

MINING COPPER IN SITU

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Introduction

This paper presents an old method in the light of new progress, recent research, and economic adjustments. The author does not lay claim to any new discovery. He has attempted to present all the pertinent facts relative to the consideration of an effort to produce a mine from a copper deposit by the adoption of a particular mining method.

Geologists have long noted that in abandoned copper mines the decomposition of the ore may take place indefinitely producing cupriferous water. The decomposition of iron sulphides, usually associated with copper ores, produces weak sulphuric acid and soluble ferric sulphate. Both these products are capable of dissolving various copper minerals. Attempts to imitate this natural process have been made on several continents. The deposit may be developed as in the exploration of a mine, the workings all leading to a centralized point for solution collection. After the copper is removed from the collected solution the water may be recirculated over the ore body, or, it may be simply discarded.

The science and chemistry of the method has been developed by years of experience with surface leaching plants. This long experience has added much to the literature of the process which treats profusely on the relative merits of various procedures, reagents, and operations. In this paper those particulars are presented about the methods that have come to stand highest in the estimation of the experts and practitioners.

The author expects to find disagreement among his readers. He hopes, however, to influence one reader who will carefully consider the method in conjunction with some known deposit of copper, and who may therefrom develop a copper mine.

If any part of this paper suggests a solution to the problem it will have served its purpose.

The Selection of a Stoping Method

-There are many important details which must be taken into consideration when choosing a particular mining method. These details are concerned with the structural geology of the mine being considered and can be arranged under two headings.¹

- 1. The character of the deposit. This includes the size, shape, dip, wall conditions, extent and consistency of the ore.
- 2. The character of the ore. This is the value per ton, percent extraction required for a profit, fire hazard, and the metallurgical requirements for winning the metals.

The method selected must embody the principles of SAFETY, EF-FICIENCY, and ECONOMY. Safety of the men is paramount. If the method is not safe it must be ruled out at once. Efficiency comprises flexibility of output, good working conditions for the men, and the elimination of wasted efforts. Economy calls for a reasonable outlay for the original development work. It demands the lowest cost per ton mined consistent with good business principles. Fixed costs should be carefully weighed before they are established. They do not decrease when production falls off.

Labor has established itself in the past few years as a dominant item to be reckoned in any endeavor. A mining method today must be considered in the light of what injury labor may do to it. Mining methods using the forces of gravity will not wait for a labor dispute to be settled. The cost of rehabilitating a stope may exceed the worth of the ore recovered. The present wage-hour laws call for a method of mining whereby the work can be allocated and immethodically rotated among the men. Each job must be composed so that the swingman can quickly and efficiently assume the duties of the man who must lay off for the duration of the week.

The capital and time required to place a property on a paying basis should be considered. Quick development may be the aim of capital in order to realize on high, transitory, metal prices. This type of policy may require a mining method that would ultimately ruin the mine. Flexibility of output without a sacrifice of efficiency is an important point in any mining method. The goal of industry is stabilization, but supply and demand still governs in most cases. Therefore, a mining method should be flexible to meet the broad fluctuations peculiar to the marketing of metals and the idiosyncrasies of modern labor dictation.

Rock that is "non-commercial" one year may be commercial ore the next as a result of marked advance in mining and metallurgical processes. Due to the exhaustion of higher grade deposits, increasing demand for metal, and lower market values, low cost mining methods are imperative. Twenty years ago the mining of 0.7% copper ore at a profit would have been considered an impossibility. Today it is one of the world's biggest mining operation and profit maker.* This example indicates that within certain limitations tonnage is becoming increasingly more important than grade. Large scale operations, and the liberal expenditure of sufficient money at the start to insure the most economical operation, is the secret of many mining successes.²

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The fact that a profit is being made by an enterprise does not signify that it is being managed and engineered to the best advantage. Mining methods showing a profit may be changed and consequently produce a much improved condition and a higher capital return. The same reasoning can be applied to properties showing a working loss. Methods are sometimes condemned when the fault, as a rule, is not with the method but in its wrong application. Each ore body is accompanied by a certain set of conditions which will influence the method of stoping to be adopted. Careful observation of these conditions and a knowledge of all the methods will enable a decision to be made as to the particular method which is most applicable under the existing circumstances.

The constantly decreasing grade of the deposits now being considered affords only a limited choice of mining methods. This calls for the application of engineering ability, experience, and initiative, in welding together one extremely low cost operation.

The ultimate object of mining is a profit and the method used is subordinate to this fact. Ingenuity, based on sound engineering principles, can do much-towards the revivification of a method that may be able to produce a production success.

The Method

Mining "in situ," using a leach solution, is the application of a solvent to an ore body without disturbing the

² C. A. Mitke, op. cit., page 8.

³ Mitke, C. A., "Mining Methods," p. 7, Mc-Graw-Hill, 1930.

^{*} Utah Copper Company, Bingham, Utah.

position of the ore body as it is found in the earth. The method is sometimes referred to as mining "in place." Leaching, as used here, is the dissolution of the valuable metal from its ore by means of a solvent.

Mining in situ does not entail the usual costs of developing and extracting ore from within the earth. There is no expense of breaking and moving rock for subsequent mill treatment. The ore is not crushed or ground in a mill. Consequently, there is no expense for the disposal of mill tailings. These expensive operating items are all eliminated when mining in situ.

In order that an ore may be treated by leaching it must have the following characteristics:3

- 1. The metals to be mined must be soluble in the solvent used.
- The gangue minerals must be insolu-2. ble in the solvent.
- The dissolved metal must be recoverable from the solution.

The method functions with relation to the porosity of an ore body as it is found within the earth. The solvent is placed above the ore body in solution form and then permitted to disperse downward, (acting under the laws of gravity), and is later collected as "pregnant solution" at drainage points underneath the ore body. This collected solution is then led to precipitation cells where the valuable metal is recovered as cement copper. The solution, now "barren," may then be discarded, or, it may be regenerated and made to repeat its cycle of flow through the ore body until all of the valuable mineral has been recovered. This, in brief, is the mechanics of mining in situ.

The capital required for the method can be summarized into the following items which will not be considered in detail:

- 1. Precipitation plant, usually relatively small.
- Reagents for the dissolution and pre-2. cipitation of copper.
- 3. Circulation of the solvent solution.
- 4. Regeneration of the spent solution.
- 5. Development work necessary to establish points for solution drainage and application.

