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MICROCOPY RESOLUTION TEST CHART

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Indiz. **AMJHORE PYRITE PROJECT**

Process Development and

Engineering Studies.

Phase I .

DP/IND/81/018

by

Sherritt Gordon Mines Limited

Canada.

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November 1983

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April 27, 1984

Mr. D. Gardellin United Nations Industrial Development Organization (UNIDO) Purchase and Contract Service Division of Industrial Operations (PAC/DIO) P. 0. Box 300 A-1400 VIENNA AUSTRIA

Dear Mr. Gardellin:

RE: AMJHORE PYRITE STUDY (PROJECT DP/IND/81/018, STUDY NO. 3)

It is a pleasure to transmit to you fifty (50) copies of the Phase I report of the work carried out by Sherritt on the recovery of sulphur from Amjhore pyrite. In addition, three (3) copies have been transmitted to Mr. T. N. Jaggi, Managing Director of Pyrites: Phosphates and Chemicals Ltd (PPCL). The report describes the results of the laboratory testwork and preliminary process engineering studies on the recovery of sulphur, using pressure oxidation, from artificial pyrrhotite matte produced through a conventional pyrometallurgical smelting process. The report has been reviewed with PPCL and has been revised based on their comments. The commercial plant would treat 420 t/d of pyrrhotite matte producing 115 t/d of elemental sulphur in a single autoclave train.

A process has been defined to treat artificial pyrrhotite analyzing 57% Iron and 29% sulphur. Ground matte is pressure oxidized at 150°C using oxygen in an autoclave. The autoclave discharge is flash cooled to atmospheric pressure. The flashed slurry undergoes primary sulphur separation, liquid solid separation, and flotation to produce flotation
concentrate and tailings slurry. The tailings are neutralized with concentrate and tailings slurry. limestone and lime and are then sent to the tailings pond. The flotation concentrate undergoes hot filtration to produce a clean sulphur product and a filter cake residue that is recycled to the grinding circuit.

Sherritt has demonstrated 1n the laboratory that artificial pyrrhotite produced from Amjhore pyrite can be subjected to pressure oxidation followed by flotation to recover elemental sulphur.

Sherritt Gordon Mines Limited

Fort Saskatchewan, Alberta. Canada T8L 2P2 / Telephone (403) 998-6911 / Telex 037-2290

Mr. D. Garde!lin Page 2 April 27, 1984

Estimated capital costs for the pressure oxidation and sulphur recovery plant, consisting of grinding, pressure oxidation, liquid solid separation, tailings neutralization, flotation, molten sulphur filtration and oxygen plant, are \$17 million (U.S.). All costs are estimated for the third quarter of 1983 for an Indian location. Costs were converted to an Indian location based on information supplied by PPCL and the results have been reviewed with PPCL. Annual operating costs are estimated to be \$3 100 000 (U.S.).

The next phase of work leading to commercialization of this project, is Phase II, confirmatory tests. Sherritt's subsequent involvement beyond Phase II would involve detailed laboratory minipilot plant demonstration of the process and preparation of a process engineering design package. Prior to commencing subsequent work beyond Phase II, it would be necessary to agree to terms under which PPCL would be licenced by Sherritt to use Sherritt technology in the commercial scale plant.

We enjoyed working for you on Phase I of the Amjhore pyrite project and look forward to continuing involvement in further phases of the project development. Thank you for your interest in the Sherritt process. Upon transmittal of this final Phase I report, Sherritt will send you an invoice in the amount of \$20 000.

Your truly,

Altrum

H. Veltman Director, Research Centre

HV/dw enclosure

ACKNOWLEDGEMENTS

The process development and laboratory testwork was conducted by the Process Research Group under the direction of Dr. D. Robert Weir, Manager, Process Research and Dr. I. M. Masters, Manager, Extractive Metallurgy. Dr. M. E. Chalkley, Senior Research Metallurgist, was responsible for the technical aspects. The process engineering study was completed by Mr. E. McConaghy.

Those directly involved in the technical aspects of project included:

Mr. P. Amarnath, Senior Process Engineer, was responsible for overall coordination.

