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THE CEMENTING OF HYDRAULICALLY PLACED TAILING FILL BY THE OXIDATION PRODUCTS OF PYRRHOTITE

BY

STANLEY H. ALDER — 1934

A

THESIS

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ABSTRACT

This thesis has been prepared to make available basic information on the use of the oxidation products of pyrrhotite to cement hydraulic tailing stope fill.

As nothing has been published on this subject to date, a review has been made of pertinent information culled from accounts of work in related fields. From this study, a set of equations representing the most likely pyrrhotite oxidation reactions has been evolved and tests supporting these equations performed.

Samples of fill, each containing from one to six percent of pyrrhotite, were cemented in the laboratory. They were then examined microscopically, subjected to unconfined compressive strength tests and assayed.

Bonding of these samples is shown to be effected by a matrix of iron oxides mixed with iron sulphates. The main factors governing the strength of the final cemented fill are shown to be: the quantity of pyrrhotite oxidized, the stage to which its iron oxides hydrate and the particle size distribution and chemical composition of the tailing.

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I. INTRODUCTION

Hydraulic tailing fill (H.T.F.) is usually piped to the working place as a slurry of mill tailing, make-up pit sand and water containing about 70% solids.

After draining, the H.T.F. mass retains approximately 10% of its water which holds the grains lightly together by capillary tension. This bond, however, is very weak and the fill tends to yield and shrink and will not support itself vertically.

Yielding and shrinkage of a fill material causes an excessive load to be placed on the pillars which may tend to fracture heavily and cause:

1. Difficult drilling conditions.
2. Inability to use taper-fit detachable bits.
3. Inability to use cheap AN-FO explosives.
4. Poor eye bolt anchorages.
5. Ground fall hazards.

The inability of a mass of stope fill to support itself vertically causes:

1. Dilution of pillar ore.
2. Dangerous runs of fill and rock at pillar sides.
3. Lack of support at pillar edges.
4. Increase in quantity of gobbing required.
5. The necessity of building fill fences next to pillars prior to each pour of fill in the stope.

From the aforementioned, it is seen that the use of non-cemented hydraulic fill may limit the choice of pillar mining methods to those requiring heavy timbering such as square-set and undercut-and-fill.

Conversely, in some instances, if the hanging walls of adjacent stopes were better supported by cemented hydraulic tailing fill (C.H.T.F.), cheaper mining methods might be substituted for winning the pillars.

In these cases, mining cost would be reduced provided no more was spent on cementing the fill than was saved by adopting the cheaper mining method. The mines concerned would also have greater overall stability and the pillars would be mined out more quickly.

As an example, assume an ore body of width 60 feet and density 10 cubic feet per ton currently being mined with 90 foot cut-and-fill stopes and 30 foot square-set pillars. If stope fill cementation allowed the pillars to be recovered by cut-and-fill mining, about $3.50 per ton would be saved in pillar mining cost. If the pillars were 145 feet high on plane of reef, approximately $90,000 would be saved per pillar.

If the tailing fill weighed 100 lb. per dry cubic foot, up to $2.33 could be spent to cement each ton of tailing.

The author agrees that the above example is rather spectacular but points out that even if H.T.F. cementation did not permit a cheaper pillar mining method to be used it would still save money.

In working places of the aforementioned dimension, for example, approximately $3,500 would not be spent in building fill fences and, taking the average thickness of fill between pillar wall and fence to be 6", 435 tons of fill would not have to be reprocessed. In addition, blocking would be easier and working conditions safer.

A. Hydraulic Tailing Fill Cementing Materials

The qualities most valued in an H.T.F. cement are low price per unit of strength produced, simplicity of use, ability to set in a reasonably short time and freedom from offensive side effects such as evolution of gas and corrosive liquids.

Cementing materials known to have been tried are pyrrhotite, Portland Cement and lime. Little information is available on efforts to cement H.T.F. with Portland Cement and lime and neither will be dealt with in this paper.

The author's interests lie in the use of pyrrhotite, which is a waste product in many mines, to cement H.T.F.

B. Purpose of the Investigation

This paper is produced in an attempt to aid those who would like to experiment with the use of pyrrhotite to cement H.T.F. but feel handicapped by the lack of basic information on the subject.

To do this, a review is made of pertinent literature and laboratory-scale experiments are performed in an effort to produce some relationship between the quantity of pyrrhotite used and the strength of the C.H.T.F. produced.

II. REVIEW AND DISCUSSION OF LITERATURE

Pyrrhotite and Pyrite have long been used for cementing fill by Noranda Mines Ltd.[1], Quemont Mining Corp. Ltd. and Consolidated Mining and Smelting Company of Canada Ltd. (Cominco). Pyrrhotite (FeS) is used in preference to pyrite (FeS_2) as it contains less sulphur and therefore produces less sulphur dioxide and acid water when it oxidizes.

To oxidize, and cement fill particles together, pyrrhotite needs both oxygen and water. This is illustrated by the fact that, when finely ground, it can be kept fresh as a dry powder in a dry atmosphere or as a water slurry filling a sealed jar. If the same slurry is kept in an open jar it turns light brown and becomes very hard as the water evaporates.

Noranda currently uses a stope fill composed of 72% granulated slag, 25% dump slag and 3% pyrrhotite tailing. The tailing contains 56% pyrrhotite and 6% pyrite. This mixture takes less than three months to set in cut-and-fill stopes.

Cominco has used -1" material, from its sink-and-float plant, coated with 5% iron concentrate tailing and 2 1/2% moisture. The tailing, composed of 66% pyrrhotite and 12% pyrite, cemented the fill in six months.

It should be noted here that the mechanically placed fill material in each of the above examples is coarse enough to allow air to flow freely through the fill mass.