The equipment necessary for a precipitation plant consists of series connected, water-tight cells that have receptacles for the precipitating agent. The size and number of these cells will depend upon the volume of solution being handled. Some installations have found it advantageous to provide for cell aeration during the formation of cement copper.⁴ Suitable

means for the ease of handling cement copper and native iron into and out of the cells should be provided as labor saving devices for this detail will materially reduce operating costs. Sufficient cells should be built so that stand-bys are available during periodic clean-ups of cement copper. It is desirable to install the precipitation plant at the point of solution recovery, possibly far underground. In this case there will be no expense for a building and attendant repairs, and there will not arise the problem of handling and transferring corrosive copper sulphate waters.

The reagents required for the dissolution of copper as a sulphate are sulphuric acid and, (if the ore requires it), ferric sulphate. The only reagent required for the precipitation of cement copper is native iron. Theoretically, the sulphuric acid and iron required to produce one pound of copper is 1.66 pounds of H_2SO_4 and 0.95 pounds of iron. At current market prices, (less freight), this is 2.651 cents per pound of copper produced.5 Actual working conditions will change this cost figure with the possibility of one reagent compensating for the other. Water in a large amount is used. The water should not be basic because it would then increase consumption of sulphuric acid.

The solvent solution must be conducted to the upper regions of the ore body and to do so will usually require pumping. When a regenerated solution is used the solution will be pumped the entire height of the ore body being mined. The resulting pregnant solutions must be handled in other than ordinary iron pipe due to the corrosive action of copper sulphate on iron. A regenerated; (barren), solution should not be corrosive as the corrosive copper sulphate has been removed from it. Pumping costs, (for an example), at Cananea were 0.094 cents per pound of copper produced.⁶

If there is a limited quantity of water at the premises it will be necessary to re-use the barren solution as it comes away from the precipitation cells. This solution will be high in ferrous sulphate and may need to have its free acid strength increased. As the solution becomes stronger in ferrous sulphate, through re-use, there will be a tendency for the ferrous iron to form basic oxides of iron. These basic oxides will precipitate in a nearly neutral solution. If this precipitation should occur within the ore body it will clog up the natural solution channels in the ore particles and thus shut

off the valuable mineral from the dissolving solution. It is therefore necessary to rid the barren solution of excess ferrous iron, increase the free acid strength, and when treating sulphide ores, to oxidize ferrous iron to ferric iron. In the presence of sulphuric acid and oxygen, ferrous sulphate can be oxidized to ferric sulphate.7 This treatment of the barren solution is en. titled "regeneration." At the higher valence the iron will not readily form basic salts, and it will materially aid in the formation of oxide copper. Another way to rid the solution of ferrous iron is to neutralize the solution and filter away the precipitated basic salts. This method, however, raises the cost of later acidifying the solvent solution. Ferrous iron is difficult and expensive to electrolyze out of solution.^s

The development work required for any given ore body will naturally depend upon the geologic structural conditions. Access to the top of the ore may be at the surface. Under other circumstances lengthy tunnels may have to be driven to reach the point of solution application. Advantage can be taken of natural faults, bedding planes, and other geological type formations. It is essential that the solution carrying the dissolved copper be recovered with very little loss. To accomplish this the points of collection will need to be located at natural drainage channels. If natural agencies do not exist, then it will be necessary to establish artificial dams and cutoffs underneath the ore body before mining operations are begun. Good judgment and preliminary examination of structural conditions will do much to reduce the expense of developing the property for mining in situ. _

In the case of mining "lost ore," stope fill, or ground that has been mined around due to its low grade. the original development work will usually be completed. It will be only necessary to set up the equipment and pipe lines for solution circulation. Under these circumstances some planthave been able to finance themselvesolely from earnings and the junking of mills.⁹

Analysis of Possible Applications

Large disseminated copper zone are known where the preexistent de posits of copper have been attacked during the ages and generally carries away dissolved in the ground water."

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^a Joseph Newton, "Introduction to Metallurgy," p. 267, Wiley & Sons, 1938, *Lavender, H. L., Water Treatment & Under-ground Leaching at Bisbee, Mining Congress Journal, Sept. 1926, p. 663, Greenwood, C. C., Underground Leaching at Cananea, Engineering & Mining Jour.-Press, vol. 121, Mar. 1926, p. 518.

⁸ Oil, Paint, & Drug Reporter, vol. 139, no. 1, Jan. 6, 1941.

^o Greenwood, C. C., op. cit., p. 519,

⁷ McBain, J. W., Oxidation of Ferrous Solution by Free Oxygen, Jour. Phys. Chem., vol. 5, De-1901, p. 622.

^{*} Table of Standard Electrode Potentials.

Anderson and Cameron, Recovery of Copper b Leaching at the Ohio Copper Co. of Utah: Trat Am. Inst. Min. and Met. Eng., vol. 73, 1926, p. 3
 Clarke, F. W., Data of Geochemistry, U. 3
 Geol. Survey Bull. 770, 5th ed., 1924, p. 675.

TABLE I

Copper remaining in the leached zones, due to the mechanics of weathering, is found as some form of copper oxide. Copper carried away may sometimes he found at a lower depth re-precipitated as chalcocite, covellite, bornite, and other sulphides. An important thing to remember here is that these deposits are genetically related to penetrating solutions following preformed passages along cleavage planes, fractures, and fissures within the ore body. It is therefore contended that artificial solutions of predetermined strengths can be directed through these same passages for the purpose of removing the copper.

Low grade bodies of copper may become ore bodies provided they are of sufficient size, occur in a favorable position, and can meet the requirements of the method. The grade of the deposit is not confined to certain limits. The quantity, character, and extent of the deposit, together with the required development costs, plant outlay, operating costs and amortization will set the minimum tenor of the ore. Operating costs of actual operations have been as low as 3.84 cents per pound of copper produced.11 Plant investments may be as low as \$2500. One plant in mind was financed wholly from earnings.11 These figures indicate a possible application of the method to copper deposits containing as little as 0.2% copper. Costs of the process are more fully covered in a later section.

Mining in situ with the use of a leach solution has two requirements. The method uses a very dilute acid solution to maintain low operating costs and thus the locality should have a copious water supply. The ore body must be susceptible to water penetration. Any mineralized copper deposit can be considered adaptable to the method if it can meet these two conditions.

The demand for water is not as heavy as first implied because the solution can be recovered, regenerated, and then recirculated. For any solution to produce a metal it must make a contact with and dissolve some form of the metal. Hence the material in question must be permeable to the solution and the valuable metal must be soluble in that solution. There are many modes of application and the usual occurrence of mineralized zones lend themselves to the method.

