-----------------------|----------------|-----------------------|----------------|-----------------------|----------------|
| | <u>% wt.</u> | <u>% cumul</u> | <u>% wt</u> | <u>% cumul</u> | <u>% wt</u> | <u>% cumul</u> | <u>% wt</u> | <u>% cumul</u> |
| + 28 | 21.0 | 21.0 | 20.3 | 20.3 | 10.1 | 10.1 | 7.7 | 7.7 |
| + 35 | 56.0 | 77.0 | 47.2 | 67.5 | 46.7 | 56.8 | 39.9 | 47.6 |
| + 48 | 20.2 | 97.2 | 27.4 | 94.9 | 35.8 | 92.6 | 45.0 | 92.6 |
| - 48 | 2.8 | 100.0 | 5.1 | 100.0 | 7.4 | 100.0 | 17.4 | 100.0 |

— The process warrants renewed study if and when better, cheaper resins appear on the market.

As a point of general interest it should be added that during the period of these investigations the Cerro mining department doubled the production of cement copper by intensified irrigation and more effective stripping. To what extent these fine efforts were catalysed by the contemporary endeavours to establish a new process for reclaiming the copper is purely a matter for conjecture

As regards solvent extraction, this has certainly been advocated for stripping copper from mine effluents (33), (34), but so far the method has not found industrial acceptance for this purpose. We ourselves have done very little experimental work in this field, although we feel that, due to its inherent simplicity, liquid-liquid exchange could well surpass the usefulness of solid resins for sequestering copper from dilute solutions. Obviously the economic considerations are very different from those which apply to the extraction of uranium. Cost and limited selectivity of solvents have had a discouraging effect on development work so far, but this may change with time. Naphthenic acid has been recommended as an inexpensive solvent (35); unfortunately it will work for copper only at pH 6 which seems to rule it out as far as acid mine waters with a high iron content are concerned. On the credit side it is claimed that solvents of the alkyl hydrogen phosphate type are useful for sequestering zinc as well as copper (34), quite an important consideration in the case of some mine effluents. Also when handling clear effluents solvent losses would be limited to the true solubility of the organic phase in water, whereas in pulp treatment losses by mechanical dragout preponderate.

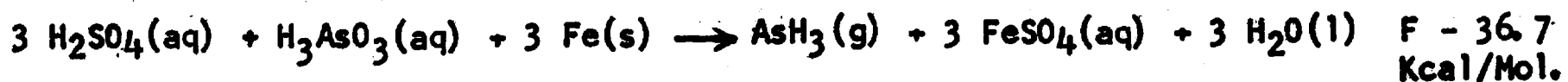
Similarly the Sebba process of ion flotation (36), (37), could have distinct possibilities for mine water treatment if only it can be made to pull the copper and zinc preferentially while keeping the iron depressed in solution. Certainly in cases where mine waters and similar effluents should happen to have a favourable copper to iron ratio, both liquid-liquid extraction and ion flotation deserve very close scrutiny.

Ideally, the hydrometallurgist needs exchange media of maximum absorption capacity and selectivity; in most cases he would wish to operate under slightly acid conditions. Solid media should be resistant to mechanical abrasion, while liquid solvents should have a low viscosity, high specific gravity and next to no solubility in water. In addition the price must be right. Admittedly this is asking for quite a lot, but the growth of ion extraction techniques for dilute process streams will depend entirely upon the degree of success with which the organic chemist can approach such ideal specifications.

RISK OF EVOLVING ARSINE GAS

When dealing with cementation or cathodic reduction methods applied to acid process streams carrying small amounts of dissolved copper, one must always be conscious of a serious potential health hazard from the evolution of arsine gas.