Hydraulically placed fill is fine as shown by the following screen analysis; the uneven size distribution noted in this sample is due to the addition of pit sand to the finer mill tailing.

Screen Size	% of Sample
+ 40	2.6
+ 60	13.3
+ 80	12.0
+ 100	9.7
+ 200	32.3
+ 325	24.0
- 325	5.9
	99.8

It is readily noted that, should pyrrhotite be added to hydraulic fill of such low porosity as the above, seven inches per hour, it would take many years to oxidize naturally due to lack of oxygen.

This is confirmed by the experience of one company which, in 1964, mined against fill poured in 1959. The fill, which originally contained 9% pyrrhotite, was found to have cemented itself together for a distance of three feet from the stope walls. This would appear to show that there was a greater supply of oxygen next to the stope walls than in the centre of the mass. This in turn, indicates the presence of a gap or gaps between fill and walls due to fill shrinkage and/or blasting vibration compaction and/or percolation channels.

The aforementioned suggests that, when full-scale cementation of H.T.F. is attempted using pyrrhotite, the deoxygenated air in the fill mass will have to be replaced at frequent intervals. This could be most easily accomplished by pushing it out with compressed air from pipes buried in the fill at points dictated by stope geometry.

During initial full scale trials of H.T.F. cementation using pyrrhotite, a water line might be connected to the air pipes. This would enable any "hot spots" producing sulphur dioxide to be cooled and would absorb the highly soluble gas.

Thermocouples could be made and installed cheaply in the fill. If connected to and read in the cribbed manway raise, the taking of readings would not interrupt work in the stope.

As 80 volumes of sulphur dioxide dissolve in 1 volume of water at 0°C, damp fill could conceal the development of a hot-spot caused by the exothermic oxidation reaction until it is well established. Regular fill temperature measurements would be good insurance against development of too much heat.

These procedures might also ease the experimental pour proposal past objections stemming from zealous safety-consciousness.

Precautions should also be taken to allow as little pyrrhotite as possible to escape from the stope and to minimize segregation. Keeping the fill around cribbed raises above the general water level in the stope will cut down pyrrhotite loss. Segregation can be reduced by pouring in many points simultaneously or by frequently changing the point of discharge of a single fill hose.

A. The Chemical Reactions

It has not yet been determined conclusively just how pyrrhotite effects the cementing of fill.

F. E. Patton[1] states:

> No definite conclusions have been made as to the cementing action. Polished sections of backfill have shown the presence of iron oxide at the surface of the slag particles. Dilute acid is generated by oxidation and its action on the slag may form a cementing product.

Cominco Staff[2] states:

> Oxidation of the sulphides cements the float but produces $S0_2$ fumes, heat, acid drainage water and low oxygen content in the stope.

Only one brief note could be found on the oxidation reaction of pyrrhotite. This was written in connection with oxidation and supergene enrichment of ore bodies by A. M. Bateman[3] who states:

> Most metallic mineral deposits contain pyrite. This mineral under attack readily yields sulphur to form iron sulphate and sulphuric acid; pyrrhotite does the same.

Many **papers**[4] have been produced concerning the conversion of pyrite to ferric hydroxide in connection with research into stream polution by acid mine waters. One of the more succinct accounts is presented by Brant and Moulton[5] as follows:

> Step I: Sulfide to Sulfate
>
> When natural sulfuritic material in the form of sulfide, and usually in combination with iron, is exposed to the atmosphere (oxygen) it may theoretically oxidize in two ways with water (or water vapor) as the limiting condition. In the first circumstance, assuming the process takes place in a dry environment, an equal amount of sulfur dioxide will be generated with the formation of iron (ferrous) sulfate, thus:
>
> (1) $\mathrm{FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2}$
>
> Iron sulfide + oxygen → ferrous sulfate + sulfur dioxide
>
> If however the oxidative process proceeds in the presence of a sufficient quantity of water (or water vapor) then the direct formation of sulfuric acid as well as iron (ferrous) sulfate in equal parts may be anticipated, thus:
>
> (2) $\mathrm{2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4}$
>
> Iron sulfide+water+oxygen → ferrous sulfate + sulfuric acid
>
> It should be pointed out that in the great preponderance of mine environments, there is strong indication that the latter reaction is favored.
>
> Step II: Oxidation of Iron (Ferrous to Ferric):
>
> Iron (ferrous) sulfate in the presence of a sufficient quantity of sulfuric acid and

oxygen then itself oxidizes to the ferric state to form iron (ferric) sulfate.

(3) $4FeS0_4 + 2H_2S0_4 + 0_2 \rightarrow 2Fe_2(S0_4)_3 + 2H_20$

Ferrous sulfate + sulfuric acid + oxygen → ferric sulfate + water

Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Step III: Precipitation of Iron

The iron (ferric associated with the sulfate then commonly combines with the hydroxyl ion of water to form iron (ferric) hydroxide. In an acid environment iron (ferric) hydroxide is largely insoluble and accordinly precipitates.

(4) $Fe_2(S0_4)_3 + 6H_20 \rightarrow 2Fe(OH)_3 + 3H_2S0_4$

Ferric sulfate + water → ferric hydroxide + sulfuric acid

At the same time it should be pointed out that another possible reaction has been suggested in the case of iron (ferric) sulfate. From an energy standpoint the iron (ferric) ion may enter into an oxidation-reduction reaction with iron sulfide whereby the iron (ferric) ion "back triggers" the oxidation of the further amounts of sulfuritic materials (iron sulfide) to the sulfate form, thereby accelerating the acid-forming process.

The author suggests that in Step I of the oxidation of pyrrhotite, the following reactions take place.