If a low grade deposit should contain copper that is quickly attacked by solution, the returns from the operation may be large within a comparatively short time. The oxide ores of

COMPARATIVE RATE OF DISSOLUTION OF VARIOUS COPPER MINERALS SIZED TO MINUS 100 PLUS 200 MESH; TEMPERATURE, 35° C.

Mineral .	Time of Treatment	Solvents Used	Percent of Copper Dissolved
Azurite	1 hour	1% H ₂ SO4	100
Malachite	1 hour	1% H ₂ SO ₄	100
Tenorite	2 hours	1% H ₂ SO ₄	98
Chrysocolla	1 hour	1% H ₂ SO ₄	90
Chrysocolla	1 hour	2% H ₂ SO4	98
Cuprite	1 hour	5% H ₂ SO ₄	71
Cuprite*	12 hours	5% H ₂ SO4	99
Cuprite	24 hours	5% H ₂ SO4	100
Cuprite	1 hour	2% Fe ₂ (SO ₄) ₃ and 2% H ₂ SO ₄	100
Chalcocite	1 hour	1% Fe2(SO4)3 and 0.5% H2SO4	33
Chalcocite	1 hour	1% Fe2(SO4)3 and 0.5% H2SO4	49
Chalcocite	8 days	1% Fe2(SO4)2 and 0.5% H2SO4	90
Chalcocite	20 days	1% Fe2(SO4) and 0.5% H2SO4	97
Bornite	1 hour	1% Fes(SO4), and 0.5% H2SO4	27
Bornite	7 days	1% Fe2(SO4)3 and 0.5% H2SO4	69
Bornite	21 days	1% Fe2(SO4) and 0.5% H2SO4	99
Covellite	1 day	1% Feg(SO4)3 and 0.5% H2SO4	8
Covellite	47 days	1% Fes(SO4)s and 0.5% H2SO4	57
Chalcopyrite	43 days	1% Fe: (SO.) and 1% H2SO	2
Enargite	60 days	1% Fe2(SO4)3 and 0.5% H2SO4	2
Tennantite	30 days	2% Fes(SO4)3 and 0.5% HaSO4	7
Tetrahedrite	23 days	1% Fe2(SO4)3 and 0.5% H2SO4	95
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* * Impure samples dissolved at different speeds.

copper are quickly soluble in weak acids and it is this type of deposit that is attractive to the method.12 Sulphide ores of copper require a longer length of time for dissolution. See table I, for comparison. For this reason a much larger area of sulphide ore must be treated simultaneously to produce a yield commensurable with the investment.

Low grade deposits should lie in a position that will aid the work of gravity when applying and recovering the leach solution. Geological structural conditions should favor the application and control of solution as well as the chemistry of the method. These requirements may at first appear to be severe, but in actual instances they have been found to be present wherever ore bodies are present due to the inherent nature of ore deposition itself. The method, after all, is the reverse of nature's method of ore permeation. Where deposition has occurred, conditions for deposition must be present. These are the same conditions that should prevail for the. leaching of ore in situ. As a rule the copper deposits do not lack suitable structural and physical features required by the method.

During the course of some mining adventures certain blocks of ore have

Taken from U. S. Bur. Mines Rept. Inv. No. 3228, p. 50.

been known to become "lost." By this term is meant ore that has come to lie in a relative position too dangerous to extract; ore that requires too much development work to recover; ore that has become contaminated with waste so that it is no longer ore when considered as a block. When such bodies of ore are of sufficient size, mining them in situ can be done at a profit.^{13 14} It is not too difficult to apply solutions to a section of ground that at the same time is too dangerous to place men within. If the ground in question is badly broken, hard to hold open, or running, it would be an expensive operation to safely place workmen and establish an extractive mining method in it. However, just such conditions are favorable for efficient solution distribution necessary for effecting metal recovery by mining in situ. Solution can be led to such blocks of ore by various means. Drill holes, subsidence cracks, and caved workings can all be utilized for mining in situ.

At some of the larger mines old stopes have been filled with mill refuse. These tailings are a possible source of copper metal. It would be easy to apply the method to these stope fillings if their copper content warranted the capital outlay. Installation

¹¹ Anderson and Cameron. op. cit., p. 31.

³³ Sullivan, J. D., Dissolution of Various Oxidized Copper Minerals, U. S. Bur, Mines Rept. Inv. 2934, p. 9, 1929.

¹⁸ Anderson and Cameron, op. cit., p. 30. ³⁴ Greenwood, C. F., op. cit., p. 519.

costs for such a venture would be low. and the copper reclaimed would represent higher extraction efficiency and a metal bonus. At some mines where the mine water is acidic, a plan may possibly be worked out whereby mill tailings would be placed into the old stopes chiefly for the purpose of fur-. ther extraction of copper by circulating the acidic water through the tailings. However, the plan may need to be augmented or modified. If the ore had previously been subjected to an extractive process that placed deleterious material into the tailings then further treatment may be too costly for the method. Most copper ores are now treated by some form of flotation. A few organic reagents used in flotation will consume leaching reagents unduly. Their presence in the tailings would prohibit the installation of a stope fill leaching system.

The chemistry of the method is so simple, and the method so flexible, that copper, dissolved in solution, can be made to precipitate along a predetermined horizon provided that horizon contains the necessary precipitants. The characteristics of a particular deposit may prohibit the usual methods of exploitation. Certain lateral sections of the deposit, however, may be exploitable. Here, mining in situ can be applied, not to extract the metal, but to cause a secondary enrichment at the level of the lateral section to be mined. Descending solution will dissolve metal from gangue and reprecipitate it when contact is made with sulphides, with the water table, or when a saturated condition occurs within the solution.¹⁵ It may therefore be possible to bring about an artificial condition of secondary enrichment, thus substantially raising the tenor of the ore that is already in line for the usual mining methods. Geologic conditions and engineering technique will determine the feasibility and efficiency of such an undertaking.

Infinitesimal reactions cannot be hurried along within the boundaries of an ore deposit, but when the reaction is extended over a large area the summation of each reaction will produce a daily product measurable in tons.

Solutions Applicable to the Method

The several known chemical processes used in copper leaching may be classified on the basis of the solvent employed. They are the following:¹⁶

- 1. Alkali Process.
- 2 Sulphite Method. 3.
- Sulphate Process. 4. Chloride Process.
- 5. Nitrate Methods.