In the Cerro de Pasco mine where the chief copper mineral is enargite, arsenic is always detectable in the mine effluents. Arsenic concentration normally ranges from 0.05 to 0.2 g/l As but on occasions we have had samples running up to 1 g/l As. By introducing metallic iron it is perfectly possible to liberate arsine gas from this kind of water according to the equation:

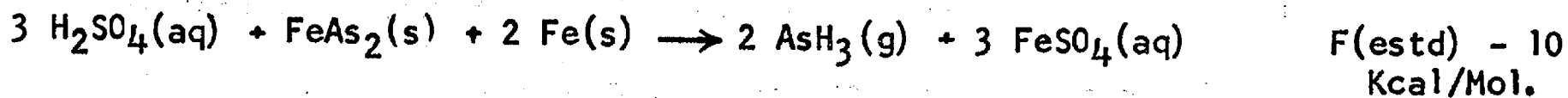


The standard energy of formation favours this reaction and laboratory tests have given positive indications of arsine gas evolution, albeit in very low concentrations.

Fortunately we have never experienced any trouble in our underground cementation launders which may be ascribed to the fact that they are usually placed along main drifts with adequate ventilation. An industrial case of arsine poisoning involving somewhat related conditions, namely the contact of an acid liquor containing arsenical compounds with a cast iron filter press, has however been reported (38).

Some years ago we carried out some heap leaching tests during which various copper minerals in contact with pyrite etc., were subjected to lixiviation by mine waters under closely controlled conditions. From a relatively high grade copper ore containing mainly pyrite and enargite, copper and arsenic were dissolved in the proportion of 4.9:1 and from a low-grade material in the proportion 18:1. The ideal weight ratio of copper to arsenic in enargite is 2.5:1. This is further evidence that some arsenic can be dissolved from such ores by natural mine waters, although with difficulty.

If sponge iron containing small amounts of arsenides is used for cementation of copper, arsine gas may also be generated by the following mechanism:



The free energy of this reaction is probably small; in actual laboratory tests we have not detected arsenic generated from sponge iron.

A more potent hazard could arise in cases where aluminium cans enter the cementation system with scrap iron. This of course is a very real possibility and aluminium will liberate the deadly gas with considerable vigor:



F - 207
Kcal/Mol.

The same problem crops up in intensified form during scavenging operations on copper refinery effluents where arsenic is always present in significant concentrations.

PROCESS CONTROL

Reverting once again to economic considerations, it is of utmost importance that a copper recovery plant treating drainage waters and similar effluents be designed to work year-in year-out, steadily and without interruptions. These waters will flow inexorably, regardless of plant breakdowns, labour disputes or slumps. Unless the mine is abandoned and flooded, there will always be drainage waters that cannot be stored or stockpiled for future treatment. Whatever process is adopted for reclamation of copper, reliability is the prime requirement for any plant design.

By the same token analytical control of tailings waters must be given careful consideration, especially in cases where there is no effluent recirculation. This is an ideal case for automatic sampling and analysis coupled with recording of analytical results. We approached several commercial firms specialising in this kind of equipment and we got relatively little help. So we decided to develop our own prototype automatic analyser for copper effluents, more particularly for determinations in the range below 50 mg/l Cu.

A polarographic technique was first investigated but here we struck a major difficulty due to the residual current caused by the high iron content of the tailings waters. It must be remembered that the iron:copper ratio in these tailings waters may be as high as 500:1. We then decided to use a

colorimetric technique, somewhat along the following lines: the sample is diluted and EDTA is added to complex the iron in the mine water; a characteristic copper colour is next developed by using diethyldiocarbamate stabilized with a colloid. These reagent additions are in the liquid form and readily controlled by a small proportioning pump system. Next the sample is fed continuously through a colorimetric cell and the results are read directly from a commercial colorimeter, the scale being graduated in milligrams copper per liter. Actually our prototype set-up is not truly continuous, but gives a sample reading automatically every five minutes.