With little water present:

(5) $4FeS + 70_2 \rightarrow 2Fe_20_3 + 4S0_2$

With ample water.

(6) $4FeS + 4H_20 + 90_2 \rightarrow Fe_2(S0_4)_3 + H_2S0_4 + 2Fe(0H)_3$

and/or

(7) $5FeS + 10H_20 + 110_2 \rightarrow FeS0_4 + 4H_2S0_4 + 4Fe(0H)_3$

Equation (6) is based on the fact that pyrrhotite is a less powerful reducing agent than pyrite. Its reducing power should be overcome if a plentiful supply of oxygen is available, permitting the formation of ferric sulphate.

E. Posnjak and H. E. Merwin[6] have shown that, when pyrite undergoes oxidation, the free acid generated tends to keep the iron in the soluble ferrous state and enables it to be removed in solution. Also that the oxidation of ferrous to ferric iron is accelerated by the presence of copper.

Thus it is apparent that for Step III to take place efficiently the pH of the solution should be above a critical value, which, in this case, is 3.5.

Bateman[7] points out that the ferrous sulphate, produced in equations 1 and 2, readily oxidizes to ferric sulphate and ferric hydroxide -

(8) $6FeSO_4 + 3O + 3H_2O \rightarrow 2\ Fe_2(SO_4)_3 + 2\ Fe(OH)_3$

He also describes Brant and Moulton's "back triggering" reaction thus:

> Ferric Sulphate is also a strong oxidizing agent and attacks pyrite and other sulphides to yield more ferrous sulphate
>
> (9) $FeS + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + S$
>
> Ferric Sulphate, in addition, changes to various basic sulphates.

The sulphur produced in reaction Number 9 is probably oxidized to sulphuric acid.

Bateman goes on to say:

> The above reactions indicate the importance of pyrite, which yields the chief solvents, ferric sulphate and sulphuric acid, and also ferric hydroxide and basic ferric sulphates. Moreover, ferric sulphate is continuously being regenerated not only from pyrite but also from chalcopyrite and other sulphides. The ferric hydroxide changes over to hematite and goethite and forms the ever-present limonite that characterizes all oxidized zones. The basic ferric sulphates, of which there are several, may be deposited as such, but generally limonite is the end product.

The reactants and products in the above equations are believed to be correct. It should be understood, however, that intermediate steps probably exist in most cases.

O. R. Grawe[8,9] states:

> The basic iron sulphates (produced by weathering of pyrite deposits) ultimately hydrolyze to goethite, limonite or hematite.

and

> The formation of goethite vs. hematite is largely controlled by temperature, acidity, and the nature of the ions present in the oxidizing solutions. Oxidation of pyrite liberates heat. This would tend to raise the temperature of the deposits and ferrous formation of hematite rather than goethite. ...The sulphate ion, with its double negative charge is capable of precipitating any ferric oxide colloid as it is formed.

Only two hydrated ferric oxide minerals are recognized, these are goethite and lepidocrocite. They have different crystal systems but share the formula $Fe_2O_3.H_2O$.

The name "Limonite" is now used to describe hydrated iron oxides with poorly crystalline characters whose real identity is not known. It is usually found as an amorphous, "earthy" material and has been given a general formula $2Fe_2O_3.3H_2O$. It is probably a mixture of ferric hydroxide and goethite.

The following table shows the various iron oxides produced by the oxidation of iron sulphides differ in chemical composition by the amount of water carried by each.

Ferric hydroxide	-	Fe_2O_3. 3 H_2O
"Limonite"	-	Fe_2O_3. 1 1/2 H_2O
Goethite	-	Fe_2O_3. H_2O
Hematite	-	Fe_2O_3

Grawe[10] states that the formation of goethite is favoured by removal of the sulphuric acid.

B. Summary of Chemical Reactions.

In dry conditions, pyrrhotite oxidizes to form sulphur dioxide and hematite

(5) $4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$

If water is present in addition to oxygen, both ferrous and ferric sulphates are formed.

(6) $4FeS + 4H_2O + 9O_2 \rightarrow Fe_2(SO_4)_3 + H_2SO_4 + 2Fe(OH)_3$

(7) $5FeS + 10H_2O + 11O_2 \rightarrow FeSO_4 + H_2SO_4 + 4Fe(OH)_3$

Ferric sulphate attacks the pyrrhotite to produce ferrous sulphate and sulphur

(9) $FeS + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + S$

The sulphur released is probably oxidized to form more sulphuric acid.

The ferrous sulphate formed in reactions (7) and (9) is oxidized to ferric sulphate and water and/or ferric hydroxide.

(3) $4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$

(8) $6FeSO_4 + 3H_2O + 3O \rightarrow 2Fe(SO_4)_3 + 2Fe(OH)_3$

If the pH of the moisture present with the reactants is above 3.5, the ferric sulphate is hydrolized to form ferric hydroxide which is precipitated by the sulphate ions and sulphuric acid which is consumed in reaction (3)

(4) $Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$

The ferric hydroxide thus deposited in the fill pores may remain unchanged or be partially or totally converted to goethite or hematite. Hematite formation is aided by heat.

Hence the products, resulting from the oxidation of pyrrhotite which can be expected to be present in C.H.T.F., are ferrous sulphate, ferric sulphate, sulphuric acid, ferric hydroxide, goethite/lepidocrocite and hematite.

C. Evidence Supporting the Suggested Reactions

The author acquired bricks of C.H.T.F. recovered from pillars being worked against old cut-and-fill stopes. The fill mass in one stope was yellow, whereas that in the other was red.

Thin sections of the yellow material showed it to contain particles of pyrrhotite. Each of these particles lay within a mass of limonite which spread around the adjacent grains of H.T.F. forming a matrix.