Campbell lists the following reagents: "In the order of their importance the chief solvent reagents used in copper leaching are: sulphuric acid, ammonia and ammonium carbonate, ferric sulphate, ferric chloride, sulphurous acid, chlorine, and nitric acid. Of these the first three are the most common today."17

Nitrate methods are frequently suggested as solvents of copper. The fixation of atmospheric nitrogen by electricity offers a cheap source of nitric acid, and nitric acid is the best known copper solvent. However, nitric acid is also an excellent solvent of almost all of the impurities found associated with copper. Their subsequent dissolution would present insurmountable difficulties in the clean precipitation of free copper and in the regeneration of the solvent. The applicability of any solvent for the extraction of copper depends on the character of the ore. All acids likely to be used in a solvent process can react with other elements in the ore, and when so consumed are unavailable for the work of dissolving the copper.

The elements most detrimental to copper leaching acid processes are these:18 calcium, magnesium, aluminum, zinc and manganese. The quantity of these elements in the ore should be determined before installing a particular leaching method. It is important to remember, however, that a chemical analysis of the ore cannot be made the criteria upon which to determine the applicability of an acid process. Lime, for example, is detrimental only in certain combinations such as the oxide or carbonate. In many copper ores it will be found as harmless sulphate or silicate. Alumina also is usually combined in such forms as not to effect an acid leach. The Cripple Creek ores, containing as much as 20% alumina, have been successfully treated with sulphuric acid in connection with their chlorination.¹⁹ The other elements mentioned are usually not found in sufficient amount with low grade copper ores to seriously interfere with the method.

The highly oxidized ores are in the most susceptible condition for the application of any solvent. Reagents may be introduced to produce an oxide of copper for the solvent to attack. See table I, which shows the ease with which oxides of copper are dissolved. Several of the copper sulphides have the property of reducing ferric sulphate to the ferrous salts,

the copper thereby being brought directly into solution as soluble copper sulphate. This reaction is employed by the ferric sulphate and ferric chloride process.*

The alkali processes have not met with success. The solubility of copper in an alkali solution is relatively low. Because many basic salts are thrown down in alkaline solutions an alkali process would soon clog up the circulation channels in the ore body, hence it is impractical for mining in situ.

Oxides and carbonates of copper are readily soluble in an ammoniacal solution but the volatility of the gas in aqueous solution is high. The presence of sulphates will decompose the reagent. An ammoniacal solution would lose most of its strength to the atmosphere if it was applied to the surface of a broken ore body. Due to these reasons reagent costs would be excessively high when attempting to mine in situ with any ammonium solvent.

The theory of the sulphite process is attractive. The chemistry of the method requires only 32 pounds of sulphur in the form of sulphurous acid to dissolve the same amount of copper as is required of 98 pounds of sulphur when in the form of sulphuric acid.20

$$CuO + SO_2 \rightarrow CuSO_3$$

$$3CuSO_3 + CuO \rightarrow Cu_2SO_3$$

$$\cdot CuSO_3 + CuSO_4$$

The sulphurous acid can be dissolved in sulphuric leach solution. The dissolved cupro-cupric sulphite which forms can be precipitated by driving excess sulphurous acid from the solution. The solution is usually heated to effect this removal of sulphurous acid. The copper sulphite so produced is quite pure in content but it must be reduced to native by the usual converter process. Only sulphite copper will precipitate in this manner. All sulphate copper must be removed by electrolysis or by metallic conversion of iron. Certain features of the process, while possible to control in a well designed plant, would prevent its atlaptation to mining in situ. It is difficult to saturate the solution merely by blowing the sulphur dioxide into it. The maximum amount of copper that can be held in the solution is two percent. The copper sulphite will separate very easily from the solution, and should it do so within the ore mass proper it would defeat the purpose of the method. Approximately 40 percent of the copper will go to sulphate and will have to be precipitated by other methods. Rare metals, such as silver,

20 Idem, p. 176.

* See Introduction for details of this reaction.

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¹⁵ Emmons, W. H., Principles of Economic Ge-ology, 2nd ed., p. 281, McGraw-Hill, 1940, ¹⁶ Greenawalt, W. E., "Hydrometallurgy of Cop-per," p. 169, McGraw-Hill Book Co., 1912,

¹⁷ Campbell, T. P., Examples of Hydrometallurgical Operations, Mines Mag., vol. 21, no. 10, Oct. 1931, p. 10.

¹⁸ Greenawalt, W. E., op. cit., p. 169. 19 Idem, p. 170.

would not be recovered with the method.

The chloride processes have been applied to the extraction of copper from its various ores.* Hvdrochloric acid, ferric and ferrous chlorides are the solvents usually employed. Hydrochloric acid has the advantage but is more expensive. The acid is less apt to form basic salts and thus the solution will hold more iron during the precipitation of the copper chloride as cement copper. It is applicable only to oxidized ores. Ferric chloride has the property of dissolving copper from its oxide, carbonate, and sulphide comhinations.²¹ The chloride of copper which forms is precipitated with iron which produces cement copper and iron chloride. The precipitation is slow in a cool solution. In a nearneutral solution, ferric chloride reacts with copper oxide to form a basic salt of iron that would soon interfere with the normal passage of the leach solution through the ore mass. The same objection is raised when treating $3CuO + 2FeCl_s \rightarrow CuCl_s + Fe_2O_s$ the sulphide of copper with ferric chloride. In this case

 $CuS + FeCl_s \rightarrow CuCl + FeCl_2 + S$ the free sulphur produced would soon choke up the natural flow of the leach solution and prevent the further dissolution of copper mineral left in the ore. These objections are sufficient to eliminate the use of any chloride processes when leaching copper in place.

Sulphate Method

It is the sulphate process that best lends itself to the mining of copper in situ. The reagents are relatively cheap. The solvent produces a high efficiency with few detrimental products. The solution is very stable and cheap to produce. Equal quantities of copper are produced for iron consumed which fact insures the economics of the method so long as iron + is cheaper than copper. The leach solution is maintained at an acid strength too weak to dissolve undesirable material but which is sufficient to dissolve any copper salts in the ore. It is possible to regenerate the barren solution at a low cost thus saving on reagent costs. Native copper, (cement copper), is produced. The percent of contained impurities in the cement copper depends upon technique and control during precipitation. The entire method is carried out at normal temperatures and pressures and requires power only for the circulation of solution. The method will function in all climates. Only extreme freezing conditions, (40 below zero underground), will stop operations.