We estimate that a robust production model suitable for permanent installation at the mine head or tailings discharge point could be made up from commercially available components at a total cost of around \$10,000 to \$15,000. This would include the sampling system, reagent dosing, colorimeter, automatic readout and chart record of the results, coupled to an alarm system which comes into action if the copper content of the tailings water rises above a pre-determined limit. This of course is much cheaper than the automatic X-ray fluorescence analytical control for mill pumps, and we are confident that such a simple system will be entirely adequate to prevent valuable copper being lost, quite literally over the dam.

CONCLUSIONS

While copper in dilute mine effluents is not a major contributing factor to world production of the metal, it can be reclaimed at an attractive cost; the gross return from such scavenging operations to the mining industry is not negligible. Copper precipitation processes merit very close metallurgical control and extraction efficiency must take precedence over other operating factors such as labour cost. Scrap iron is still universally used for the purpose of stripping copper from such dilute process streams

but one may predict a tendency towards other precipitants, particularly argentiferous or cupriferous sponge iron. It may well be that recently developed techniques for sweetening sea water will find an application in the treatment of mine effluents. Ion exchange or liquid-liquid extraction will make little progress until such time as the cost of reagents can be lowered or degradation in use be reduced.

ACKNOWLEDGMENTS

Insofar as this paper contains data obtained during technical investigations in Cerro de Pasco and in La Oroya, many colleagues in the operating and research departments have made valuable contributions. It would be impractical to list the names of all those to whom I am indebted and I trust that my friends will accept a general acknowledgment. I must single out for special mention Mr. H. P. Doettling, formerly in the service of the Corporation as Research Metallurgist, who has been very closely associated with the work on our ion exchange pilot plant and similar investigations. My sincere thanks are due to the Management of Cerro Corporation for their unfailing support and for permission to publish the data presented in this paper.

REFERENCES

- (1) G. D. Van Arsdale, "Hydrometallurgy of Base Metals", McGraw Hill Book Co., New York, (1953)
- (2) A. E. Anderson, F. K. Cameron, "Recovery of Copper by Leaching", Ohio Copper Co. of Utah, A. I. M. E., Trans. 73, 31, (1926)
- (3) A. C. Bigley, F. F. Frick et. al. "New Precipitation Plant at Butte", Mining Congr. J. 37 March, 48-53 (1951)
- (4) R. C. Weed, "Cananea's Program for Leaching in Place", Mining Eng. 8, 721-23, (1956)
- (5) Peruvian Patent 6175. "Majoras en la recuperación de valores metálicos contenidos en soluciones", to Cerro de Pasco Corpn.
- (6) Peruvian Patent 6174. "Acondicionamiento de soluciones que contienen sales ferricas disueltas", to Cerro de Pasco Corpn.
- (7) M. J. M. Pourbaix, "Thermodynamics of Dilute Aqueous Solutions", E. Arnold & Co, London (1949)
- (8) J. B. Hutt1, "How New Leach-Float Plant Handles Greater Butte's Ore". Eng. Mining. J. 154 No. 6. 90-93 (1953)
- (9) "The L. P. F. Plant - Key to the New Hayden Smelter", Eng. Mining J. 160 No. 6. 104-107.
- (10) "Tailor Metallurgy to Ore at Hayden", World Mining, 12 June, 40-49, (1959)
- (11) Peruvian Patent 3744. "Majoras en y relativas a la metalurgia y al beneficio de minerales no ferrosos, como los de cobre, plomo, zinc, etc., y de minerales ferrosos, como piritas y oxidos de hierro". to Cerro de Pasco Corpn.
- (12) Peruvian Patent 5231. "Proceso para recuperar metales contenidos especialmente en residuos de zinc". to Cerro de Pasco Corpn.
- (13) Peruvian Patent 4177, "Método de recuperación de valores metálicos contenidos en soluciones", to Cerro de Pasco Corpn.
- (14) J. B. Hutt1, "Cement Copper Begins at Bagdad", Eng. Mining, J. 162 No. 6. 86-88 (1961)
- (15) British Patent Applications 78, 287/60; Peruvian Patent Application Exp. 5707, by Stewarts & Lloyds Ltd. Glasgow.
- (16) C. R. Kuzell, et. al, U. S. Patent 3,023,454, "Hydraulic Quenching and Granulation of Molten Materials", assigned to Phelps Dodge Corpn.
- (17) Peruvian Patent Applications, Exp. 5612, 5613, 5614 by Phelps Dodge Corpn.