Thin sections of the red material showed it to be similar to the yellow C.H.T.F. but that two thirds of the mass surrounding each pyrrhotite speck was of hematite and the remaining third, that nearest the pyrrhotite, was of limonite.

Samples of cemented fill made in the laboratory from white silica sand and pyrrhotite duplicated the microscopic evidence of the thin sections made from the mine C.H.T.F. samples. These specimens were not so compact as the naturally formed examples because they contained small cavities and water/air percolation channels and because the Ottawa sand was not so well graded as the H.T.F.

It was noticed that those specimens which had been left to work long after the pyrrhotite in them had been oxidized turned pink and red. Sections showed the color change to radiate into the mass from the airways.

The above illustrates the change from ferric hydroxide to hematite.

Exhaustive x-ray diffractometer analysis of mechanically separated fine material from the specimens showed no cementing agent for the yellow C.H.T.F., thus indicating it to be amorphous, just like limonite. The red C.H.T.F. was shown to contain hematite.

Reaction (5) was verified by heating pieces of pyrrhotite and yellow C.H.T.F. In all cases much sulphur dioxide was produced and the red masses remaining gave off no hydrogen sulphide when covered with hydrochloric acid. This showed all sulphide had been oxidized.

X-ray powder patterns, using the Straumanis technique, showed the presence of ferrous and ferric sulphates in soluble extracts from the cemented masses.

The red specimens of C.H.T.F., which contained 17.3% total iron, 6.3% magnetic iron and 5.5% sulphur, were noted to be much weaker than the yellow samples which contained 18.4% total iron, 6.6% magnetic iron and 7.2% sulphur. Cylindrical specimens with diameter to height ratio of one showed their unconfined compressive strengths to be 408 psi and 1675 psi, respectively.

When burned to the red state, the yellow material was found to become weaker and the conclusion was drawn that hematite is a weaker bonding agent than hydrated iron oxides.

To test this, cylinders of the yellow C.H.T.F. were gently heated to 400°C., kept at that temperature for four hours and slowly cooled in the oven for eight hours. Their compressive strength was found to have been reduced to 1045 psi.

As the dissociation temperature of ferrous and ferric sulphates are 666°C and 480°C, respectively, this test indicates the loss in compressive strength was due to the dehydration of the limonite. Hence it is suggested that efforts should be made to ensure the temperature in a mass of cementing H.T.F. is not allowed to rise too high.

D. Microbiological Considerations

In his investigations of stream polution by acid mine water Braley[11] discovered a new bacillus, he writes:

> The un-named bacillus is capable of oxidizing ferrous iron to the ferric state at an extremely rapid rate, a rate which cannot be equalled by a strictly chemical reaction under aseptic conditions. Mine waters, or synthetic inorganic media, containing approximately 300 p.p.m. ferrous iron were completely oxidized by the bacterium in 5 days, whereas in the absence of the organism, such waters were only 48% oxidized at the end of two years.

This bacillus was later named Ferrobacillus ferrooxidans. The "catalytic" role of the bacillus is described by Braley[12]:

> Ferric sulphate also oxidizes iron sulphides to ferrous sulphate being itself reduced to ferrous sulphate at the same time. The increased amount of ferrous sulphate when now

> oxidized by the influence of bacteria furnishes a large amount of ferric sulphate, which can in turn bring into solution a large amount of the ferric sulphide. It will then be seen that the iron oxidizing bacteria responsible largely for the oxidation of ferrous sulphate to ferric sulphate, may also act as an accelerator by promoting indirectly the oxidation of insoluble sulphide to soluble iron sulphate.

E. Strength Required of C.H.T.F.

Due to the many variables affecting the strength of C.H.T.F. and to the fact that the magnitude of present and future wall pressures are known in few mines, a trial-and-error method of producing satisfactory C.H.T.F. seems preferable to any other.

Published research work gives little indication of the strength required of such a body of fill. The only lead found was in confidential experimental work using another cementing agent.

In this, a mixture, which when made under controlled conditions in the laboratory gave 30-50 p.s.i. unconfined compressive strength, was placed hydraulically underground in a full-scale test.

When the adjacent stope worked up to this C.H.T.F. it was exposed over a length of 100 feet to a height of 10 feet and appeared to stand well. Blasting of adjacent ore and repeated pounding of the scraper produced only 6" of slough.

The exposed wall showed clearly layers containing low and high amounts of bonding agent. This bonding or segregation could account for the wide range of uniaxial compression test results, namely 0-72 p.s.i.

The author made laboratory size batches of C.T.F. employing the same formula used by the original investigators and obtained compressive strengths averaging 75 p.s.i. for dry specimens and 67 p.s.i. for specimens containing 13% water.

He believes an unconfined compressive strength of 50 p.s.i. might be sufficient for applications of C.H.T.F. in which the main requirement is the ability of the material to support itself on exposed vertical faces.

III. EXPERIMENTAL WORK

A. Apparatus

The equipment consisted of 8 glass tubes, each 2' long x 3" in diameter supported vertically in a frame and heated by steam jackets.

Compressed air was fed through a regulator to a porous fish tank aerating stone from which it bubbled through heated water.

The wet air was distributed by a manifold to the top of each glass tube in which it passed through a sample of fill and was released to the atmosphere after being bubbled through a beaker of water which acted as a sight glass.

B. Fill Preparation

It was originally intended to cement mine tailing fill with the oxidation products of pyrrhotite but, on assaying the fill available, it was found to contain 8.1% total iron and 5.9% magnetic iron. It was therefore decided to substitute clean, white, Ottawa, silica sand for the tailing.

Great care was taken to ensure the only materials present in the fill samples were clear pyrrhotite concentrate, silica sand, air and water.

