AN EXPERIMENTAL INVESTIGATION OF SOME FACTORS INFLUENCING THE RATE OF LEACHING OF THE BRITANNIA ORE

by

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ABSTRACT

Experimental investigations are carried out to establish a satisfactory technique and to study some factors -- variations in the chemical character of the attacking solutions, rate of flow, and the effect of pyrite -- influencing the rate of leaching of the Britannia copper ore.

The natural leaching phenomenon at the Britannia Mine is described and brief geological descriptions are listed of other mines from which copper recovery is made from the mine water.

The general chemical and physical principles involved in the leaching of copper sulphide ores are reviewed.

Samples taken from the Britannia Mine are crushed, sorted according to size, oven heated to destroy any bacteria, packed in glass tubes, and leached with different chemical solutions at various rates of flow.

The chemical character of the attacking solutions is the key factor in determining the rate of leaching. Ferric sulphate and sulphuric acid increase the rate of leaching up to 600 times and 33 times that of pure water respectively.

Changes in the rate of flow are of secondary importance and determine the range of fluctuations in the
rate of leaching around an order of magnitude dependent on the chemical character of the attacking solutions.

The ore with the smaller chalcopyrite to pyrite ratio is more readily attacked than the one with the greater ratio.

Leaching of copper ores in place may be increased by attacking them with solutions of sulphuric acid and/or ferric sulphate. This may be accomplished by the recirculating of the conditioned mine waters after the extraction of the copper.
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AN EXPERIMENTAL INVESTIGATION OF SOME FACTORS
INFLUENCING THE RATE OF LEACHING OF THE BRITANNIA ORE

CHAPTER I

INTRODUCTION

Leaching is essentially the oxidation of metallic minerals and their subsequent removal as soluble salts. The principles involved in natural leaching appear to be relatively simple and their application on an economic basis would seem to be easy. Proof of the converse is witnessed in the limited success of human attempts to leach copper from the ores in place. Only from mines possessing unique natural conditions has a favourable recovery of copper been made from the mine waters. The Britannia Mine of British Columbia is an example of such an unique, yet commercially advantageous, situation.

An experimental study has been undertaken to investigate some factors influencing the rate of the observed leaching. The investigation was designed to establish an experimental technique for studying the effects of variations
in the chemical properties of the attacking solutions on the rate of leaching. This experimental technique might be applied in investigating other influences, such as temperature, particle size, and rate of flow, effecting the leaching of the Britannia ore. Other copper ores from deposits possessing favourable physical conditions might also be investigated.

Leaching in hydrometallurgy refers to the processes by which copper bearing material is chemically attacked with a solvent in order to dissolve the copper, and separate it from the residual solid. The copper may then be extracted from the solution either by electrolysis or precipitation.

A distinction should be made between leaching "in-place", a natural phenomenon, and leaching as employed in the hydrometallurgical treatment of ore. Although the chemistry of both is essentially the same, the conditions under which each operates and the units of measurement (parts per million compared to per cent) are quite different. Leaching in place, although probably helped to some extent by man, is not a well controlled process in which a fairly complete recovery is made of the available metal in the ore. The ore leached is either in its original natural environment, or is partly broken by mining developments. For purpose of discussion in this paper, leaching refers to those chemical processes which occur under the more natural conditions.
CHAPTER II

LEACHING AT BRITANNIA

The Britannia Mine\(^1\) was discovered in 1898 and the first production of copper was in 1905. The upper main adit on the 1050 level was developed at an elevation of 3,300 feet above sea level. The present workings extend from a height of 4,200 feet above sea level to a depth of over 1,000 feet below sea level. The first attempt to extract copper from the mine waters by precipitation on scrap iron was in 1926. Since then, the recovery plant has been moved and expanded considerably and its present output is in the order of over three-quarters of a million pounds of copper a year.\(^2\) In addition to the copper plant at the 2,200 level townsite, another plant has just been put into operation at sea level which is fed with water from the 4,100 level. Diagram 1 shows the positions and source of the water of the respective plants.

The Britannia copper deposit is in a prominent ridge on the Pacific coast about twenty miles north of Vancouver. The mine area is underlain by Mesozoic clastic volcanics, tuffs, and slates of the Britannia group which form a roof

\(^1\) For a detailed description of the geology and early mining development see H.T. James (1928)

\(^2\) For a description of the early history of the copper plant see Ebbut and Selnes (1928)
pendant that has suffered local and regional dynamic metamorphism, and has been hydrothermally altered to a fissile quartz-sericite or quartz-chlorite sericite schist. Depending on the local structure, the orebodies consist of stringer lodes, massive replacements or a combination of both. The most favourable host rock is the locally termed "green mottled" schist. It derives its name from the green coloured blotches of exceedingly fine aggregate of chlorite in the quartose rock.

Chalcopryrite is by far the most abundant copper ore mineral with minor amounts of supergene chalcocite and covellite. Sphalerite is widespread and locally abundant in some sections of the mine but pyrite is the most widespread sulphide mineral throughout the whole area.

The gangue is comprised chiefly of quartz with subordinate amounts of sericite and chlorite. Barite and anhydrite are locally conspicuous in some orebodies. Accessory minerals include titanite, apatite, leucoxene and alhite.

Three significant facts are noted concerning the mineralogy; there is a negligible amount of secondary enrichment; there is an abundance of pyrite scattered throughout the ore; there is relatively little reactive carbonate gangue.

Samples of ore used in the laboratory investigations
DIAGRAM 1. SKETCH SHOWING GENERAL RELATION OF THE OREBODIES AND SOURCE AREA OF MINE WATER FOR THE COPPER PLANTS
were taken from the Empress orebody. A more detailed description of this ore is given later.

The topography coupled with the heavy precipitation of the Britannia area plays an important role in the leaching phenomenon. A series of steep cirques in the north slopes were formed by hanging glaciers after the retreat of the main ice sheet. The south slope is not as abrupt and the cirques are typically absent. Mining developments have shown oxidation to be more severe on the southerly exposure, the one of least glaciation, where both rocks and ore are badly oxidized to a depth of over 200 feet. The highest orebodies have been mined by a series of shrinkage stopes and glory holes resulting in the caving and crushing of large portions of the surface and upper mine levels.

The average annual precipitation is approximately one hundred and ten inches made up of heavy autumn and spring rains and deep winter snows. Large quantities of snow are collected in the cirques, glory holes and caved areas, ensuring a good supply of melt waters from these reservoirs in the summer months. A great deal of the run-off of the heavy precipitation is caught in the many crevices and cracks in the porous surface, and seeps down through the crushed ore zone. The amount of water seeping into the mine has a seasonal variation; the greatest being in the early summer when heavy rainfalls combine with melt waters and the least in the late winter months of March and April.
From the surface to the 2200 level where it is removed to the copper plant, the mine water has a vertical descent of some 2,000 feet or more. In this journey the water has changed from a barren surface water to a potent leaching solution by the interaction with the sulphides. In the migration downward the waters pass through crushed and fractured rock and, in many places, along mine openings. Orebodies above the 1050 level in the Empress, Fairview and No. 5 mines have not been mined for the past few years and are now inaccessible. As a result, the mine waters are not observed until they have reached the 1050 level. At this level they are already rich in copper and it is estimated that over 80% of the copper taken into solution comes from the broken ore in these inaccessible mine workings. The copper content of the broken ore in these sections varies from about 3.00% to trace with an overall estimated average of 1.00%. The inaccessibility of the sections providing the greatest source of copper makes it impossible to correlate the copper content of the ore with that of the mine waters from any given section.

At certain levels below the 1050 level, troughs are used to collect and control the flow of the copper rich solutions. Where possible, the solutions are directed through old stopes containing broken rock in order to increase the potential copper recovery. The mine waters from the various sections of the mine are combined at a common point near the
Diagram 2. West-East Schematic Showing Idealized Path of Mine Water

From the Surface Through the Orebodies to the 2200 Tunnel
No. 1 Shaft and are directed in a wooden flume out of the tunnel to the surface. Diagram 2 shows the idealized path of the percolating solutions from the surface to the 2200 level tunnel. The average for analyses of the heads solutions at the plant in 1955 gave the following concentrations expressed in milligrams per litre (parts per million)—copper 651; ferric iron 270; ferrous iron 37; sulphate 310. The average rate of flow in the same year was 10,522 imperial gallons per hour.

The acidity of 310 parts per million is equivalent to a sulphate ion concentration of a .006 N sulphuric acid solution or a pH of 2.4. In sections where the pH was greater than 3, considerable iron oxide precipitated from the mine water onto the floor and walls of the mine opening. The copper content of the water in these sections is lower than in places where the water is more acid.

In periods of medium to low flow, the mine waters in the natural basins of the stopes have a greatly diminished rate of flow, or may even stagnate, with the result that their copper concentrations become abnormally high. During periods of high flow, these pools are flushed out, the net result being a greater flow with a higher copper content.

The Britannia leaching is a natural continuous process with seasonal variations due to the natural precipitation. Diagram 3 shows the seasonal variations and the relation of volume to copper concentration. It is noted that the highest
grade water is obtained during the spring run-off and the late fall rainy season, when the flow of water is also at a maximum.

The abnormally low copper content of the mine waters at the copper plant in the summer months of 1946 has been correlated with the cessation of active mining during a company strike. This suggests that the blasting in the upper levels of the present workings combined with drawing the ore in certain sections appreciably moves the broken ore in the abandoned sections above the 1050 level, thereby exposing new surfaces to, and creating new channels for, the percolating solutions.
Rate of Flow in thousands of Imp. gal./hr.

Conc. of Copper in grs./litre (ppt)


Diagram 3. Seasonal Variations in Rate of Flow and Copper Content of the Mine Waters, Britannia Mine, B.C.
CHAPTER III

OTHER EXAMPLES OF COPPER RECOVERY FROM MINE WATERS

Mine waters are chiefly sulphate waters, and carry only small amounts of the carbonates and chlorides. There is a remarkable uniformity in their characters as they are nearly all sulphates of metals. But they differ greatly in their acidity and oxidation.

Copper dissolved as sulphates is abundant in many mines. In some mines the waters, during certain periods of development, have been sufficiently cupriferous to yield marketable quantities of copper. Several mines from which copper recovery is reportedly made from the natural mine waters are described briefly.

Butte, Montana--The orebodies consist of steeply dipping vein systems cutting quartz monzonite. They are pyritic replacements along fissures and contain pyrite, enargite, tennantite, bornite and chalcocite, but little covellite and chalcopyrite. There is a scant gangue of quartz. Considerable secondary enrichment has taken place with the formation of chalcocite. The copper tenor of the ore is 4 to 5%. The copper concentrations of the mine waters vary in different sections of the various mines. The highest concentration given by Emmons (1916) of 45,633 ppm. was taken from the Mountain View Mine.
Ducktown, Tennessee—The deposit is in the form of elongated tabular masses lying concordantly in a highly compressed, metamorphosed, schistose series. The ore is massive pyrrhotite and pyrite containing chalcopyrite and sphalerite. There is some secondary enrichment to chalcocite. The average copper assay is 2.5%. The six analyses of the mine water reported by Emmons (1916) ranged from 11 to 200 ppm.