- (18) S. J. Wallden, S. T. Henriksson, et. al, "Electrolytic Copper Refining at High Current Densities", J. Metals, 11 528-34 (1959)
- (19) C. B. Kenahan, D. Schlain, "Deposition of Copper and Zinc from Sulfate and Cyanide Electrolytes", U. S. B. M. RI 5890 (1961)
- (20) C. H. Keller, U. S. Patent 2,390,540, "Recovery of Copper from Copper-bearing Solutions", assigned to The Dow Chemical Co.
- (21) J. S. Sutton, T. D. Carrick, "Possible Uses for Bacteria on Metallurgical Operations", U. S. B. M. IC 8003 (1961)
- (22) B. F. Dodge, "Fresh Waters from Saline Waters", Am. Scientist, 48 476-513 (1960)
- (23) "Saline Water Conversion", Advances in Chemistry Series No. 27, Am. Chem. Soc, Washington, D. C. (1960)
- (24) E. D. Howe, "Desalting Water", International Science & Technology, April 1962, 47-52
- (25) W. E. Donath, U. S. Patent 2,904,511, "Method and Apparatus for Producing Purified Water from Aqueous Saline Solutions", assigned to Koppers Co. Inc.
- (26) W. H. Moyers, "Desalting Mine Water on a Large Scale", Optima, vol. 7. No. 3. 134-140 (Sept. 1957)
- (27) E. A. Mason, W. Juda, "Applications of Ion-Exchange Membranes in Electro-dialysis", Am. Inst. Chem. Eng. (Baltimore Meeting - Sept. 1957)
- (28) W. E. Katz, "Some Practical 1959 Advances in Electric Membrane Demineralization, (A. C. S. Meeting - Cleveland, April 1960)
- (29) N. P. Chapey, "Water Desalting Plant to Prove out Electrodialysis", Chem. Eng. 69 No. 11. 104-106 (1962)
- (30) B. H. Vromen, "Dialysis a Sleeper?", Ind. Eng. Chem (Intern. Edition) 54 No. 6. 20-28 (1962)
- (31) T. A. A. Quarm, "Recovery of Copper from Mine Drainage Water by Ion Exchange", Trans, Inst. Mining Met. 64 109-117 (1954-55)
- (32) Peruvian Patent 3578, "Procedimiento para recobrar cobre puro de soluciones impuras y diluidas especialmente de aquellas que contengan hierro", to Cerro de Pasco Corpn.
- (33) R. S. Olsen, M. F. McCarty, "Solvent extraction in the Metallurgical Industry", Mining Congr. J. 43 July, 50-55, 80-81 (1957)
- (34) W. C. Hazen & A. V. Henrickson, U. S. Patent 2,992,894, "Process for Concentrating Copper and Zinc Values Present in Aqueous Solution", assigned to Kerr-McGee Oil Industries, Inc.

- (35) A. W. Fletcher, J. C. Wilson, "Naphthenic Acid as a Liquid-Liquid Extraction Reagent for Metals", *Trans. Inst. Mining Met.* 70 355-366 (1960-61)
- (36) F. Sebba, "Concentration by Ion Flotation", *Nature* 184 1062-63, (1959)
- (37) Peruvian Patent 5942, "Un procedimiento de flotación mineral", to Armour & Company, Chicago.
- (38) W. D. Buchanan, "Toxicity of Arsenic Compounds", Elsevier Publishing Co., London (1962) 86-87.