As silica is stable in all acid environments, except those containing hydrofluoric acid, the formation of silicates within the mix was impossible. Hence, all reaction

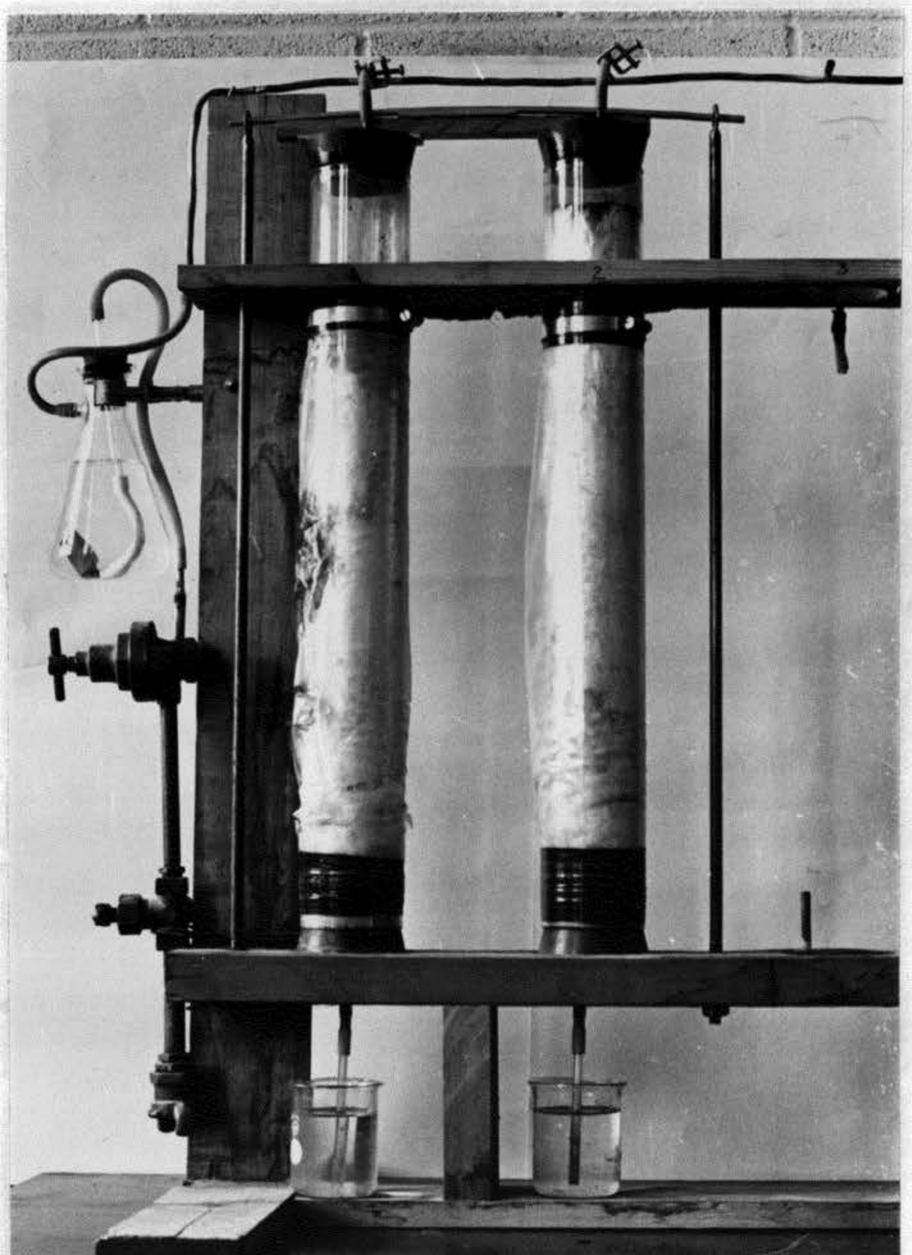

Fig. 1 Front View of Apparatus

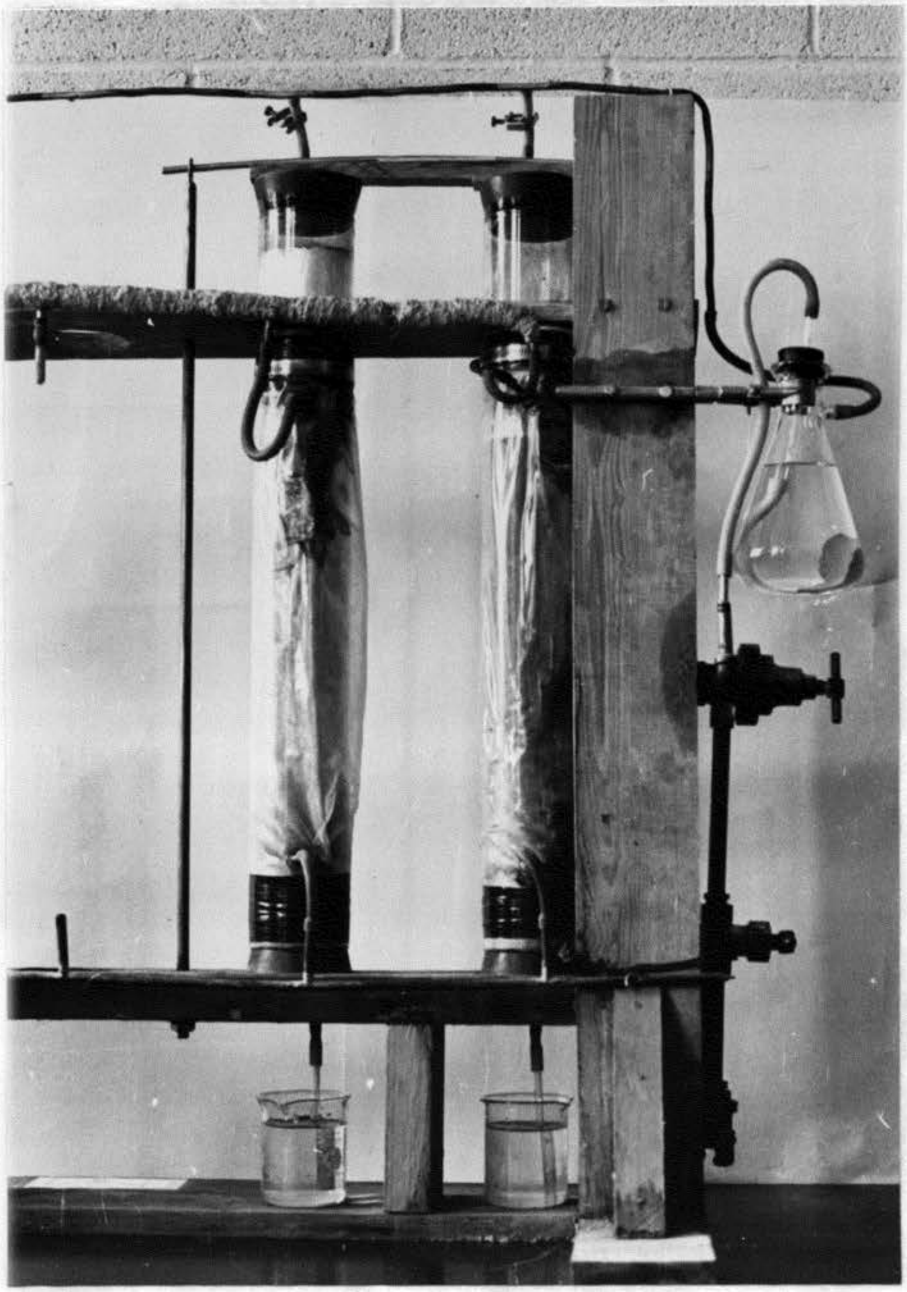

Fig. 2 Rear View of Apparatus

products formed were derived solely from pyrrhotite, air and water.

Each sample was prepared according to the following table.

Tube No.	% Pyrrhotite	Weight grams (Solid)	Volume mls. (Water)
1	1	3000	1285
2	2	3000	1285
3	6	3000	1285
4	3	3000	1285
5	6	3000	1285
6	4	3000	1285
7	5	3000	1285
8	6	3000	1285

C. Mixing Procedure

The sample of finely ground pyrrhotite was diluted by stirring it thoroughly into about 100 grams of the previously weighed sand component.

The water was then measured into a one gallon can which was clipped onto a "Hamilton Beach" milk shake mixer.

Half the remaining sand was slowly poured into the agitated water followed by the pyrrhotite/sand mixture. This slurry was allowed to blend thoroughly before the remainder of the sand was poured in.

While blending, sand was found to build up on the bottom of the can farthest from the mixing vanes. This build-up was prevented by agitating that portion of the can with a stick.

The whole 70% solids slurry was blended for two minutes then quickly taken from the mixer and poured directly into the sample tubes.

As each sample settled, its tube was tapped heavily in an attempt to consolidate the mass and to prevent the formation of percolation channels. This was later found to have been only partially successful.

D. Starting and Running The Equipment

When all tubes were filled, their upper stoppers were coated with Goodyear cement and clamped in place to prevent air leaks. After the glue had set, the damp air feed valve was turned on at low pressure to drive excess water from the fill. With this completed, a hose clamp was put on each of the rubber tubes connecting the air distribution manifold to the copper pipe passing through each top tube stopper. The beakers through which air escaped from the sample tubes were filled with water so each exhaust pipe had the same back-pressure head.