It is taken for granted that extraction is exceedingly slow, and that, for the venture to be successful, the extraction must be spread over a large area so that the daily recovery can be measured in terms equitable with the costs. It is also granted that the operation will usually have a fairly long life in order to make an efficient extraction from a given ore body.

The two basic chemical equations of the sulphate method are:22

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$CuSO_4 + Fe \rightarrow Cu + FeSO_4$$

The copper minerals found in disseminated deposits are usually oxides or sulphides. The following sub-group of copper minerals are fairly easily decomposed and converted into copper oxide by weak oxidizing agents: Chalcanthite, copper sulphate; Brochantite, basic copper sulphate; Malachite and Azurite, basic copper carbonates; Atacamite, basic copper chloride; and Chrysocolla, copper silicate.28 These sub-group minerals are often dissolved in nature by underground waters and re-deposited at lower depths on contact with iron pyrite. They do not form true primary copper sulphides and are a class of sulphides that are susceptible to a weak acid leach.

Ferrous iron has been the biggest problem in the sulphate method of leaching. Properly controlled it can be turned into an asset, if it is disregarded it will eventually ruin the operation. From the second equation above, 2.38 pounds of ferrous sulphate is formed for every pound of copper recovered. This ferrous sulphate will remain dissolved in solution up to certain solution strengths. It is very desirable that this ferrous sulphate stay dissolved. The production of copper will quickly decline if the ferrous iron should come out of solution in the small leaching channels in the ore mass. This item is covered extensively in the section on control of the solution.

The question of oxidizing sulphide copper has been given considerable attention by metallurgists. Mining in situ, of course, precludes any roasting operation. Weinig states that, "sulphide minerals promptly start to oxidize when exposed to water and air, and that the result of this oxidation, among other things, is the production of films on the mineral composed of its own salts or oxidation products. It has been found that sulphide minerals occurring in the older geological formations are more stable



▼ Table II—Graph showing the Rapid and then Partial Dissolution of Chalcocite. Compiled from data taken from U.S. Bureau of Mines Tech. Paper No. 473.

than those of more recent date."24 He has also found that copper sulphate acts as a catalyst during the oxidation of sulphides to oxides.

When cupriferous pyrite is treated with a solution of ferric sulphate in the presence of sulphuric acid and oxygen, copper will go into solution in proportion to the quantity of iron that has been reduced from the ferric to the ferrous condition.²⁵²⁶ When chalcocite, (Cu₂S), is leached with ferric sulphate, one-half of the copper dissolves rapidly, and the residue has the approximate formula of covellite.

$$Cu_{2}S + Fe_{3}(SO_{4})_{3} \rightarrow CuS$$
$$+ CuSO_{4} + 2FeSO_{4}$$

This CuS does not remain constant, but continually undergoes change as more copper is dissolved until the atomic ratio of copper to sulphur becomes 0.9 or less.

$$CuS + Fe_2(SO_4)_s \rightarrow CuSO_4 + 2FeSO_4 + S$$

This is shown graphically by table II. Artificial covellite produced by the leaching of chalcocite, dissolves at a much faster rate than does natural covellite.27 Table III illustrates this difference in leaching speed.

Sullivan has found that the size of the ore particle has no effect upon the rate of dissolution provided the solution was able to enter the sample. Ore samples ranging in size from plus ten to minus two hundred mesh gave practically identical rates of dissolution.²⁸ (Table IV.) Ores of copper are usually of the disseminated type and solid particles larger than ten mesh would be rare.

^{*} At Rio Tinto. Spain; Helsingborg, Sweden; Chiquicamata, in Chile. ²¹ Idem, p. 216.

²² Idem, p. 180.

²³ Sullivan, J. D., Dissolution of Various Oxidized Copper Minerals, U. S. Bur. Mines Rept. Inv. 2934, p. 7, 1929.

 ³⁴ Weinig & Carpenter, The Trend of Flotation, Colo. Sch. of Mines Quarterly, vol. 32, no. 4, 4th ed. Oct. 1937, p. 16.
 ³⁵ Greenawalt, W. E., op. eit., p. 193.
 ³⁵ Sullivan, J. D., Chemistry of Leaching Chalco-cite, U. S. Bur. Mines Tech. Paper 473, p. 24, 1930.
 ³⁷ Sullivan, J. D., Chemistry of Leaching Covellite, U. S. Bur. Mines Tech. Paper 487, p. 16, 1930.
 ³⁸ Sullivan, J. D., Chemistry of Leaching Chalco-cite, U. S. Bur. Mines Tech. Paper 487, p. 23, 1930.



TIME IN DAYS

▼Table 111—Comparison of the speed of dissolution of artificial covellite, impure covellite, and pure, natural covellite. Compiled from data taken from U.S. Bureau of Mines Tech. Paper No. 487.

The rate of dissolution of chalcocite has been found to be independent of the acid strength of the solution. Sullivan's experiments on chalcocite with solutions containing one percent of ferric iton plus sulphuric acid ranging in strengths from 0.25% to 10.0% showed practically identical rates of dissolution. This fact, that only a very weak concentration of sulphuric acid is required, greatly decreases the operating costs of the method and is very important to the leaching of sulphide copper ores in situ. It is a distinct advantage because a weak acidic solution will not dissolve the many impurities found associated in the disseminated ores of copper.

Oxidized copper minerals are readily dissolved by ferric sulphate. The ferric sulphate is decomposed and converted into the oxide; hydroxide, or basic sulphate. These products will precipitate from the solution unless it is acidic. When sulphuric acid is present the ferric sulphate is decomposed and converted into ferrous sulphate which is soluble in the leach solution. The presence of sulphuric acid is, therefore, desirable in leaching mixed ores of copper.

It is important to keep the concentration of ferric iron as low as possible because the ferric ion will consume native iron in the precipitation cells during the formation of cement copper. All the ferric sulphate introduced into the leach solution should be consumed within the ore body and produce soluble copper sulphate. If it is not completely consumed it will materially increase the cost of the operation by consuming raw iron intended for the copper reduction.

By repeatedly re-using the barrensolutions after the precipitation of cement copper, the concentration of ferrous sulphate increases far beyond reaction concentrations and there will result a retardation in the dissolution of chalcocite. However, the formation of basic salts of iron within the ore body by the re-use of barren solutions is of more serious consequence.