Jerome, Arizona—The copper deposit is a pyritic replacement in the form of a pipe cutting Precambrian schists. The ore consists of pyrite, sphalerite, chalcopyrite and tennantite in a quartz, sericite, chlorite and dolomite gangue. The copper content of the ore ranges from 4 to 6%. No analyses of the mine water were found.

Rio Tinto, Spain—This is the greatest pyritic deposit in the world, and has been mined by heap leaching methods since 1752. The orebodies consist of enormous lenticular masses lying conformably between slate and porphyry. Chalcopyrite occurs in minute scattered grains or as threads cutting the granular pyrite. Considerable secondary enrichment with the deposition of chalcocite has taken place to a depth of 200 to 1200 feet. The tenor of the enriched ore is 3 to 12% copper and of the primary ore .5 to 2% copper. Analyses of the mine waters were not found.

Quirvicula, Peru—The orebody is a steep vein fissure
filling type of deposit located in bedded basic volcanics. The ore is composed of enargite, tennantite and tetrahedrite disseminated throughout massive pyrite. The ore assays at 4.4% copper. The gangue is mostly quartz with minor carbonate. Considerable pre and post mineralization fracturing has occurred. According to Lewis (1956), the copper recovery from the mine waters in 1951 was 485,470 pounds.

Chuquicamata, Chile—This deposit is a highly oxidized series of lodes in a granitic host rock and from these, supergene mineralization has spread until it occupies a large area. The primary ore, known only from the drill core, consists mainly of pyrite and enargite and some disseminated chalcopyrite in a silicified and sericitized gangue. The supergene minerals are cuprite, melaconite, brochantite, antlerite and chalcocite. Jarrells (1948) reports the mine water to contain up to 1,150 ppm of copper.

In the above examples several characteristics are common to almost all the deposits. There is considerable pyrite intimately associated with the copper sulphides; there is secondary enrichment; there is little, if any, carbonate gangue; the host rock is generally a siliceous schistose rock. It is noteworthy that the Britannia Mine possesses these features with the exception of secondary enrichment. In this respect the leaching at the Britannia Mine is rather distinctive.
Recovery of copper from the natural mine waters is also reported from the Ballgahan Mine, Ireland, and the Black Ores, Kuiko, Japan. No information was obtained concerning them. Other examples doubtlessly exist but none were uncovered in the survey of the literature.

Two examples of human attempts to leach copper sulphide ores "in-place" are described in the literature. These are the Ohio Copper Company, Utah, and the Ray Mines, Arizona. A brief description is given of both along with the reported recoveries of copper.

Ohio Copper Company—Anderson and Cameron (1926) give a detailed discussion of the leaching operations. The ore-body consists of a vein system in a porous quartzite and shattered monzonite. The ore minerals are pyrite, pyrrhotite, bornite, chalcopyrite and sphalerite. They are irregularly disseminated and/or occur in streaks and stringers. Considerable secondary enrichment has taken place and chalcocite is now the dominant ore mineral. The veins are almost completely worked out and the original stopes and intermediate regions are broken down so that the orebody consists of a zone of broken ore, surrounded by consolidated rock. The caved area may be described as an inverted truncated cone standing at an angle of forty degrees to the vertical. The axis of the cone is approximately 1,200 feet in length and the upper transverse dimensions are 1400 and 600 feet. The truncation at the bottom is about one-quarter of the top area. The
cone is believed to be quite uniformly and completely filled with broken material of approximately four inches in diameter on the average. All this material carries copper and it is estimated that there are over thirty-eight million tons having a .88% copper average.

In the leaching operation, water from the Bingham Canyon Creek is pumped onto the surface overlying the caved zone. The solutions, after percolating through the broken ore, contain .31% copper. A total of seventeen million pounds of copper was recovered in the first fourteen months of operations at a cost of 5.8 cents per pound. Considering an annual production of ten million pounds, Anderson and Cameron (1926) estimated that the life of the operation would be twenty years. With the exception of their paper, no other data were found concerning the leaching operation and it seems doubtful that it continued for many years.

Ray, Arizona—The Ray Mine is in the form of an extensive chalcocite blanket situated in an area of Precambrian schist cut by dikes of granite porphyry and diabase. The protore consists of disseminated pyrite with a little chalcopyrite. Enrichment has taken place through the replacement of pyrite by chalcocite. The oxidized orebody averages 1% copper.

The leaching operation is described by Thomas (1938), and summarized by Newton (1942). By 1933 active mining had ceased in the western part of the mine. During 1935 and
and 1936, there was a heavy rainfall and the copper content of the surface water, after percolating through the broken rock, averaged 1%. As no further mining was contemplated in this sector of the mine, it was decided to prepare it for leaching. Considerable underground work was required to control the flow of the mine water. Drainage drifts were driven and concrete dams installed to prevent the flooding of the active mining areas in the lower levels. Concrete ditches were constructed together with the necessary pumping stations for handling the water.

The leaching operation extended over an area of ten acres. An estimated copper content of the abandoned ore and protore above it indicated that the ground amenable to leaching contained over fifty million pounds of copper. Water was pumped to the caved area and distributed by a series of sprinklers which were moved from section to section. By alternating the periods of spraying and draining, the pyrite was considered to oxidize faster to form ferric sulphate, the principal leaching solvent of the copper minerals. According to Newton (1942), the leaching attack up until 1938 was conducted entirely with fresh water although mention was made of the possibility of employing a leaching agent at some future time.

In the first eighteen months of the operation, ten million pounds of copper were recovered. After a high initial recovery, it decreased rapidly and the entire operation
was not an economic success. The reason for the failure is believed to have been the channelling of the solutions.¹

The writer was unable to find any further examples of leaching of ores "in-place" in his survey of the literature.

¹ Personal communication - H.C. Gunning, University of British Columbia.
CHAPTER IV

PREVIOUS LABORATORY INVESTIGATIONS OF LEACHING

There is little published data on the chemical and physical factors influencing the rate of leaching of ores. The available data and theories are found to be scattered in the various geological, mining, engineering and metallurgical publications. Such publications pertinent to the subject are rather sporadic in time, depending on the recognition of an important phase of the leaching processes. A probable explanation for the lack of any published laboratory research on the natural leaching of an ore is that oxidation of sulphides depends on so many factors that general statements cannot be applied to all conditions. A problem on leaching with clear cut observations cannot be expected because of the heterogeneity of the chemical reactions and the unlimited number of combinations of the influential factors.

Numerous papers on secondary enrichment were published in the early nineteen hundreds and are well summarized by W.H. Emmons (1916). These include a series of experiments on the reactions of specific minerals with different chemical solutions. The closest approach to the leaching of an ore was on mixtures of various sulphides with pyrite.
With regard to the hydrometallurgical treatment of ore, J.D. Sullivan (1933) carried out experiments on the effect of temperature and size on the dissolution of certain copper sulphides. Rather than list them here, the experimental data taken from the literature will be referred to where they are most relevant to the laboratory study.

The first attempt at an experimental investigation of the leaching of the Britannia ore was started in January 1955 by the writer at the suggestion of the Britannia Mining and Smelting Company. After considerable experimentation under the supervision of Dr. R.E. Delavault, a technique was established which produced some encouraging results. These results provided the impetus for continuing the study, and served as a guide in conducting the present work. A summary of the results of the preliminary work is presented in Chapter VII.
CHAPTER V

PRINCIPLES OF LEACHING

Leaching is dependent on the mineralogy of the ore and gangue, the physical nature of the rock, climate, rainfall, water level, topography and to some extent, the openings left from mining developments. A combination of these factors determines the chemical and physical nature of the mine water. In its turn, the mine water governs the degree of leaching.

Man is able to intervene in the leaching processes in two ways; chemically and physically. Chemically, he is able to add certain reagents to the mine water. Physically, he can increase the permeability of the ore. Because of economic limitations, the chemical approach is more practical for a laboratory study.

There are three reasons why investigating the chemical nature of the mine water becomes the primary concern of this thesis subject: it is determined by the factors upon which leaching is dependent; it is prone to human intervention; it lends itself to a laboratory study.

Chemistry of Leaching

The general principles of the chemistry involved in the leaching of the Britannia ore minerals are reviewed in
order to elucidate the laboratory approach to the problem and to serve as a basis for a discussion of the experimental results.

Leaching, as concerned here, occurs in two steps—reaction and removal. Reaction involves the oxidation and solution of the ore minerals and removal involves the transfer of the soluble metal compounds so-formed.

The main oxidizing solvents in a natural leaching process, in order of their increasing potency, are aerated water, sulphuric acid and ferric sulphate. These solvents react at different rates and in slightly different manners with the various sulphides. They are always present at any given time in the mine water (see equations 1). Their proportions may vary considerably and the reactions of each solvent with each mineral should be known in order to understand the net effect of the numerous reactions involved in the leaching of a given mineral association.

The equations expressing the various reactions indicate only the initial and final products. A number of intermediate products probably are formed with the reactions occurring in more than one step. It should be emphasized that, except for equation 1c, the reverse reaction cannot take place under normal temperature and pressure without the presence of reducing agents.

The sulphides are virtually insoluble in water and the only copper mineral of any appreciable solubility is
the cupric sulphate—chalcanthite. Although no chalcanthite is present in the ore, it is important because it is to this form that all the other copper sulphides, oxides and silicates are converted. Its high solubility (316 grams per litre of water at 0 degrees centigrade)—(Handbook of Chemistry and Physics) permits the ready transfer of large amounts of copper in the mine waters from their mineral source to the recovery plant.

The solubilities in cold water of other sulphates involved in the experiments, according to the Handbook of Chemistry and Physics, are, in grams per litre—Fe$_2$(SO$_4$)$_3$·9H$_2$O - 444; FeSO$_4$·7H$_2$O - 156.5; ZnSO$_4$·7H$_2$O - 965.

**Water Reactions:** Pyrite reacts with water to form the more important leaching agents sulphuric acid and ferric sulphate. The persistent association of pyrite with sulphide deposits and its chemical reactions with pure water has resulted in pyrite being referred to as the "spark plug" of sulphide oxidation. Buehler and Gottschalk (1910) showed experimentally that no thiosulphate, hydrogen sulphide or sulphur dioxide was generated in the oxidation of pyrite. They concluded that oxidation of pyrite is most correctly described according to the reactions expressed in the following equations:
(1) \( \text{FeS}_2 + 7 \, \text{O} + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4 \)

(1a) \( 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \)

(1b) \( 6\text{FeSO}_4 + 3 \, \text{O} + 3\text{H}_2\text{O} = 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe(OH)}_3 \)

(1c) \( \text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Fe(OH)}_3 + 3\text{H}_2\text{SO}_4 \)

Reaction 1 is quite slow but the subsequent reactions proceed faster. Ferrous sulphate is unstable so that reactions 1a and 1b follow as natural consequences of equation 1. The preference of either 1a or 1b will depend on the availability of sulphuric acid. When the solutions are too dilute, such as in ores where there is little pyrite to generate sulphuric acid and/or ferric sulphate, reactions 1b and 1c will occur. The leaching action will then be decreased due to the reduced permeability caused by the plugging of the pores with ferric hydroxide. The importance of the reaction of pyrite with water is its ability to generate the more potent reagents sulphuric acid and ferric sulphate, thereby accelerating the oxidation of, not only the other sulphides, but itself as well. Gottschalk and Buehler (1910) found that in mixtures of other sulphides, pyrite accelerated their oxidation by 8 to 20 times.