Using the emerging bubbles as guides, the hose clips were then adjusted to ensure each pipe had an equal supply of air. It was found necessary to re-adjust this air flow daily.

The steam supply was then turned on very slowly to avoid cracking the glass tubes. When the equipment had warmed sufficiently, the steam pressure was adjusted so each of the plastic steam jackets was under enough pressure to balloon it out from the tube sides.

The contents of the tubes were allowed to oxidize for four weeks, after which period, tube Number 5 was taken from the frame.

The cemented sand was cut from the tube with a coring bit made from a piece of thin-walled pipe of 2 7/8 inches outside diameter.

Testing with hydrochloric acid produced a trace of hydrogen sulphide showing a little of the pyrrhotite had not been oxidized.

The apparatus was left to work for a further three weeks when tube Number 8 was removed and its contents tested.

No sulphide was detected in this tube so tube Number 3 was removed and tested also. This test confirmed that all sulphides in the tubes containing 6% pyrrhotite had been oxidized.

Since the remaining tubes had had more oxidation time per unit of contained iron than the tubes tested, their sulphide contents were assumed to have been digested. They were removed from the frame and the cylinders of cemented sand drilled out using the coring bit.

The contents of tube Number 1 were too soft to be removed as a cylinder and were discarded.

E. Segregation Check

Specific quantities of pyrrhotite were originally added to the silica sand with the intention of obtaining directly the strength imparted to the mass by various percentages of this mineral.

To confirm the uniformity of the cylinder, samples were taken from the top (A), middle (B) and bottom (C) of each and assayed for iron.

These analyses, shown in Table 1, show segregation occurred as the 70% solids slurry settled in each tube.

Visual examination revealed that the top inch of material in each cylinder contained much fine material amongst which much of the 300 mesh pyrrhotite must have gathered.

Due to this segregation it was decided to discard the top three inches of each column of cemented sand and to assay each test sample individually.