Control of the Method

There are several essential factors pertaining to the successful leaching of any copper deposit "in situ!" Among the factors that need to be considered these four are of particular importance in the regulation of the process.

- 1. An economical solution that will attack the copper minerals must penetrate the body of the ore particles and make contact with the copper mineral.
- 2. The copper mineral must be dissolved solely by the chemical action of that solution.
- 3. The solution containing the dissolved copper must find its way out of the voids of the rock and into the points of collection.
- 4. The copper in the leach solution must be easily recovered by an economic means of precipitation.²⁹

In order to insure continued operation close watch should be maintained to prevent the introduction of deleterious constituents into the solution or into the ore mass proper. It is propitious to replenish the spent solutions with fresh water. The re-use of the barren solution will eventually lead to difficulty due to its constantly increasing iron content. Surveillancemust be maintained over the free acid strength of the leach solution. A slightly higher strength will produce considerable acid loss with attending increases in reagent expense. Constant care of the precipitation cells is necessary. Neglect will result in contamination of the cement copper as well as excess losses of iron reagent and decreased efficiency of copper recovery. Once-begun the operation should be constantly attended until all leach solution has passed through the precipitation cells. Labor for the work

²⁹ Sullivan, Keck & Oldright, Factors Governing the Entry of Solutions, Into Ores, Düring Leaching, U. S. Bur, Mines Tech, Paper (441, p. 1, 1929). presence of one technical man would be sufficient to maintain operations once they were started.

Control of the solution can be kept at the point of application, during regeneration, and in the feeder reservoirs. The dissolved copper must be removed from the pregnant solution as it is received and in the quantity in which it arrives. Should the pregnant solution contain excesses of reagents the remedy will be applied to the feeding solution. If difficulties should arise during the extraction of the dissolved copper, due possibly to certain concentrations in the solution, it would be perfectly safe to feed the "semi" pregnant solution back over the ore body together with the correction needed for efficient extraction.

Copper is soluble, (at usual conditions of temperature and pressure), in very weak acid solution up to 0.4 pounds of copper per gallon of solution.30 The usual copper content of leach solution coming from ore in place may be 0.04 pounds of copper per gallon of leach solution. This copper content can be increased by increasing the ferric iron concentration in the leach. Careful control, however, must be kept on the ferric iron concentration to insure its consumption solely in the ore mass. It is important that very little ferric iron. enters the precipitation cells as no copper will precipitate while ferric iron is present. The presence of ferric iron in the cells is also expensive as it consumes the native iron intended for the reduction of the copper. The system should not be loaded down with ferrous iron. Ferrous iron has no useful work to perform and its elimination is beneficial. Its elimination, however, is expensive unless the entire barren solution is discarded. The iron content of the batch can be determined easily by simple titration.

An important item is the application of the solution to the ore body. The ore should be subjected to alternate cycles of wetting and drying. When soluble copper is extracted from the interior of a rock by alternate wetting and drying, evaporation draws copper salts to the surface of the rock during the drying period. These salts are subsequently removed by the next application of the leach solution. Some of the solution will penetrate into the cavities, cleavage planes, and interstices within the rock during the time that the surface salts are being removed by washing. The distance the solution penetrates into the rock is a function of the time of washing. If all of the moisture within the rock is removed

30 Greenawalt, W. E., op. cit., p. 162,

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during the drying cycle, the soluble copper salts will be crystallized, partly at the surface and partly inside the rock. The amount of copper brought to the surface will depend upon the size, shape, and general character of the voids within the ore. The ore mass particles will become saturated if the washing period is long enough regardless of whether or not the moisture was completely removed in the previous drying process.³¹ This scheme produces soluble copper faster than chemical diffusion. It will also aid in the oxidation of any sulphide copper present in the ore body. It can be accomplished by dividing the ore body into sections, one section can be receiving the solution during the time another is drying.

When the leach solution is applied its temperature should be the same as the ore body's. Higher temperatures will raise the vapor pressure of the solution and prevent its efficient penetration into the voids of the rock. In this connection it has been suggested that the solution be saturated with a non-acting gas having a lower vapor pressure than that of the ore body's.32 However, the cost of processing the leach may not compensate for the increased production. Evidence has been offered to show that the solubility of the gas contained within the ore, with respect to the penetrating liquid, is the deciding factor that determines the rate of ingress of solution.38

It has been agreed that the solution must make contact with the ore particle. There will be questions raised as to the possibility of any solution making contact with an ore particle far inside the interior of an ore mass. It is the author's contention that an ore mass is susceptible to circulating waters and solutions, otherwise it would not contain ore particles. Tolman states that, "confined flow in fractures commonly extends to considerable depths and rises along master fractures to the discharge point of the major fractures. A tunnel, by interception, may drain an entire fracture system and its tributaries. The lowering of the water table in fractured rock by artificial excavations has been the subject of many actions at law."34 For example, hydrothermally altered granite is generally very porous. When a specimen of such rock is dipped in dye it instantly becomes colored, and the dye will permeate deeply.³⁵ Many of the copper ores owe their origin to the circulation of hydrothermal solutions. It is thus logical to presume

²³ Sullivan, Keck, & Oldright, op. cit., pp. 35-7.
 ²⁴ Tolman, C. F., "Ground Water," 1st ed., pp. 297-8, McGraw-Hill Book Co., 1937.

⁴⁵ Emmons, W. H., op. cit., p. 160.



▼Table IV—Dissolution of various sized chalcocite in a 1% Ferric sulphate, 0.5% Sulphuric acid, solution. Taken from U. S. Bureau of Mines Tech. Paper No. 473.

A... Kennecott, -100 +200 mesh. B... Bisbee, -10 +28 mesh. C... Bisbee, -2 +3 mesh.

that cold solutions will penetrate altered rock as well as hydrothermal solutions because of their lower vapor pressure.

Sullivan, Keck, and Oldright found that the size of an ore particle did not determine the speed of solution ingress. Their solutions always penetrated the rocks rapidly at first, then the rate of penetration decreased and finally became nearly constant.³⁰ Table V shows the results of some of their work. There is an initial rapid penetration of solution into the ore along the larger fractures and openings. From these larger avenues the solution seeps into smaller fractures, crevices, and interspaces. Actually, the solution does not have to penetrate three inches of minute openings to reach the center of a six-inch piece; rather. it enters through larger arteries and travels to smaller ones. As copper is removed, more space is made for further ingress of later solutions. "With the rocks studied it has been found that the solutions enter along fractures and cleavage planes; from these larger fractures it gradually seeps into the rest of the rock. The first 50 to 75 percent of the total penetration takes place very rapidly along these crevices and fractures, and the smaller voids are then filled more slowly from these points of initial penetration. This explains why only 59 percent more time is needed to saturate a six-inch piece than a one-inch piece."37

³⁶ Sullivan, Keck, and Oldright, op. cit., p. 8.