The copper sulphides dissolve very slowly in aerated water, and will preferentially react with the more potent solvents which have undoubtedly been generated by virtue of the reactions with the associated pyrite. Insignificant as they are believed to be quantitatively, for the sake of
completeness, the reactions of chalcopyrite and chalcocite are expressed in the following equations:

(2) \( \text{Cu}_2\text{FeS}_4 + 8 \text{O} = \text{CuSO}_4 + \text{FeSO}_4 \)

(3) \( \text{Cu}_2\text{S} + \text{H}_2\text{O} = \text{CuSO}_4 + \text{Cu(OH)}_2 \)

Sphalerite is attacked slowly by aerated water. No satisfactory equation has been given for the reaction. In an experimental study, Carmichael (1926) found the sulphides to oxidize in water in the following order starting with the most easily attacked—chalcocite, pyrite, sphalerite, chalcopyrite and bornite.

**Sulphuric Acid Reactions:** Sulphuric acid, while a strong solvent for the copper carbonates, oxides and silicates, is considered only slightly reactive in directly dissolving the copper and iron sulphides. However, when acting on a mixed sulphide ore, it appreciably increases the rate of leaching in an indirect manner. Sulphuric acid converts the ferrous sulphate and possibly the ferric hydrate, which have been generated by pyrite in a too dilute solution, into ferric sulphate. This reaction is expressed in equations 1b and 1c.

Little, if any, chalcopyrite is dissolved directly by the sulphuric acid and no equation expressing such a reaction was found in the literature available. According to Lindgren (1933) p-832, the copper sulphides are only
slightly attacked by dilute sulphuric acid in the decreasing order of bornite, chalcopyrite, chalcocite and covellite.

The copper oxides, although not identified in the Britannia ore, may be formed as an intermediate compound in the leaching processes and, hence, their reactions are included here. Tenorite (CuO) dissolves readily, but cuprite (Cu₂O) less readily and only half its copper enters solution. If intermediate copper oxides do form, the sulphuric acid would readily dissolve them and, hence, accelerate the conversion of copper from the sulphide to the soluble sulphate.

(4) \[ \text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O} \]

(5) \[ \text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{Cu} + \text{H}_2\text{O} \]

Sphalerite is fairly soluble in dilute sulphuric acid with the evolution of \( \text{H}_2\text{S} \).

(6) \[ \text{ZnS} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{S} \]

**Ferric Sulphate Reactions:** Ferric sulphate is an active solvent of nearly all the sulphides and is by far the most powerful oxidizing agent in the chemistry of the leaching of copper ores. A ferric sulphate solution is an acid one because it reacts with water to generate sulphuric acid as shown in equation lc. In too dilute solutions, the ferric sulphate will hydrolize and precipitate ferric hydroxide as expressed in equation lc. In oxidizing copper sulphides, the ferric sulphate is reduced to its ferrous form which is in turn converted back to the ferric form in the presence of
available oxygen and sulphuric acid. The ferric sulphate reactions then, are of a partial self-generating nature. This chemical characteristic coupled with its potency renders ferric sulphate the most important reagent in the leaching processes.

The sulphides dissolve in dilute ferric sulphate according to Emmons (1916), in the decreasing order of sphalerite, chalcocite, bornite, covellite, chalcopyrite and pyrite. The first three react considerably faster than the last three. Chalcopyrite and bornite react with ferric sulphate in the following manner:

(7) \[ \text{Cu}_2\text{FeS}_2 \ + \ 2\text{Fe}_2\left(\text{SO}_4\right)_3 \ \rightarrow \ \text{CuSO}_4 \ + \ 5 \ \text{FeSO}_4 \ + \ 2 \ \text{S} \]

(8) \[ \text{Cu}_4\text{FeS}_5 \ + \ 20 \ \text{Fe}_2\left(\text{SO}_4\right)_3 \ + \ 20 \ \text{H}_2\text{O} \ \rightarrow \ 4\text{CuSO}_4 \ + \ 41 \ \text{FeSO}_4 \ + \ 20 \ \text{H}_2\text{SO}_4 \]

J.D.Sullivan (1933) shows that the Cu:Fe:S ratio remains constant throughout the dissolution of chalcopyrite. Therefore he concludes that there is no selective breakdown of any part of the chalcopyrite molecule.

The rate of dissolution of chalcocite is so rapid that it is practically independent of the size of the particles or the strength of the solutions. It appears that chalcocite in its normal condition has sufficient porosity to permit the ready ingress of the solutions. Chalcocite has been shown to dissolve in two stages. In the first stage it gives up half its copper rapidly and changes into a form
approximating covellite. In the second stage the covellite-like residue dissolves comparatively slowly. The reactions of chalcocite and covellite are expressed in the following equations:

(9) \[ \text{Cu}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuS} \cdot \text{CuSO}_4 + 2\text{FeSO}_4 \]

(10) \[ \text{CuS} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 2\text{FeSO}_4 + \text{S} \]

Pyrite dissolves slowly, but faster than in pure water according to the reaction below:

(11) \[ \text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 = 3\text{FeSO}_4 + 2\text{S} \]

In the oxidizing environment any sulphur produced is immediately converted to sulphuric acid.

(12) \[ \text{S} + 3\text{O} \cdot \text{H}_2\text{O} = \text{H}_2\text{SO}_4 \]

Sphalerite is readily attacked to form ferrous sulphate and free sulphuric acid.

(13) \[ \text{ZnS} + 4\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} = \text{ZnSO}_4 + 8\text{FeSO}_4 + 4\text{H}_2\text{SO}_4 \]

All the above reactions involved in leaching are doubtlessly simpler than those actually taking place in nature. Nevertheless, they represent the beginning and some of the end products, and also indicate the general tendencies that might be expected.

The effect of electrolytic action on the rate of dissolution of mixed sulphides was examined by Gottschalk and Buehler (1912). Experimental work on mixtures of two sulphides showed a large increase in the solution of the mineral having the lowest electrode potential, whereas, the
mineral of higher potential was protected. The minerals were arranged according to their electromotive series and the further apart two minerals were in the series, the greater was their influence. The electrolytic action varied with the nature of the solution and the condition of the minerals and, hence, there was no general rule that could be formulated. As a result, application of electrolytic action was so difficult that it was of little service in the current study.

The relative reactivity of certain minerals in reducing the acidity of such solutions as sulphuric acid, ferric sulphate and cupric sulphate was investigated by G. S. Nishihara (1941). The experiment showed that quartz, mica, chalcopyrite and pyrite had little, or no effect on the acidity of the solutions but calcite, olivine, rhodocrosite, siderite and pyrrhotite did have a noticeable reducing effect. The Britannia ore used is comprised mostly of the four, above mentioned, inert minerals and therefore, the reactivity of the minerals in reducing the acidity is of no consequence to the thesis study and may be dismissed.

Physical Aspects of Leaching

Although leaching is fundamentally a chemical process, certain physical factors must also be considered. Before the chemical reactions can take place, the attacking solutions have to come in contact with the ore minerals. The amount of solution and solid that comes in contact will
depend on the permeability of the ore, the porosity of the minerals and the distribution of the mineral in the ore. The allowance of the ore for the ready ingress of solutions is, therefore, a prerequisite to a high degree of leaching.

**Ingress of Solutions:** The ingress of the solutions depends on the amount of void space available. In general, there are two classes of voids; firstly, there are fractures and cleavages, and secondly, there are pores of capillary size or smaller. The natural distribution of the minerals is related to the first class for, if the sulphides are located along the fractures and cleavages, the solutions can more readily come in contact with them than if they are disseminated.

The openings between the crushed ore particles are included in the first class because the extent to which man may appreciably increase the permeability of the ore by crushing is restricted by an economic limit. After a certain point it would be more practical to mine the ore by the conventional methods.

Since leaching in place refers to ore approximating a massive condition, the porosity of the individual minerals is important in determining the rate of leaching. The solutions absorbed in the capillary spaces will be in very thin films, perhaps even layers of molecular dimensions.

The invading solutions, when in contact with the sulphides, will react at the interface of the solid and
liquid to form the soluble salts according to the reactions discussed above. The reaction will continue as long as there is a fresh solution in contact with the sulphides. This necessitates the removal of the soluble salts from the interface. The removal of the salts and the replenishing of the fresh solutions in these sub-microscopic pores will depend on the diffusion phenomenon.

Diffusion: The rate of diffusion of a given solute depends on the nature of the solvent and the solute, the temperature and, in particular, the concentration. Diffusion takes place with the transfer of the solute from a state of highest concentration to a state of lower concentration. The greater the difference in the relative concentrations, the faster will be the diffusion. The copper sulphate formed at the interface will then tend to diffuse to the surface of the mineral, and will ultimately be carried away by the percolating solutions. The diffusion of copper sulphate is considered by J.D. Sullivan (1933) to be a relatively rapid process, and independent of temperature. In effect, as the copper sulphate is produced, an equal amount is removed.

An optimum removal of copper requires an ideal balance between the chemical reaction forming the copper salt and the rate of flow of the percolating solutions replenishing the spent solutions. A very dilute solution and a very fast rate of flow gives a fast diffusion but a slow chemical
reaction and, therefore, a low concentration of copper per unit volume of percolating solution. On the other hand, a strong solution and a slow rate of flow will not remove the copper sulphate that could be chemically produced. The rate of leaching is determined by the chemical reaction rate and by the diffusion phenomenon. Leaching is, therefore, a time-chemical phenomenon.
CHAPTER VI

EXPERIMENTAL TECHNIQUE

The main problem in establishing a satisfactory experimental technique was to design an apparatus which would simulate actual leaching conditions as closely as possible, be relatively simple and inexpensive, and be capable of giving reproducible results within the recognized limits of control. In doing this, the many factors influencing the rate of leaching were recognized and their relative importance assessed. The factors considered most influential were taken into account, and controlled where possible. The experimental technique which was finally adopted satisfied the necessary prerequisites, and gave results similar to those observed at the Britannia mine.