F. Sample Preparation

It was noted that the cylinders bore surface patches of hard crust.

Each of these patches had formed next to that portion of the glass tube upon which the steam entering the jacket had impinged.

Analysis showed these crusts to contain approximately 0.25% iron in sulphate form which is equivalent to

0.94% as ferric sulphate - $Fe_2(SO_4)_3\ H_2O$
or 1.06% as ferrous sulphate tetra hydrate - $FeSo_4.4H_2O$
or 0.71% as ferrous sulphate - $FeSO_4$

These patches of hard material were probably formed by excessive heat evaporating droplets of water carrying iron sulphate down the tube from the rich top layer of sulphides.

In selecting sections of the cylinders for compression test specimens, the less uniform portions were discarded. These included, in addition to those containing hard patches, portions containing drainage channels which the precautions taken in pouring had failed to eliminate.

Those sections selected for testing were cut off with a band saw and the ends made parallel by lapping on a sheet of sandpaper. This lapping process was also used to make the length of each specimen equal to its diameter.

G. Compression Testing

As the specimens from each tube were not uniform, triaxial testing was not practical.

Uniaxial tests were made with a Farnell testing machine using a dual - 100 and 400 - proving ring and set at a compression rate of 0.002 inches per minute.

On loading each specimen, three thicknesses of well greased paper were put between each of its ends and the plattens.

The load at which each specimen broke is shown in Table II.

H. Assays

A representative sample taken from each broken specimen was assayed for total iron and sulphur. This was done in an attempt to equate compressive strength with content of either or both of these elements.

Sulphur content was determined by the A.S.T.M. iodate titration method using a Leco Sulphur Determinator.

Iron content was found by the standard dichromate titration method.

The results of these assays are shown in Tables II and III.

I. Effect of Moisture.

It was noticed that when the specimens were moistened with distilled water they became weaker.

This lead the author to believe a substantial quantity of soluble cement to be present.

Surprisingly small samples of this cement were obtained by evaporating the water from thrice-filtered solutions made by grinding quantities of cemented sand and C.H.T.F. in warm distilled water.

The Straumanis technique in x-ray diffraction powder pattern analysis showed these green **crystalline** samples to be a mixture of ferrous sulphate, ferrous sulphate monohydrate, ferrous sulphate tetrahydrate and a little ferric sulphate which is only slightly soluble in water.

These crystals probably escaped detection under the microscope due to their small size and to their almost colorless state being overshadowed by the limonite.

All compression test samples were assayed for iron present as soluble sulphate. The results of these analyses are seen in Tables II and III.

In this assay, the size of samples available, only ten grams each, and the small quantities of soluble iron being dealt with made it necessary to substitute a Jones

Reductor for the more usual stannous chloride reduction method and to use approximately 0.01 N. potassium permangarate solution, 1cc ≡ 0.00050 grams iron, for the titration.

A Chromel/Alumel pyrometer embedded in samples of cemented sand recorded a maximum decrease in temperature of 2°C. when the samples were moistened. This reading was deemed too small for consideration in this instance.

J. Results

Table III, in which the samples are arranged in order of unconfined compressive strength, shows the strength of the cemented material to be influenced in a rather haphazard manner by the iron and sulphur content.

To try and calculate reasonable curve equations, a least squares polynomial method was used from one to ten degrees. Both linear and logarithmic data were fed into the IBM 1620 computer but average per cent errors of 62% to 55% were shown.

This showed the relationship to be so vague that attempts to equate the assays and strength of all twenty two samples were abandoned.

Table II shows the samples arranged in seven groups, each group being composed of samples taken from one tube.

With the exception of samples 6, 13, 16, 17 and 21, the iron content of the samples in each tube drops with compressive strength.

Now the reaction conditions at each point, with the exception of the hot spot, in any one tube should have been similar. This hot spot, incidentally, could well account for some of the last four samples mentioned above, all being stronger and therefore probably harder than their iron contents might warrant.

The conditions in each tube though were definitely not identical because of:

1. Time on the equipment not being proportional to pyrrhotite content.
2. Pressure and moisture content of air not necessarily being constant throughout the length of the feed manifold.
3. Difficulties experienced with bursting and leaking steam jackets.

This is borne out by the difference in appearance of each column of cemented sand. Each cylinder had its own peculiar colour or shade which altered little throughout its length.

These colours ranged from light ochre to dark red. Samples below Number 11 on Table III with the exception of

Number 7 and Number 12 range from ochre with a tinge of pink to dark red. Samples above Number 13 are all shades of ochre.

From the above evidence, the author reasons that the strength produced in the cementation of silica sand by the oxidation products of pyrrhotite is due both to the percentage of pyrrhotite in the sample and to the degree of dehydration which the ferric hydroxide has undergone.

The quantity of iron present as soluble sulphate does not seem to be large enough to account directly for much of the loss in strength of the cemented sand when wet. It must be remembered, though, that the sulphate is crystaline, is adhesive as well as cohesive and that the true percentage of iron sulphate in the material ranges from 2.85 to 4.23 times the percentage of soluble iron present depending upon how much water is contained in the sulphate molecule.

It is most unlikely that the iron hydroxides in "limonite" would quickly hydrate further by merely adding water to them. The author therefore concludes that the loss in strength on wetting is due to:

1. Slaking - in extreme cases
2. The fact that saturated rock has lower shear and compressive strength than dry rock.

Sowers and Sowers[13] describe slaking thus:

> If a soil that has dried well beyond the shrinkage limit is suddenly inundated or immersed in water, it may disintegrate into a soft wet mass, a process known as slaking.
>
> Two factors are involved in slaking. First, the unequal expansion of the soil as the water penetrates from the surface causes pieces of soil to flake off the mass. Second, when the soil dries beyond the shrinkage limit, some of the voids fill with air. When the dried soil is immersed, water enters these air-filled voids on all sides. The air is trapped between the meriscuses of the entering water, and its pressure builds up as water fills the void. The result is an explosion of the void and disintegration of the soil.