⁸⁷ Idem, p. 38.





TIME IN HOURS

 ³¹ Guggenheim & Sullivan, Acceleration of Extraction of Soluble Copper from Leached Ores, U. S. Bur, Mines Tech. Paper 472, p. 29, 1930.
 ³² B Sullivan, Keck, & Oldright, op. cit., pp. 35-7.

The chemical action of the solvent must be strong enough to dissolve the copper mineral. Yet the dissolving action of the solvent must not be great enough to spend itself upon the worthless material present with the copper. Experience has shown that a sulphuric acid leach containing about 0.5 percent free acid is sufficient to dissolve copper oxide and at the same time not effect silicates and the other gangue minerals usually present with copper 4 deposits. The acid strength needed must be determined before the method can be passed upon as applicable to a certain deposit. The presence of ferric sulphate, (or other ferric compounds), will speed the dissolution of copper oxide in the acid leach. Regulation is thus required to maintain a predetermined strength of ferric ion and sulphuric acid in the leach solution. It should be remembered that too high a ferric strength will result in ferric ion appearing at the precipitation cells and causing excessive raw iron losses. Control is entirely in the hands of the laws of physics and chemistry after the solution has been distributed at the points of application. Not until the solution appears at the point of recovery can the technician remedy any difficulties.

The fourth named essential is that the copper be removed economically from the pregnant solution. The amount of solution appearing at the receiving point will be equal to the amount delivered at the distributing point if the plant has been developed correctly and solution losses have been prevented. The quantity of leach solution for a good economic basis should be about 100 gallons per minute. Larger volumes are recommended. A solution volume of 1500 gallons per minute has been successfully re-circulated against a head of 1000 feet.38 At the same installation, solution velocities of 40 feet per minute were maintained in the precipitation cells to insure a clean product of cement copper. A poor grade of cement copper will increase refining costs. Control is needed to see that the cement copper is not precipitated in a contaminated condition. Foreign material would be included in the cement copper if the solution were not quickly circulated. The plant at Britannia Beach could not produce a high grade cement copper because of difficulties in the precipitation cells.³⁰ Air agitation-has been practiced during precipitation to produce uncontaminated cement copper. Air agitation tends to oxidize ferrous sulphate forming ferric ions and causing an increased raw iron consumption.

As copper is formed, native iron is dissolved, and a convenient method of handling both will do much to lower operating costs. A constant supply of raw iron must be kept in the precipitation cells. It is this phase of the method that requires the largest portion of man-hours. If there is a large and sufficient supply of scrap iron on the premises it may be economical to use it in the cells rather than buy raw iron. Cutting and handling costs of scrap material is high. De-tinned scrap iron makes the best precipitating reagent. It is a most efficient copper precipitant, and full value in iron content is received for its cost. This type of scrap has a large surface area, and is nearly pure iron due to the method in which it is processed. Its large surface area is objectionable to iron scrap foundries and thus de-tinned scrap does not command a market price equivalent to its iron content. When placed in a moving solution of copper sulphate, the large surface of the scrap allows the precipitation of copper to occur quickly and efficiently. The same advantages would hold for machine cuttings and shop waste provided the material is not alloyed with elements that have a retarding effect in the cells.

Due to the corrosive action of copper sulphate upon iron pipe it is advisable to precipitate all the copper at, or near, the point where the pregnant solution comes from the ore body. This can be done because the precipitation cells are not large and can be strung along both sides of a moderately sized tunnel. Copper sulphate solution can be transported through lead pipe, wooden launders, wooden pipe, and copper-alloyed materials. Pumps used for the circulation of copper sulphate solution should be made of bronze parts. The precipitation cells are usually made of wood, copper nails, and are fitted with lead connections.

Examples of Past Practices

Mining in situ is not something that is new and untried. The method has been applied in several localities and has met with varying degrees of successfulness. In Sonora, Mexico, the Cananea Consolidated Copper Company recovered 189 tons of copper from the leaching of one single stope. In British Columbia the Britannia people made a profitable extraction of 600 tons of copper per year using the method. During a four year period in Utah, the Ohio Copper Corporation extracted 8500 tons of copper from a caved section of low grade ore. The method has also met with reverses. The Bagdad people of Arizona abandoned, in 1924, an attempt to leach in situ because of excessive reagent consumption and serious losses of pregnant solution.⁴⁰ Mining in place has been successful as a rule on ore bodies that have been subjected to caving action of some kind or other which has developed the natural occurring solution channels.

An outstanding example of successful stope leaching is the record made by the Ohio Copper Corporation of Utah in the years 1922 through 1926.41 An immense body of low grade copper ore had been developed and the usual methods of block-caving mining had met with financial losses. Much development work had been done up to 1922, and the caving stopes had been closed down because of an insufficient grade of ore and a poor metallurgical recovery. The ore was chiefly oxidized copper, disseminated in shattered quartzite. The sulphide copper in the ore oxidized fairly easily when it was exposed to the arid climate of the region. In 1922, Messrs. S. K. Kellock and F. E. Turner junked the equipment of the metallurgical mill and began the installation of an underground leaching plant.42 The cost of the leaching plant was paid for by the sale of junk from the old mill. These men began operations by dispersing 250 gallons of sulphuric acid leach solution per minute over the top of broken rock overlying a caved stope. The solution drained through 1000 feet of vertical distance and emerged through four raises into the Mascotte tunnel. This point was two miles underground from the portal. Precipitation cells had been constructed there, and the pregnant solution was made to precipitate its copper content using scrap iron. Improvements were made until the volume of leach solution recovered from the stope was 1500 gallons per minute. This volume required the services of 15 men attending the cells, replenishing the iron, and removing the cement copper. It was found that a high speed flow of pregnant solution, through 32inch cells containing de-tinned scrap iron held on a false bottom 17 inches high, would produce cement copper of about 85 percent purity. The recovery of copper from the pregnant solution was 98 percent of the head assay. The raw iron consumption was

³³ Anderson & Cameron, Recovery of Copper by Leaching at the Ohio Copper Co. of Utah: Trans. Am. Inst. Min. & Met. Eng., vol. 73, p. 31, 1926.
³⁵ Brennan, C. V., Mining Operations at the Prop. of the Britannia Min. & Stnelt. Co., U. S. Bur. Mines Inf. Circ. 6815, p. 27, January 1935.