Method

The ore was examined, crushed, sorted, assayed, packed in glass tubes (hereinafter known as the ore tubes) and chemically attacked with various solutions (hereinafter known as the heads). The reacted solution (hereinafter known as the tails) were collected daily irrespective of their volume, unless extreme rates of flow necessitated more frequent collection. The tails were analysed for copper, zinc, iron and acidity. Concentrations are expressed in
milligrams per litre which is equivalent to parts per million. The amount of copper leached from the ore column totals less than one tenth of the over all copper content and represents, at any time, a negligible proportion of the visible chalcopyrite.

All pertinent data were recorded on charts. The results were plotted on graphs in a manner which best illustrated the effects of the known factors influencing the degree of leaching.

Description of the Ore

Thin sections and polished surfaces of the ore were studied in the laboratory. The Empress orebodies consist of numerous discontinuous quartz stringers forming an ore zone rather than a distinctly defined vein. The host rock is a highly silicified, sheared chlorite-sericite schist. The original rock is believed to have been acid fragmental volcanics interbedded with tuffs. The Empress orebody shown in Diagrams 1 and 2 extends from the surface to the 1600 level. The 12 E 1 stope is located seventy feet below the 1000 level. The samples were selected by the company engineer and were evidently taken from a rich portion of the stope as they assayed considerably higher than the average 2.35% copper of the Empress ore.

1 Personal communication with A.L. Killin, Britannia Explorations Ltd.
The ore is a hard, massive, pale green rock carrying numerous, well-defined, white, quartz stringers and replacement masses. The quartz stringers measure less than one inch in width, and, more or less, parallel the schistosity for distances up to several feet. Most of the sulphides are in the stringers or in fractures in the wall rock. Irregular masses of chalcopyrite are intermixed with a dull, porous pyrite. Small crystals of lustrous pyrite are scattered throughout the schistose host rock. Much of the chalcopyrite is coated with a thin layer of black, sooty chalcocite, or is tarnished with a film of bornite.

In thin section the host rock has a fine grained, mylonitic texture. It is composed of interlocking quartz grains surrounded by numerous, minute shreds of chlorite and sericite. In places, the quartz groundmass grades into a coarser phase taking the form of irregular veinlets and augen structures. During the silicification of the original rock, the coarser quartz formed veinlets in the fractures, and selectively replaced the fragments in the volcanics to give augen structures. Both the finer and coarser phases were heavily mylonitized and cut by shreds of sericite.

A second generation of quartz cuts and replaces both phases of the earlier one. This generation is clearer and coarser and forms veinlets possessing a cross grained structure. The veinlets occur in two general directions; parallel to and oblique to the schistosity.
A striking feature in the crystallization of the second generation quartz is its occurrence in the form of fibrous grains radiating from the boarders of euhedral pyrite.

In places, chlorite and sericite form small lenticular aggregates in the plain of schistosity. The chlorite is too fine grained and intergrown with the sericite to permit determination of its composition. The pleochroicism suggests the varieties ripodolite or prochlorite. In the report by H.T. James (1929) the optical properties of chlorite are considered to be similar to those of the variety aphrosiderite.

Small, irregular masses of leucoxene are scattered throughout the rock and are presumably formed from the alteration titanite as referred to by James' report.

Chalcopyrite occurs in irregular masses, and is slightly fractured. Narrow veinlets of supergene, feathery covellite partially fill most of the fractures. Subhedral crystals of pyrite are moderately fractured and veined with quartz. Where the two sulphides are in contact, the chalcopyrite surrounds and, in many places, replaces some, or all, of the pyrite. The chalcopyrite does not vein the fractures in the pyrite. A few fractures cut both minerals indicating late movement. Unlike the lustrous pyrite scattered throughout the host rock, the pyrite associated with the chalcopyrite is dull, porous and fractured. These character-
istics suggest that it would be readily attacked by leaching solutions.

A few minute grains of sphalerite were observed in the study of the crushed ore under the binocular microscope. None was identified in the polished sections.

The textural relationships observed in hand specimen and thin and polished sections suggest, the following sequence of events:

(a) original interbedded clastic volcanics, tuffs and slates.
(b) shearing with widespread silicification in fine and coarse phases
(c) intense shearing with mylonization of the entire rock, and development of sericite along the shears
(d) deposition and fracturing in the following order: pyrite, fracturing, quartz, chalcopyrite and fracturing.
(e) formation of supergene covellite, chalcocite and bornite.

The mineralogical composition has been calculated from a chemical analysis in conjunction with the thin and polished sections study. The data are listed in the following tables:
Table I
Chemical Analysis of Ore from the 12 E 1 Empress Stope

Britannia Mine, B.C. Analyst
British Columbia Research Council

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>73.35</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.46</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.97</td>
</tr>
<tr>
<td>MgO</td>
<td>.98</td>
</tr>
<tr>
<td>K₂O</td>
<td>.48</td>
</tr>
<tr>
<td>Na</td>
<td>.14</td>
</tr>
<tr>
<td>CaO</td>
<td>--</td>
</tr>
<tr>
<td>H₂O₀    (105°C)</td>
<td>1.10</td>
</tr>
<tr>
<td>H₂O₀</td>
<td>.13</td>
</tr>
<tr>
<td>Residue</td>
<td>.66</td>
</tr>
<tr>
<td>Cu</td>
<td>4.02</td>
</tr>
<tr>
<td>Zn</td>
<td>.19</td>
</tr>
<tr>
<td>S</td>
<td>5.38</td>
</tr>
<tr>
<td>Fe</td>
<td>4.69</td>
</tr>
</tbody>
</table>

99.55 per cent

The weight percentages of the various minerals are given in the order of their calculation with the indicated assumptions.
Table 2
Calculated Mode Composition of 12E 1 Empress Stope

<table>
<thead>
<tr>
<th>Component</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite (assume all copper to be pure chalcopyrite)</td>
<td>11.65</td>
</tr>
<tr>
<td>Sphalerite (assume all zinc to be pure sphalerite)</td>
<td>.28</td>
</tr>
<tr>
<td>Pyrite (assume remaining sulphur in form of pure pyrite)</td>
<td>2.33</td>
</tr>
<tr>
<td>Sericite ((\text{Na}_2\text{O} \cdot \text{K}_2\text{O})2\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}) (assume all \text{NaO} and \text{K}_2\text{O} in sericite)</td>
<td>5.03</td>
</tr>
<tr>
<td>Chlorite ((\text{MgO} \cdot \text{Fe}_2\text{O}_3) \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}) (assumed the \text{MgO}, \text{Fe}_2\text{O}_3, \text{H}_2\text{O} and remaining \text{Al}_2\text{O}_3 form a chlorite) -- this gives the variety ripodolite)</td>
<td>11.07</td>
</tr>
<tr>
<td>Quartz (assume remainder of silica as quartz)</td>
<td>68.38</td>
</tr>
<tr>
<td>Residue as leucoxene</td>
<td>.66</td>
</tr>
<tr>
<td></td>
<td>99.40%</td>
</tr>
</tbody>
</table>

The study of the ore samples draws attention to several facts that may be relevant to the leaching phenomenon:

(1) the host rock is a highly silicified brittle schist that is moderately fractured.

(2) the concentration of chalcopyrite in the fractures.

(3) the close association of a dull porous pyrite with chalcopyrite indicative of rapid weathering.

(4) the absence of reactive gangue minerals (carbonates).

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1 Winchell (1951), from diagram p-381
Preparation of the Ore for Leaching

The ore samples were crushed in the ore dressing laboratory of the Department of Metallurgy. The crushed ore ranged in size from dust particles to one-half inch, and was sorted into three fractions:

1.5 to 3 mm. (-8\*10 mesh); 3 to 5 mm. (-5\*8 mesh); and 5 to 7 mm. (-3\*5 mesh).

In dealing with concentrations of parts per million, the conventional brass or steel sieves and screens could not be used. To avoid salting, special sieves were made by drilling holes in small aluminum pans. A thin finishing coat containing appreciable quantities of zinc was removed from the pans with hydrochloric cleaning solution.

Crushing the ore makes it more amenable to leaching by increasing the surface area per unit weight, by opening fractures and cleavages and by shortening the path required for the solutions to come in contact with the copper minerals within the particles. The size of the ore particles, therefore, requires careful consideration in the experimental approach. The size used should react chemically at a rate similar to that of the particles in the crushed ore zone of the mine, yet be of a suitable size for a laboratory study. J.D. Sullivan (1933), investigated the influence of size on
the rate of dissolution of some specific copper sulphides and found the relationship to be neither linear nor as great as might be expected. Several experiments proved that for sizes finer than ten mesh the effect is considerable, whereas for sizes coarser than that the effect rapidly lessens. As the particles approach the massive state the effect of size becomes less significant. This is illustrated in diagram 4.

![Diagram 4. Relation of size of particles to dissolution of covellite in acidified ferric sulphate. (after Sullivan, 1933, p. 326).](image)

The relationship of size and rate of dissolution on specific minerals is similar for a mineral association and may be applied to the leaching of ore. In order to test the
validity of this statement, the three different size fractions of the Empress ore were similarly attacked by water and sulphuric acid solutions. The rate of leaching was almost identical in the two coarsest sizes, and only slightly higher in the finest. This relationship was in close agreement with Sullivan's results. Although there was a difference of about 2% in the copper content of the three sizes (the finest being the richest), the amounts of copper leached were a negligible proportion of the copper content of the ore. Therefore, the differences in the copper content of the ore would not effect the rate of leaching. The influence of the size factor satisfactorily explained the difference in the observed leaching. The 3 to 5 millimetre size (-5-8 mesh) used in most of the experimental investigations of the Britannia ore may be considered a reasonable approximation, chemically speaking with regard to its dissolution, to the average size of the particles in the crushed ore zone of the mine.

Assay samples were taken from each of the size fractions by quartering with a sample splitter. The samples were assayed for copper and zinc by the company analyst. The chemical analysis was done on the 3 to 5 mm. size fraction through the courtesy of Dr. Strickland of the British Columbia Research Council.

The bacteria thiobacillus thioxidans is known to occur in the Britannia mine water, and may have an effect
on the leaching processes. According to Bergy (1948) p-79, this bacteria thrives in an acid environment, and derives its energy from oxidizing sulphides and by producing sulphuric acid. No foreign organic material is necessary for its life. The optimum reaction is at a pH of 2.2 and a temperature of fifteen to twenty degrees centigrade. The quantitative importance of the bacteria in the leaching is not known and its presence in the samples leached seems unlikely. Nevertheless, to ensure against any possible bacteria influences, the ore was heated to sixty degrees centigrade for one hour at which temperature the bacteria is destroyed.

Two hundred and fifty grams of the sorted and heat-treated ore were weighed and washed with distilled water to remove any fines adhering to the particles. The ore was then funnelled into the ore tube, and packed so that it filled a length of approximately ninety centimetres. The packing was accomplished by immersing the ore in distilled water and shaking until the ore column was reduced to the desired length. The packing ratio (defined as the per cent by volume of ore in the ore column divided by the per cent by volume of solution) was kept constant in all the experiments. The ore was packed as tightly as possible because it was too difficult to obtain a constant value when it was loosely packed.