When plunged into water, pieces of the softer samples behaved according to both factors but as harder and harder samples were tested in the same manner the effect of wetting became less and less.

This showed that, with increasing hardness, the properties of the cemented material graded from those considered in the sphere of soil mechanics to those dealt with in the realm of rock mechanics.

TABLE I

Assays of Samples Taken from Top (A) Centre (B) and Bottom (C) of tubes 3 to 8

Sample	Original Percentage of Pyrrhotite	Assay after Cementation % Iron	% Sulphur
3 A	6	2.7	2.23
B		1.0	0.84
C		2.4	1.36
4 A	3	4.9	2.29
B		0.5	0.75
C		0.6	0.78
5 A	6	9.2	5.40
B		2.0	1.03
C		1.2	1.58
6 A	4	2.1	1.68
B		0.8	1.21
C		0.9	1.11
7 A	5	4.9	2.91
B		1.2	1.51
C		1.4	1.21
8 A	6	2.5	2.78
B		1.2	2.55
C		1.8	2.43

TABLE II

Unconfined Compressive Strength And Assay Values of Cemented Sand.

Sample	Tube	P.S.I.	% Sulphur	% Iron	% Iron as Soluble Sulphate
1	2	25.3	0.72	1.3	0.026
2		11.3	0.56	1.2	0.054
3	3	86.6	2.40	3.4	0.167
4		79.0	2.12	2.9	0.004
5		47.0	1.68	2.6	0.001
6		41.4	2.40	2.9	0.002
7		26.2	1.56	2.4	0.004
8	4	17.3	0.96	2.0	0.099
9		3.1	0.81	1.6	0.003
10	5	43.7	1.74	3.3	0.006
11		34.8	2.49	2.9	0.024
12		24.6	1.49	2.4	0.009
13	6	32.2	0.98	1.7	0.001
14		26.2	1.37	1.9	0.001
15		20.5	1.75	1.9	0.000
16	7	63.7	1.37	1.9	0.035
17		49.0	1.49	1.1	0.000
18		48.7	1.82	2.9	0.001
19		43.0	1.91	2.7	0.002
20		38.6	1.49	2.0	0.002
21	8	94.3	2.67	3.1	0.124
22		51.9	2.11	3.8	0.015

TABLE III

Assay Values of Cemented Sand Arranged In Order of Unconfined Compressive Strength

Sample	P.S.I.	% Sulphur	% Iron Total	% Iron as Soluble Sulphate
21	94.3	2.67	3.1	0.124
3	86.6	2.40	3.4	0.167
4	79.0	2.12	2.9	0.004
16	63.7	1.37	1.9	0.035
22	51.9	2.11	3.8	0.015
17	49.0	1.49	1.1	0.000
18	48.7	1.82	2.9	0.001
5	47.0	1.68	2.6	0.001
10	43.7	1.74	3.3	0.006
19	43.0	1.91	2.7	0.002
6	41.4	2.40	2.9	0.002
20	38.6	1.49	2.0	0.002
11	34.8	2.49	2.9	0.024
13	32.2	0.98	1.7	0.001
7	26.2	1.56	2.4	0.004
14	26.2	1.37	1.9	0.001
1	25.3	0.72	1.3	0.026
12	24.6	1.49	2.4	0.009
15	20.5	1.75	1.9	0.000
8	17.0	0.96	2.0	0.099
2	11.3	0.56	1.2	0.054
9	3.1	0.81	1.6	0.003

IV. CONCLUSIONS

1. The reactions taking place in the oxidation of pyrrhotite are very similar to those involved in the oxidation of pyrite.

2. The bonding is effected by a matrix of iron oxide mixed with ferric and ferrous sulphates.

3. Strength of C.H.T.F. cannot be predicted in advance due to the variable conditions under which oxidation may - or may not - take place.

4. Strength of the final C.H.T.F. is governed by:
    a. The quantity of pyrrhotite oxidized
    b. The stage to which its iron oxides dehydrate
    c. The density, or gradation of the fill in place.
    d. The chemical composition of the fill.
    e. Moisture content.

5. Goethite is the best cementing iron oxide followed by hematite and hydrated ferric oxide. The formation of these is governed by acidity and heat and by the supply of water and oxygen.

6. The inside of the H.T.F. mass will not cement unless the air contained therein is frequently replaced.

7. In making experimental full-scale pours, the pouring

procedure must be carefully planned and supervised to cut segregation of materials to a minimum. On completion of the fill placement, manways, mill holes and chutes must be hosed down to prevent accumulation of spilled material which could be a fire hazard and could also cement broken rock and the chute. Ditches carrying the fill water must also be cleaned out promptly.

8. The odor of sulphur dioxide indicates a "hot spot" has developed due to lack of water.

9. This method of fill cementation should not be attempted in areas containing much timber.

10. If the fill in wet stopes is cemented by the oxidation products of pyrrhotite, water flowing through the fill mass will carry iron sulphates to the levels below. These solutions may increase corrosion in the mine.

RECOMMENDATIONS

The author suggests that further study of the cementation of H.T.F. include detailed microscopic and chemical analysis of the bonding action of each of the oxidation products of pyrrhotite.

If the investigator wishes to use apparatus similar to that described in this thesis, it is recommended that he reduce segregation to a minimum. This would be most easily accomplished by packing the tubes with dry mixtures of sand and pyrrhotite.

An electrical method of heating would be more convenient than steam heating and might provide more uniform heat distribution.

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VITA

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