⁴⁰ Private correspondence with Gen. Mgr. J. W. Still, Dec. 1940.

⁴¹ Anderson & Cameron, op. cit., pp. 30-33. ⁴² Leaching a Copper Mine, Eng. & Min. Jour., vol. 116, p. 668. Oct. 1923.

found to average pound for pound of copper produced. This is only 14 percent above the theoretical and indicates fairly good technical control of the leach solution. The district did not furnish an unlimited supply of fresh water hence the company was forced to re-use its barren solution. Additions of fresh water were made from time to time to decrease the ferrous iron content. It is believed, however, that the ferrous iron was allowed to build up in the circuit until it began to precipitate in the ore body as basic salts of iron.43 This resulted in a decreased copper content in the pregnant solution due to the formation of basic iron pipes leading directly through the stope and shunting the leach solution away from fresh ore.

Operations of the company had advanced in 1925 until the cost of producing copper at the mine was 3.847 cents per pound. After refining costs and freight charges on the cement copper were paid, they realized a profit on any price of copper above 6.324 cents per pound. Their production of pure copper from leaching in place had reached 17 million pounds at the end of 1925.

A copper mine in Mexico turned a curse into a profit by applying the leaching method to old, filled, shrinkage stopes. At Cananea the mine was troubled with acidic copper bearing water that attacked the pumps and pipes through which it was transferred. This mine water running through the workings ate away the rails and any other iron that it contacted. In an attempt to reduce maintenance costs, precipitation cells were placed at vantage points in the mine. These cells produced so much inexpensive copper, the idea was expanded and improvements installed to expedite results. Mine water was dispersed over the surfaces of the old filled stopes which were estimated to carry about 1.0 percent copper. Of this 1.0 percent only 0.05 percent was acid soluble. The remaining 0.95 percent was sulphide copper. This sulphide copper was held in tiny seams and veinlets as secondary chalcocite.

Their installation in 1926 was not on a large scale. The volume of solution running through the precipitation cells averaged 50 gallons per minute. They, too, re-circulated the leach solution to effect savings on fresh water. Wooden pipe and bronzed pumps were installed to prevent corrosion of the equipment. Air agitation in the precipitation cells was practiced to give a higher grade of cement copper as the slow moving solution produced slow precipitation and contamination of the cement copper with attendant coating of the raw scrap iron.

The company had a plentiful supply of scrap iron on hand which they used for precipitation. They acknowledged, however, the efficiency could have been doubled by using de-tinned scrap iron. The operating costs of a plant handling and using heavy scrap iron would be high. The iron must be cleaned and cut down in size so that it can be used inside the cells. Their production costs in 1926 were 4.69 cents per pound of copper which included the entire cost of plant and equipment of \$2600. They did not have a shortage of water and were thus able to discard the barren solution when it became too highly concentrated with ferrous iron.

It was here that the leaching of "lost" ore proved to be feasible and possible. In the Veta stope they leached 42.000 tons of broken ore that had been left in an old shrinkage stope and that had subsequently been caved upon from the back and walls. This contamination resulted in a copper content of less than 0.8 percent. In ten months time, using a leach solution of 70.5 gallons per minute, they realized 142 tons of copper from the stope, a recovery of 42 percent. Leaching was still in progress on the stope when these figures were released.44

Ideal conditions suitable for mining in situ were found at the mine of the Britannia Mining and Smelting Company, Britannia Beach, British Columbia. A large body of low grade copper ore had caved subsequent to glory holing. This ground was connected to the lower levels by caved-in stopes and raises. A bountiful fresh water supply was available above the ore, and it had only to be led to the upper horizon of the caved zone. A volume of leach solution from 100 to 650 gallons per minute was caught in the lower workings and sent through large, five-foot, precipitation cells. As the ore contained copper oxides with sulphates and some pyrites, the solution made its own sulphuric acid of sufficient strength to dissolve the copper in the caved ore. The analysis of the pregnant solution was:

	Per Litre
Free sulphuric acid	0.023
Copper	
Ferrous iron	0.17
Ferric iron	
Air privation to the provint	

Grams

was practiced. They used low air pressures which were fed into the cells through lead pipe. Precipitation was effected with local scrap iron, tin cans, and other junk. They secured a cement copper product of 67 percent purity. This was rather low but was due to the type of precipitant used and the cell construction. As the only reagent cost was for raw iron. production costs were, of course, very low. Copper was produced at the mine for 2.14 cents per pound. The magnitude of the deposit and volume of leach solution handled was sufficient to produce 600 tons of copper per year.45

Conclusion

There is no doubt that a number of the copper minerals are soluble in a very weak acid leach. The technical information on this phase of the subject is profuse. It is quite possible that a particular leach solution may be developed in the near-future strictly for mining in situ. New ideas applied to leach solutions may quickly popularize the method and give it distinction. As already pointed out, the sulphate leach contains much to recommend it. However, it can stand considerable improvement in connection with the regeneration of the barren solution. So far, few attempts have been made to develop a particular leach solution for mining ore in situ.

Today the method is adaptable to certain deposits, developed in certain details, as proved by several, already mentioned, successful ventures. That the method is adaptable to deposits that have not been subjected to certain development remains to be seen.

We know the formation of ore deposits is usually an orderly process of progressive concentration through the agency of mineralizers. The circulation of these mineralizers is facilitated by fault fractures, planes of bedding or schistosity, and by porous strata. Experience has shown that most veins are formed along just such passages.46

Eminent geologists have shown where nature, using solutions, has deposited ore "in place." Can the technical engineer reverse this concentration through the agency of a chemical process? Can ore material be leached in place without first disturbing it? These questions remain to be proved by a full-sized, practical operation, applied to a geological structure that meets the requirements of the method.

⁴³ Private correspondence with A. E. Anderson, Oct. 1940.

Air agitation in the precipitation cells

⁴⁴ Greenwood, C. C., Underground Leaching at Cananea, Eng. & Min. Jour., vol. 121, p. 518, Mar. 1926.

⁴⁵ Brennan, C. V., op. cit., pp. 27 etc.

⁴⁶ Stephen Taber, Mechanics of Vein Formation, A. I. M. E. Transactions, vol. 161, p. 36.