When using two hundred and fifty grams of ore, the
largest packing ratio that could be obtained without breaking the glass tube was 9. (90% by volume of ore and 10% by volume of solution).

The ore tube was held on an iron rod rack, and was attacked with the various solutions.

Apparatus

In the preliminary experiments the heads solutions simply percolated through the crushed ore column. Although this method gave satisfactory results, objections were made concerning the possibilities of the solutions channelling and the measurement of only a time reaction. Another method was to immerse the ore column in the attacking solutions for a given time, after which, the pregnant solutions were drawn off and replaced with fresh solutions. Objections to this method concerned the lack of a continuous flow and the measurement of only a chemical reaction. After months of considerable experiment, the apparatus described below was finally adopted because it measured a combined time-chemical reaction. At the observed rate of leaching, an adequate supply of oxygen was supplied by oxygen dissolved in the heads and in the atmosphere.

The reproducibility of the experimental technique was tested in three ways:

(a) by two identical leaching histories of the same ore.
(b) by two leaching histories of the same ore using the
same heads but in a different order. 
(c) by one leaching history in which the heads were water, increasing strengths of sulphuric acid and back to water.

In all three the order of magnitude of the leaching was constant for a given heads solution.

In order to establish the fact that the apparatus was measuring a continuous chemical reaction and not just a solubility limit, the tails were recirculated. With each recirculation there was an increase in the copper concentration approximately equal in value to that of the original stabilized concentration. For example, in the sulphuric acid attack the rate of leaching was stable at 33 ppm, and with each recirculation the concentration of the tails increased by about 30 ppm. This indicated that a chemical reaction is continually taking place and the rate of leaching, as measured by the concentration of the tails, represents a time-chemical reaction. Had only dissolution taken place, the concentration of copper in the tails would not have increased upon recirculation as it already would have been in equilibrium with the ore.

Since the experimental technique was measuring a time-chemical reaction, by standardizing the rate of flow (time), valid comparisons could be made between the rates of leaching of the different solutions.
A complete unit of apparatus, as it was assembled on the grid, is shown in diagram 5. The different parts are briefly discussed under their respective headings.

**Glassware:** A complete set of glassware consists of a heads flask, a feeder decanter, an ore tube and several tails containers.

The heads flask is a one litre, flat-bottomed, Florence flask with two glass tubes attached to the neck—an outlet tube and an air intake tube. The latter is one inch longer than the former, and is fitted with a stopcock to allow the flask to be mounted on the rack without spilling.

The feeder decanter is an one inch diameter vertical tube with an 'S' shaped smaller tube attached about two inches from the bottom of the larger tube. The smaller tube ends in an upward capillary and is partially obstructed by an inserted platinum wire (No. 28 B and 3 gauge). By adjusting the length of this wire in the capillary, the rate of flow may be varied within the limits of 2 ml./hour to 200 ml./hour. The original feeders had smaller glass capillaries and no controlled obstruction. These were found to be easily plugged by fine solid particles. After several weeks of trial and error, the platinum wire method was adopted. It combined the advantages of being easily and quickly flushed out in the event of plugging and allowing for the regulation of the rate of flow.
HEADS
FLASK

FEEDER
DECANTER

ORE
TUBE

heads

adjustable platinum wire partly obstructing the glass capillary

crushed ore

tails

TAILS
CONTAINER

DIAGRAM 5. UNIT OF APPARATUS
The ore tube is a Pyrex glass tube thirty-six inches in length and one-half an inch in diameter. One end is left open, and is fitted with a small funnel to catch the heads dripping from the feeder decanter. Near the closed end the glass has been pushed in and the indentations so-formed act as stoppers for the ore, and allow for the unobstructed passage of the tails. In order to keep the ore submerged, the tails are removed by a small glass tube that is attached to the ore tube beneath the ore column. It extends upwards beside the ore tube for a length of ninety-five centimetres where it is bent about 135 degrees to form a spout. The level of the end of the spout is at least five centimetres higher than the top of the ore column and, in this way, the ore is always immersed in solution.

The tails are collected in 500 ml. Pyrex measuring cylinders. Large size tubes are used (100 ml.) to keep samples of the tails until they are analysed.

**Mountings:** The iron rod grid consists of two stationary horizontal rods bracketted to the wall and four adjustable vertical rods.

Burrett clamps and ring clamps are used to hold the pieces of apparatus in a near vertical position on the grid. A two inch gap has been cut in the ring clamp holding the heads flask to permit the removal of the flask without the lowering of the clamp.
Chemicals: The only chemicals used in the leaching processes are sulphuric acid and ferric sulphate. Solutions of the desired strength are made from the chemically pure stock supplies. The stock ferric sulphate powder is factory assayed at seventy per cent with less than .02 per cent trace element content. Check tests proved that it contained insignificant concentrations of copper and zinc within the limits of the experiments.

The chemicals and procedure used in the trace element analyses are those used and described in the literature by the Biogeochemical Laboratory of the University of British Columbia. The classical dithizone method was used in analysing for copper and zinc. The total iron concentration was obtained by the dipyridyle technique. The iron test was less accurate when brown ferric hydroxide and blue copper sulphate tinged the red colour of the dipyridyle. The acidity was determined by a Berkman Model N pH meter.

Consideration of Temperature

No allowance is made for temperature as this would involve costly equipment. However, a Zeal maximum-minimum thermometer was used to determine the range of temperature in the laboratory.

Temperature is an important factor in reaction kinetics and, as a general rule, a rise of ten degrees centigrade doubles the rate of the chemical reaction. In re-
actions involved in secondary copper sulphide enrichment

Zies, Allen and Merwin (1916) concluded that increased
temperatures accelerate the reactions rather than change
their character. An experimental investigation by J.D.
Sullivan (1933) on the dissolution of several copper sulphides
shows that an increase in temperature is most effective for
temperatures above twenty-five degrees centigrade and the
effect becomes less significant for those lower than this, as
illustrated in diagram 6. Although Sullivan's work was

![Diagram 6. Effect of temperature on rate of dissolution of covellite (200 mesh) in acidified ferric sulphate. (After Sullivan 1933, p. 223)](image)

concerned with a severe attack on fine particles, a similar
trend is undoubtedly true of in-place leaching conditions.
The fact that his results, with respect to size, seem to
apply to the Empress ore suggests that his observations on
temperature would also be applicable. Therefore, the range
of temperature (5 degrees centigrade to 25 degrees centigrade) under which the thesis experiments were conducted would not be expected to seriously influence the interpretation of results. However, diurnal temperature variations may be responsible for many minor, and otherwise unexplained, changes in the rate of leaching.
CHAPTER VII

SUMMARY OF THE PRELIMINARY INVESTIGATION

The preliminary investigation was primarily concerned with establishing a satisfactory experimental technique. During this investigation, several significant facts were noted which determined the course of the present study of the Empress ore. Before discussing the leaching history of the Empress ore however, the observations and their significance will be briefly reviewed.

There were two sets of experiments. The ore was attacked in one with pure water and in the other with sulphuric acid and/or ferric sulphate. Each set consisted of a sample of the Fairview ore and a specimen of high grade chalcopyrite. The high grade chalcopyrite specimen was selected to act as a control in evaluating the relative importance of the influence of pyrite on the rate of leaching.

The estimated copper contents of the Fairview ore and the high grade chalcopyrite specimen were 1% and 20% respectively. The corresponding chalcopyrite to pyrite ratios were 2:1 and 50:1. The methods of leaching of the two samples were similar and a comparison of the results could be readily made.

The only difference in the apparatus from the one described previously was that the attacking solutions
percolated through the crushed ore without submerging it.

The preparation of the ore was the same for the Empress with the following exceptions. The crushed ore was unsorted and ranged in size from fine dust to particles measuring one-quarter of an inch in diameter. The ore was neither heated nor assayed. Consideration of these factors was deemed unessential until the order of the magnitude of the leaching was established for the devised experimental technique.

Description of the Fairview ore is similar to that of the Empress. Both ores would be expected to give the same rate of leaching under an identical set of conditions.

Sulphuric acid and ferric sulphate solutions both appreciably increased the rate of leaching of both types of ore. The key factor in determining the rate of leaching was found to be the chemical character of the attacking solutions. Absolute values are not given because the effects of variation in the chemical nature of the attacking solutions on the rate of leaching are investigated more fully in the study of the Empress ore.

With regard to the mineralogy of the ore, the concentration of pyrite and not chalcopyrite determined the amount of copper that was leached. The influence of pyrite was illustrated by comparing the Fairview and high grade chalcopyrite ores in two ways:
(a) the relative rates of leaching when attacked by the same solution
(b) the relative effects on the rate of leaching caused by changes in the rate of flow.

The rate of leaching for a given attacking solution was faster in the lean Fairview ore (containing one-twentieth the amount of copper) than in the high grade chalcopyrite. The difference is accounted for by the greater concentration of pyrite per unit of chalcopyrite (twenty-five times greater in the Fairview). The reactions of the solutions with the pyrite produced sulphuric acid and ferric sulphate which in turn attacked the chalcopyrite, thereby determining the rate of leaching. Although the ore with the lower concentration of copper gave the slower rate of leaching, the richer ore would, in time, provide more copper.

Changes in the rate of flow had an inverse effect on the rate of leaching with respect to concentration, but did not appreciably alter the amount of copper extracted. As the rate of flow increased, the concentration of copper in the tails decreased because the solutions had less time to react with the sulphides. However, the amount of copper remained about the same. The effect was found to vary with respect to the nature of the attacking solutions and with the concentration of pyrite in the ore. It was most pronounced in the pure water attack and in the high grade chalcopyrite.
In the pure water attack the presence of sulphuric acid and ferric sulphate in the heads solutions is wholly dependent on the reaction of water and pyrite. These reagents, in turn, react with the chalcopyrite to determine the rate of leaching of the copper. This particular process then, may be considered to occur in two steps. On the other hand, in the sulphuric acid plus ferric sulphate attack, both of these reagents are present in the heads solutions, and do not depend on the reactions with pyrite for their presence. The chalcopyrite is attacked directly by the reagents in the heads solutions. This process may be considered to occur in one step. With respect to the element of time, a comparison of the two processes indicates that the rate of flow has a greater influence on the two step process. Consequently, changes in the rate of flow are more effective in the pure water attack.

In the high grade chalcopyrite there is less pyrite to react with pure water than in the Fairview ore. The amount of sulphuric acid and ferric sulphate generated by the pyrite are proportionally smaller and more sensitive to changes in the rate of flow. Since the rate of leaching is directly proportional to the concentrations of these reagents generated, any changes in the rate of flow would have a greater influence where there is less pyrite. The high grade chalcopyrite ore is, consequently, more sensitive to changes in the rate of flow than is the Fairview ore.
It was impossible to maintain a completely stable rate of flow over a period of days. Consequently, changes in the rate of flow were made in order to estimate the value giving the most consistent rate of leaching. A rate of 8 ml./hour gave this result in the water attack on both the Fairview and the high grade chalcopyrite ores. A deviation of 2 ml./hour in either direction did not appreciably effect the rate of leaching. This rate was also found to be in the range most easily controlled in the apparatus set-up. For purposes of comparison of other factors affecting the rate of leaching, the rate of 8 ml./hour was taken as the standard. It is the rate at which the study of the Empress ore was conducted.

The preliminary investigation indicated that the chemical character of the attacking solutions and the chalcopyrite to pyrite ratio were the main factors in determining the rate of leaching. Changes in the rate of flow were of secondary importance and established only the range of fluctuation over a predetermined order of magnitude. Since the mineralogy of the ore is a fixed factor and the rate of flow is of a subordinate nature, the chemical character of the heads solutions becomes the most interesting factor influencing the rate of leaching of the Britannia ore. As a result, a detailed study was conducted on the effect of variations in the chemical character of the attacking solutions.
In order to ascertain the effect of the variations in the chemical nature of the attacking solution on the rate of leaching, the experiments were carried out under similar sets of conditions. These conditions are listed below.

Ore - 12 E 1 stope of the Empress mine
Assay - 4.02% copper, .19% zinc, 2.33% pyrite;
chalcopyrite to pyrite ratio - 5.1
Size - 3-5 mm. (-5+8 mesh)
Heated to 60° C. - to destroy bacteria
Weight - 250 grams
Packing ratio - 9(90% ore to 10% solutions by volume)
Height of ore column - approximately 90 cm.
Apparatus - ore submerged in flowing solution
Rate of flow - stabilized within limits of 6 to 10 ml./hour except where there were unexpected interruptions. Standard rate for comparison - 8 ml./hour.
Temperature - Not controlled. Range - 5° to 25° C
Estimated average of 18° C.
Tails analysed for - copper, zinc, total iron and acidity.
According to the chemical character of the attacking solutions, there were five experiments. The solutions used were pure water, sulphuric acid, ferric sulphate, constant sulphuric acid plus ferric sulphate, and constant ferric sulphate plus sulphuric acid. In the sulphuric acid and ferric sulphate attacks the concentrations were increased in order to determine the limit at which an increase in concentration no longer had any appreciable effect on the rate of leaching. These limits (hereafter referred to as the effective limits) were then used in determining the combinations of sulphuric acid and ferric sulphate. In one case, a constant concentration of sulphuric acid was added to varying concentrations of ferric sulphate. This constant concentration was above the effective limit observed in the sulphuric acid experiment. In the other case, a constant concentration of ferric sulphate was added to varying concentrations of sulphuric acid. This constant concentration was the lowest (.001M) one used in the ferric sulphate experiment.

Leaching Histories

The leaching histories of the five experiments are best illustrated by means of tables and graphs. From these the relative effects on the rate of leaching caused by the different solutions and variations in their chemical strength are easily observed.
The concentration of copper in the tails and the amount of copper extracted are plotted in logarithmic scale against the volume on the graphs. The rate of flow is also shown in order to draw attention to variations in the concentration caused by changes in the rate of flow. Reference to the graphs shows that although the rate of flow was not constant, it was mostly confined within the limits of 6 to 10 ml./hour.

Unexpected changes in the rate of flow were caused by several factors. The factor causing the greatest change was solid particles plugging the feeder capillary. These particles were either contained in the heads solutions or introduced from the atmosphere into the open end of the feeder decanter. The least stability of the rate of flow occurred when ferric sulphate was in the heads solutions. This was a result of the formation of colloidal iron sulphate and/or iron oxide precipitate.

Changes in the viscosity may be responsible for some minor variations in the rate of flow as the viscosity of the solution depends on its chemical character and the temperature.

Diurnal changes in the temperature probably have a direct effect on the rate of the chemical reactions and, hence, account for many of the minor deviations in the rate of leaching.

In all the experiments the ore was leached with
distilled water until a constant concentration of 1 ppm. was obtained. This was done to ensure against any salting when handling the ore and to remove any fine particles that might have adhered to it. This process usually took no longer than three days. The ore was attacked by the same heads until the rate of leaching became reasonably stable over a period of at least a week.

The concentrations of the zinc in the tails are not included in the tables and discussions as they were rather erratic. This inconsistancy is explained by the following facts: the lack of uniform distribution of the sphalerite in the ore; the fast rate at which sphalerite is leached; the greater sensitivity of the analytical method for zinc determinations. In general, the copper to zinc ratio was 3:1 for low rates of leaching under a water and sulphuric acid attack. At high rates of leaching under a ferric sulphate attack, the copper to zinc ratio ranged from 3:1 to 20:1.

The leaching history of each experiment is given in Table form with a brief discussion of the results. The values given in the tables are the average concentrations over the stabilized period.

**Pure Water:** The ore was attacked with pure water for a period of several weeks at a rate of flow of 6 to 9 ml./hour. The concentration of the tails remained constant at a value of 1 ppm.
Table 3
Pure Water Attack

<table>
<thead>
<tr>
<th>Heads</th>
<th>pH</th>
<th>Copper Conc.</th>
<th>Tails</th>
<th>pH</th>
<th>Iron Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure water</td>
<td>5.6</td>
<td>1 ppm.</td>
<td></td>
<td>5.9</td>
<td>none detected</td>
</tr>
</tbody>
</table>

The rate of leaching of 1 ppm. for pure water attack provides a convenient value for comparison purposes with the rate of leaching caused by sulphuric acid and ferric sulphate solutions.

Sulphuric Acid: (Diagram 7) Increasing concentrations of sulphuric acid were used. Each solution was ten times as strong as the one preceding it.

Table 4
Sulphuric Acid Attack

<table>
<thead>
<tr>
<th>Heads</th>
<th>Concentration</th>
<th>pH</th>
<th>Copper Conc.</th>
<th>pH</th>
<th>Iron Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0001N</td>
<td>4.2</td>
<td>4 ppm.</td>
<td>5.2</td>
<td>not detected</td>
<td></td>
</tr>
<tr>
<td>.001N</td>
<td>3.1</td>
<td>33</td>
<td>4.3</td>
<td>N.D.</td>
<td></td>
</tr>
<tr>
<td>.01N</td>
<td>2.2</td>
<td>33</td>
<td>2.5</td>
<td>2ppm.</td>
<td></td>
</tr>
<tr>
<td>.1N</td>
<td>1.4</td>
<td>34</td>
<td>1.7</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>1.0N</td>
<td>.7</td>
<td>35</td>
<td>1.0</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
CONCENTRATION OF THE HEADS

Copper Extracted in Gammas (1x10^-6 gr.)

Conc. of Copper in ppm.

Rate of Flow in ml./hr.

Total Volume in Litres

Diagram 7. Graph of Sulphuric Acid Attack
Increasing the acidity was effective up to a concentration of .001N, after which a further increase had practically no effect.

Beyond the effective limit, further increase in the concentration of the heads solutions causes an initial increase in the rate of leaching but it returns to the 30 to 35 ppm. level within a few days. These initial higher rates, after a change in the heads, may possibly be accounted for by either of the following explanations.

(a) In the dissolution of the copper sulphides, copper oxide forms on the sulphides as an intermediate product and accumulates as a backlog. By increasing the strength of the heads, the copper oxide would be more readily attacked than the sulphides, thereby creating a high concentration of copper in the tails. This phenomenon is best illustrated in the change from a .001N to a .01N solution. Here, the copper concentration rises from 33 to 130 ppm, but soon returns to the 33 ppm. level. The overall effect becomes less noticeable for further increases of acidity as the stronger solutions react with the copper oxide and prevent the accumulation of an appreciable backlog.

(b) The sericite and chlorite absorb copper ions which are released by an increase in the strength of the solutions.

The negligible reactivity of sericite and chlorite plus the experimental observations favours the first explanation as being the most plausible.

Quantitatively, the increment in the rate of
leaching caused by a change in the heads is significant. This is shown in the graph by the sharp rise in the extraction curve at the point where the heads are increased.

The acidity of the tails remained less than that of the heads regardless of the strength of the heads. This bears witness to the importance of sulphuric acid in converting the ferrous sulphate into the ferric form.

The effective limit appears to be somewhere between .001N and .01N. It is suspected to be closer to the former because of the large increment in the rate of the leaching when proceeding from the lower to the higher of these concentrations.

The relation of the concentration of sulphuric acid in the heads to the rate of leaching is shown in diagram 8.

![Diagram 8](image_url)

**Diagram 8.** Relation of the concentration of Sulphuric Acid in heads to the rate of leaching.
**Ferric Sulphate** (Diagram 9.) The strength of the ferric sulphate solutions was increased by factors of five and two alternatively. There were two reasons for this procedure. Firstly, the influence of ferric sulphate on the rate of leaching warranted intermediate concentrations as well as the multiples of ten. Secondly, the .005M solution was the lowest stable concentration. Consequently, the resultant concentration values of ten and five were used for the rest of the experiment.

The yellow to brown colour of the ferric sulphate solution is due to its hydrolysis. Abegg (1930) p. 134, states that the colour vanished on adding sufficient acid. For purposes of comparison, the concentrations of the iron in the heads and tails are determined by the dipyridyle method, and may differ from the theoretical concentrations, probably because of hydrolysis.

The .001M solution gradually hydrolized (equation 1c) and became consistently weaker with a corresponding decrease in the rate of leaching. The precipitated iron hydroxide caused the plugging of the feeder capillary with the result that the rate of flow was extremely erratic.

Increasing the concentration five times to .005M increased the rate of leaching three to five times. The tails became a faint blue colour due to the concentration of copper sulphate. Powder x-ray diffraction confirmed the copper sulphate to be in the form of chalcanthite.
## Table 5
Ferric Sulphate Attack

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>.001M</td>
<td>pale yellow</td>
<td>2.9</td>
<td>300 ppm.</td>
<td>115 - 70 ppm.</td>
<td>colourless</td>
<td>3.5</td>
<td>N.D.</td>
</tr>
<tr>
<td>.005M</td>
<td>orange brown</td>
<td>2.6</td>
<td>500</td>
<td>330</td>
<td>pale blue</td>
<td>2.9</td>
<td>N.D.</td>
</tr>
<tr>
<td>.01M</td>
<td>brown</td>
<td>2.4</td>
<td>750</td>
<td>610</td>
<td>blue green</td>
<td>2.7</td>
<td>20</td>
</tr>
<tr>
<td>.05M</td>
<td>medium brown</td>
<td>2.0</td>
<td>1000</td>
<td>170</td>
<td>medium brown</td>
<td>2.0</td>
<td>1000</td>
</tr>
<tr>
<td>.1M</td>
<td>dark brown</td>
<td>1.88</td>
<td>1500</td>
<td>130</td>
<td>dark brown</td>
<td>1.8</td>
<td>1500</td>
</tr>
</tbody>
</table>
Diagram 9. Graph of Ferric Sulphate Attack

Concentration of the Heads

Conc. of Copper in ppm.

Rate of Flow in ml./hr.

Copper Extracted in Gammas (1x10^-6 gr.)

Total Volume in Litres
Doubling the concentration of the heads approximately doubled the rate of leaching. The concentration of 610 ppm. of copper in the tails is almost the same as the average concentration of the heads at the Britannia copper plant. The tails became a dirty green colour indicating that some of the hydrolized ferric sulphate was passing through the ore without reacting. The concentration of the ore was so low that its colour was masked by the blue copper sulphate, and could not be determined.

Increasing the concentration still further by a factor of five caused a sudden decrease in the rate of leaching to one-quarter of the former value. At the same time, the tails were a dark brown colour almost identical to that of the heads. The concentration of iron in the tails was about 1,000 ppm., the same as that detected in the heads.

Doubling the strength of the heads decreased the rate of leaching even more. The tails were the same colour as the heads and the iron content of both was 1,500 ppm.

In attacking the sulphides, the ferric sulphate did not increase the acidity at any stage in the experiments. A similar observation was made by Nishihara (1914) in studying the chemical effects of various minerals on ferric sulphate solutions.

The effectiveness of ferric sulphate in the heads can be seen by comparing the pH’s, colour and iron concen-
trations of the heads and the tails. In concentrations below .01M, there was an appreciable decrease in the acidity of the tails. However, with a lower rate of leaching under the stronger attack there was no difference, indicating that little, if any, of the sulphuric acid in the heads was consumed in the reactions beyond the effective limit.

Since the brown colour of the solutions is due to the concentration of iron, these two factors may be considered together. The colourless to blue tails below the effective limit are in marked contrast to the yellow to brown heads. This provides evidence of iron entering into the reactions with the sulphides. Above the effective limit, the heads and tails are essentially the same colour, indicating that the solutions have passed through the ore with little reaction taking place.

The effective limit of ferric sulphate is approximately .01M after which, an increase is no longer effective and, on the contrary, causes a decrease in the rate of leaching. The colour of the tails suggests that the actual effective limit would be slightly lower than the .01M value. The relationship of the concentration of the heads and the rate of leaching, as shown in diagram 10, indicates that maximum leaching occurs at a concentration of about .01M, on either side of which is a rapid decrease. In contrast to
that of sulphuric acid, the effective limit of the ferric sulphate attack is of critical chemical importance.

Diagram 10  Relation of the concentration of ferric sulphate in the heads to the rate of leaching.

The effect of the ferric sulphate heads are shown in diagram 10. In contrast to the rate of leaching curve which has a maximum, the efficiency curve has a gradual decrease with an increased concentration in the heads. Below the effective limit, the rate of leaching is increasing and the efficiency is gradually decreasing. This indicates that, although the iron remaining in the ore has lowered the efficiency of the ferric sulphate, it has not prevented the more concentrated solutions from reacting faster with the sulphides. Above the effective limit, iron seriously
efficiency retards the rate of leaching with the result that both the efficiency and the rate of leaching abruptly decrease. The effective limit, therefore, is not only of critical chemical importance but also of practical importance.

**Constant Sulphuric Acid Plus Ferric Sulphate:** (Diagram 12.)

In order to investigate whether or not sulphuric acid would increase the rate of leaching of a given concentration of ferric sulphate, a constant concentration of sulphuric acid was added to increasing concentrations of ferric sulphate.
Table 6
Constant (.01N) Sulphuric Acid Plus Ferric Sulphate Attack

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>.001M</td>
<td>pale yellow</td>
<td>2.3</td>
<td>300 ppm.</td>
<td>105 ppm.</td>
<td>faint blue</td>
<td>3.0</td>
<td>N.D.</td>
</tr>
<tr>
<td>.005M</td>
<td>orange yellow</td>
<td>2.2</td>
<td>500</td>
<td>320</td>
<td>light blue</td>
<td>2.5</td>
<td>N.D.</td>
</tr>
<tr>
<td>.01M</td>
<td>brown</td>
<td>2.1</td>
<td>750</td>
<td>580^1</td>
<td>blue green</td>
<td>2.4</td>
<td>15</td>
</tr>
<tr>
<td>.05M</td>
<td>medium brown</td>
<td>2.0</td>
<td>1000</td>
<td>350</td>
<td>green brown</td>
<td>2.2</td>
<td>400</td>
</tr>
<tr>
<td>.1M</td>
<td>dark brown</td>
<td>1.8</td>
<td>1500</td>
<td>170</td>
<td>dark brown</td>
<td>1.8</td>
<td>750</td>
</tr>
</tbody>
</table>

^1 Note: an unusually low mean temperature probably accounts for the discrepancy between this value and the 610 value of the .01M ferric sulphate without sulphuric acid.
Diagram 12. Graph of constant sulphuric acid plus ferric sulphate attack.
In the .001M ferric sulphate solution, the sulphuric acid prevented hydrolysis (see equation 1c) with the result that the rate of leaching remained at 100 ppm. This rate is the one observed in .0001M ferric sulphate without sulphuric acid before it started to hydrolize. The relatively large decrease in the acidity of the tails bears witness to the consumption of the sulphuric acid in reacting with ferrous sulphate and possibly ferric hydroxide to form ferric sulphate (equations la and lc).

The rate of leaching for the .005M and .01M ferric sulphate plus sulphuric acid is in the same order of magnitude as for the same concentrations of ferric sulphate without sulphuric acid. The extra sulphuric acid appears to be of no consequence. Therefore, there must have been sufficient sulphuric acid generated by the sulphides and by the ferric sulphate to react with the ferrous sulphate produced.

In the .05M ferric sulphate plus .01N sulphuric acid, the rate of leaching was roughly double the one of the same strength of ferric sulphate without any acid (diagram 10). This implies that the sulphuric acid has reduced the amount of ferric, and possibly ferrous, sulphate reacting with water to form iron hydroxide. Evidence of this is seen in the difference between the acidity of the heads and tails when sulphuric acid is present in the .1M ferric sulphate solution, as compared to no difference in the same solution without sulphuric acid. The colour of the tails when sulphuric acid...
is present is yellow green, indicating the presence of only a small amount of iron. This is opposed to the dark brown of the tails in the ferric sulphate without sulphuric acid attack.

The sulphuric acid is effective only when added to ferric sulphate solutions which are too dilute or too strong. In the former, it reacts directly in the heads to prevent or retard the hydrolysis of the ferric sulphate (equation lc). In the latter, it retards the precipitation of iron hydroxide on and in the sulphides, and may react with ferrous sulphate to form ferric sulphate and water (equation la) rather than ferric sulphate and ferric hydroxide (equation lb). By increasing the rate of leaching, the sulphuric acid similarly increases the efficiency of the ferric sulphate. The effect of the sulphuric acid is seen in the curves in diagram 10, and in comparing the graphs in diagrams 9 and 12. The trends of the curves and graphs are similar with a slight difference only in their order of magnitude.

Constant Ferric Sulphate Plus Sulphuric Acid: The following experiment was carried out in order to confirm the fact that ferric sulphate and NOT sulphuric acid was the vital reagent in determining the rate of leaching. A constant concentration of ferric sulphate was added to a decreasing concentration of sulphuric acid. To best illustrate the purpose of the experiment the concentrations of both the re-
Table 7

Constant (.001M) Ferric Sulphate Plus Sulphuric Acid

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>.01N</td>
<td>pale orange</td>
<td>2.3</td>
<td>300 ppm</td>
<td>96 ppm</td>
<td>colourless</td>
<td>2.5</td>
<td>N.D.</td>
</tr>
<tr>
<td>.001N</td>
<td>yellow</td>
<td>2.8</td>
<td>300</td>
<td>88</td>
<td>colourless</td>
<td>3.2</td>
<td>N.D.</td>
</tr>
<tr>
<td>.0001N</td>
<td>pale yellow</td>
<td>2.9</td>
<td>300</td>
<td>88</td>
<td>colourless</td>
<td>3.3</td>
<td>N.D.</td>
</tr>
</tbody>
</table>
agents should be below the range of their effective limits. The concentration of ferric sulphate was taken as low as possible to ensure the greatest sensitivity to additions of sulphuric acid. The .001M solution was used because it was the lowest concentration that would be comparable to the other experiments. The concentrations of sulphuric acid were decreased from just above their effective limit of .01N down to .0001N (the lowest used in the other experiments).

The copper concentration remained in approximately the same order of magnitude throughout the entire experiment as compared to the respective concentrations of 4,33 and 33 ppm. copper in the sulphuric acid attack without ferric sulphate. The relative acidity suggests that the ferric sulphate consumed sufficient acid to prevent it from hydrolyzing after which, the concentration of sulphuric acid was immaterial. The slightly higher rate of leaching in the .01N solution may be due to the lower average temperature during the period of investigation.

The observations indicate that, when sulphuric acid is present in the heads, its concentration determines the rate of leaching regardless of the concentration of the sulphuric acid.
DISCUSSION OF THE RESULTS

The absolute concentrations of copper in the tails are all relative to a concentration of 1 ppm. under a pure water attack at a rate of flow of 8 ml./hour in the specified apparatus.

The leaching of copper by pure water is considered to be the result of the oxidation of pyrite to sulphuric acid and ferric sulphate which in turn react with the copper sulphides.

Weak sulphuric acid solutions (.001N) increase the rate of leaching 30 to 35 times. Stronger solutions have little, if any, effect and the efficiency of the sulphuric acid decreases rapidly. Sulphuric acid increases the rate of leaching by accelerating the conversion of the intermediate copper oxides into soluble copper sulphate. It also ensures the oxidation of ferrous sulphate to the potent ferric form without any ferric hydroxide precipitating. When added to ferric sulphate solution, the concentration of ferric sulphate and not sulphuric acid determines the rate of leaching. Sulphuric acid is effective in preventing hydrolysis only when added to ferric sulphate solutions which are too dilute or too concentrated.

Weak ferric sulphate solutions (less than .01M) have a tremendous effect on the rate of leaching by increasing
it up to 600 times. Further increases above the effective limit of .01M cause an abrupt decrease. Ferric sulphate is the key reagent in determining the order of magnitude of leaching. The relation of the concentration of the heads, the rate of leaching and the concentration of the iron in the tails does not suggest the simple chemistry of iron as expressed by the equations in Chapter IV. The difference between the concentrations of iron in the heads and tails in attacks below the effective limit suggests that most of it must have remained in the ore column, presumably in the hydrate form. If such is the case, the rate of leaching would be expected to steadily decrease with an increased ferric sulphate concentration in the heads. On the contrary, it increases to a maximum and then abruptly decreases. The problem then, is to account for the role of iron in the leaching processes and its disappearance.

The chemistry of iron sulphates and hydrates is extremely complex and not fully known. The manner in which iron participates in the leaching processes is a complicated series of reactions and interreactions among the different iron compounds, sulphides and other reagents in the solutions.

Anderson and Cameron (1926) believe that many erroneous concepts of what may be occurring in the leaching of an orebody have resulted from confusion regarding the iron phenomenon. They state:
It is assumed that ferrous sulphate is hydrolized in solution, which is true; that oxygen is absorbed and converts the hydrolized ferrous hydrate to ferric hydrate, which is true; and that the ferric hydrate then precipitates, which is not true, as one may quickly learn by trying the experiments under controlled conditions in the laboratory.

The stability fields of the system $\text{Fe}_2\text{O}_3 - \text{SO}_3 - \sqrt{n}\text{H}_2\text{O}$ investigated by Tunnell and Psnjak (1931) apply only to oxidation of pyrite in the presence of a given quantity of water and in the absence of other substances except inert gangue. They cannot be used in mixed sulphide ores, and are not applicable to the thesis discussion.

In view of the limited number of influences investigated and taking all factors into consideration, the writer offers the following hypothesis to explain the observed phenomenon. The ferric sulphate in the heads reacts with the sulphides to form considerably more ferrous sulphate than sulphuric acid. (equations 7,8,9 and 13). Some of the ferrous sulphate may be oxidized by sulphuric acid and reform ferric sulphate (equation 1a) but because of the lack of sufficient sulphuric acid, most of it reacts with the dissolved oxygen to form ferric sulphate and ferric hydrate (equation 1b). At the time that ferric hydrate is forming, the ferric sulphate reacts with the sulphides to produce more ferrous sulphate and sulphuric acid. The iron compounds and sulphuric acid enter into a complex system of interreactions in which there is a cycling of the iron from one form to another (ferric to ferrous sulphate to ferric
hydrate to ferric sulphate). The hypothetical ferric hydroxide, reversibly soluble in sulphuric acid, that has hydrolized in the heads enters into this "iron system".

At some step in the cycle, the hypothetical ferric hydrate Fe(OH)$_3$ turns into some form of FeO-OH which is insoluble in dilute sulphuric acid, and is, consequently, removed from the cycle. The sulphuric acid generated at the interface through oxidation of the sulphides dissolves some of the soluble ferric hydrate and removes it, thereby exposing the surface to further reaction with the ferric sulphate. The iron that remains cycling at the interface of the sulphides does not mechanically hinder the catalytic effect of the ferric sulphate and the rate of leaching is not affected. That is, the efficiency of the ferric sulphate is not seriously hindered by the iron hydrate.

Above the effective limit more ferric sulphate is added to the solutions than can react with the sulphides. As a result, it cannot enter into the 'iron system' and considerably more iron is left behind than corresponds to the copper being leached. The ferric sulphate produces ferric hydroxide (equation lc) which coats the sulphides and plugs their pores. Consequently, the iron cycle is disturbed, the needful contact between solvent and sulphide is reduced and most of the iron remains in the hydrate form. The large amount of hydrate reduces the surface area and hinders diffusion thus, causing a rapid decrease in the
rate of leaching. The iron that has hydrolyzed in the heads has no opportunity to enter the 'iron system' and, therefore, passes through the ore column and into the tails where it imparts a brown colour similar to that of the heads. The efficiency relationship suggests that iron is being continually removed from the iron cycle but only in significant amounts for concentrations above the effective limit.

When sulphuric acid is added to the heads above the effective limit, it retards the hydrolysis of ferric and ferrous sulphate. By doing so, it decreases the precipitation of ferric hydroxide from ferric sulphate in the 'iron system' and the rate of leaching is not so drastically reduced. The influence of sulphuric acid on ferric sulphate solution is shown in diagram 10.
CHAPTER IX

ECONOMIC SIGNIFICANCE OF THE RESULTS

The results suggest that the rate of leaching of ores in place may be considerably increased by attacking them with solutions containing sulphuric acid and ferric sulphate. The concentrations of these reagents in the leaching solutions would have to be carefully controlled, otherwise they might lead to results contrary to those desired. Both economic and chemical consideration should be given to deciding what concentrations of these reagents should be used in the leaching solutions. The experimental results indicate that beyond the effective limits of both sulphuric acid and ferric sulphate the efficiency rapidly decreases. Therefore, concentrations above this value would be of little practical advantage.

Leaching with sulphuric acid alone has only an economic significance because above the effective limit, further increases in acidity have little, or no, effect on the rate of leaching. Hence, the amount of sulphuric acid added to the leaching solutions would be determined by the cost of the reagent in comparison to the increased leaching. The results suggest that in attacking copper sulphide ores in which there is very little secondary enrichment, the efficiency of sulphuric acid would not be great enough to
warrant its addition to the leaching solutions. However, in ores carrying appreciable quantities of copper oxide minerals, sulphuric acid would be expected to increase the rate of leaching and might prove to be of economic importance.

When ferric sulphate is used as the leaching reagent, it must be given careful chemical consideration before even the economic factors are weighed. Adding too much ferric sulphate abruptly decreases the rate of leaching and might destroy the entire leaching operation. Also, allowance must be made for the amount of iron produced by the dissolution of the sulphides. Therefore, in adding ferric sulphate to the leaching solutions, the concentrations must be kept far enough below the effective limit to provide a safety margin for the increasing iron content. Tobelmann and Potter (1919) in discussing the leaching operations at the New Cornelia Copper Company, emphasize the fact that ferric iron in solution must be kept low for successful treatment of mined ore.

In order that the concentration of iron in the solutions is kept low enough to prevent it from hydrolyzing, an adequate supply of sulphuric acid is required. The concentration of sulphuric acid is, therefore, an important consideration in the leaching of ores with ferric sulphate and the two are inseparable. A sufficient supply of sulphuric acid safeguards against any undesired consequences caused by the hydrolysis of ferrous or ferric sulphate. In dis-
cussing the effects of the formation of iron hydroxide, Anderson and Cameron (1926) state:

but catastrophe it might be if the precipitation were long continued, hence, the wisdom of not taking the chance and removing the possibility.

The question of what concentrations to use is a difficult one and the answer varies with each particular situation, especially with different types of ores. Scott (1951) gives some concentration figures when describing a method of leaching non-pyritic copper sulphide ores in place by recycling the mine waters. The recirculated water is characterized by the amount of iron being less than 10 grams/litre and sulphuric acid is added until the solution, after having passed through the ore, has a pH of not greater than two. In the case of pyritic ores, the concentrations of the added reagents would have to be adjusted to take into account the amounts produced by the pyrite.

The mine waters, having percolated through the ore, contain appreciable quantities of iron and, hence, they afford a source of ferric sulphate. In extracting the copper from the water, the iron is reduced to the ferrous form and must be converted back to the ferric form if it is to be re-circulated. This could be accomplished in several ways. Scott's method is to collect the waters in a "pond" having the largest surface area possible per unit volume of solution and by exposing it long enough to the atmosphere, oxidize it to the ferric form. The excess iron will precipitate as
hydroxide and may be removed. In cases where all the ferrous iron is to be converted to the ferric form, sulphuric acid may be added to the solutions. The places where additions of ferric sulphate and sulphuric acid solutions seem most practical are:

(a) at the surface in order that the mine water will immediately be a potent leaching solution, and not first have to react with pyrite to form sulphuric acid and ferric sulphate.

(b) in sections of the mine where the volume of water is either too small or not potent enough to appreciably leach the sulphides.

The recycling of the mine waters offers an interesting possibility. The iron content of the tails of the copper plant may be oxidized to the ferric sulphate form and, hence, provide a ready source of ferric sulphate.

It must be emphasized that, although the laboratory results establish the relative importance of some of the factors influencing the rate of leaching, their absolute values are not necessarily applicable to actual mining situations. These absolute values are relative only to the specified experimental technique and consequently, application of them would depend on how closely the technique simulates the actual mine conditions. Small scale results are not conclusive evidence of large scale results because of the time factor and the difficulty in reproducing large
scale conditions. It is difficult to assess how closely the results would hold in field conditions, and this could only be verified by putting them into actual practice. However, the fact that concentrations paralleled those observed at the Britannia Mine suggests that the experimental technique has reasonably simulated field conditions.

It should be noted that economic failure of attempts to artificially leach copper ores in place at Ray, Arizona, offers evidence that application of laboratory results does not necessarily indicate their feasibility under natural conditions.
CHAPTER X

GENERAL CONCLUSIONS

An experimental technique was established and the relative importance of some factors influencing the rate of leaching of the Britannia copper ore were determined. The technique and results may be used as a basis for further experimental investigations.

The technique proved to be satisfactory in measuring the rate of chemical reaction, in giving reproducible results within the limits of control, and in duplicating some concentrations observed at the Britannia Mine. In applying the technique to future work some refinements, especially with regard to the rate of flow, may be necessary if precise work is required.

The results are relative to the standard experimental conditions and must, therefore, be interpreted with this in mind. Leaching, under standard conditions with pure water at a rate of flow of 8 ml. per hour gives a copper concentration of 1 ppm. in the spent solutions.

The chemical character of the attacking solutions was the key factor in determining the rate of leaching. Ferric sulphate was the key reagent. It increased the rate of copper leaching up to 600 times that of pure water. The
optimum copper removed from the ore occurred at a ferric sulphate concentration of .01M. This concentration was of critical value because on either side, there was an abrupt decrease in the rate of leaching.

Sulphuric acid in the attacking solutions increased the rate of leaching up to 33 times that of pure water. The rate increased with increased acidity up to a .001N solution, after which further increases in acidity had little, or no, effect.

Adding sulphuric acid to ferric sulphate solutions which were too dilute or too concentrated, slightly increased their rates of leaching.

Changes in the rate of flow were of secondary importance, and determined the range of fluctuations in the rate of leaching around an order of magnitude dependent on the chemical character of the attacking solutions.

The ratio of chalcopyrite to pyrite was important in determining the rate of leaching. In general the ore with the greater concentration of pyrite was more readily attacked, and was less sensitive to changes in the rate of flow. The influence of pyrite became less significant when the ore was attacked by sulphuric acid and/or ferric sulphate solutions.

The investigation has established the importance of the oxidation of pyrite in the natural leaching of
copper mineralization to form sulphuric acid and ferric sulphate.

Temperatures within the range of 5°C to 25°C did not seriously effect the rate of leaching.

Difference in the size of the ore particles varying from 1.5 to 7 mm. in diameter had little, if any, effect on the rate of dissolution of the sulphides.

The results suggest the possibility of increasing the rate of leaching of copper sulphides ores in-place by attacking them with solutions of sulphuric acid and/or ferric sulphate. Such solutions may be obtained by recirculating the mine waters after the copper has been extracted from them. The fact that considerable quantities of ferric hydroxide were precipitated in the leaching processes was evidence that it would be an important factor in any human attempt to increase the rate of leaching of ores in place by attacking them with ferric sulphate.
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