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1.0 INTRODUCTION

Pyrites, Phosphates and Chemicals Ltd. of India (PPCL) own and mine the Amjhore pyrite deposit located in Bihar State, India. The pyrite is used in the manufacture of sulphuric acid. However, there have been difficulties with handling and transporting the pyrite and utilizing the material in conventional roasting plants, and very little of this pyrite is being used at the present time. PPCL are therefore considering production of elemental sulphur from the pyrite. An added advantage to this processing route would be the minimizing of sulphur imports and the attendant saving in foreign exchange.

PPCL are considering producing elemental sulphur and pyrrhotite matte by the Outokumpu flash smelting process. The matte could be further treated to recover elemental sulphur in Sherritt's aqueous pressure oxidation process. Representatives of PPCL visited Sherritt on November 29 and 30, 1982 to discuss the application of Sherritt's pressure leaching technology to the recovery of elemental sulphur from pyrrhotite matte. As a result of the discussions, Sherritt was requested to submit a proposal to PPCL and the United Nations Industrial Development Organization (UNIDO). The proposal, entitled 'Recovery of Sulphur from Amjhore Pyrites, Phases I and 1Г, was submitted to UNIDO on December 21, 1982 and approved on March 4, 1983.

The objectives of the Phase I study were:

to define a process flowsheet for the treatment of matte, obtained from Amjhore pyrite, to recover elemental sulphur;

to carry out laboratory pressure oxidation tests, solid-liquid separation and flotation tests; and

to prepare an order of magnitude estimate of the capital and operating costs for the commercial plant.

The scope of the laboratory program was to include the following:

conversion of pyrite to a matte of similar composition to Outokumpu p.ocess matte;

approximately twenty batch leach tests in laboratory autoclaves of 4 to 5 L volume to define process parameters such as grind, temperature, retention time, oxygen or air sparging rate, pressure, pulp density and acid concentration, and

INTRODUCTION 1-2

one continuous leaching test at a feed rate of 2 to 4 kg/h natte for a period of 2Ü to 24 h. The test circuit would include continuous pressure oxidation and liquid-solid separation, and flotation of sulphur from the residue. The composition of the tailings solution will be defined to provide information for a neutralization circuit with limestone and lime.

The engineering study was to include a process flowsheet, an equipment list, an outline specification of the major equipment, and order of magnitude capital and operating cost estimates.

This report on the treatment of a pyrrhotite matte produced from Amjhore pyrite summarizes the results of the laboratory tests performed, and includes results of the process engineering study.

PROJECT SUMMARY 2-1

2.0 PROJECT SUMMARY

Large deposits of pyrite ores occur in India. Exploitation of these ores for the recovery of sulphuric acid began in the 1960's. Difficulties experienced with conventional plants for direct roasting of pyrite led PPCL to investigate alternative routes for the recovery of sulphur from these deposits. This report summarizes the results of laboratory testwork carried out to develop a process for the recovery of elemental s lphur, by a pressure oxidation route, from a pyrrhotite matte.

The major objective of the study was to investigate pressure oxidation as a means of treating a pyrrhotite matte of similar composition to that which would be produced in an Outokumpu flash smelter.

Major process steps for a process based upon pressure oxidation of pyrrhotite matte were shown to be technically viable in batch experiments on a laboratory scale. It is recommended that the process chosen for the engineering study, based upon pressure oxidation at 150° C, be further examined in Phase II of this project in a continuous mode of operation in Sherritt's laboratory miniplant autoclave.

2.1 LABORATORY STUDY

Experimental work was carried out on a pyrrhotite matte produced by smelting Amjhore pyrite in an electric furnace in the presence of an iron oxide flux. The pyrrhotite matte was crushed and ground prior to the leaching testwork.

Pressure oxidation at both 100°C and 150°C was examined and both routes yielded high conversions of sulphide sulphur to elemental sulphur. Difficulties were experienced with obtaining good separation of elemental sulphur from the iron oxide fraction of residues generated at 100°C. Consequently the 150°C pressure oxidation process was chosen for the engineering study. The process is depicted in Figure 2.1.

Ground pyrrhotite matte was leached in simulated thickener overflow recycle for 1.0 h at 150°C. Conversion of sulphide sulphur to elemental sulphur exceeded 85% and the iron was precipitated as hydrated iron oxide. The oxidation residue was thickened, repulped in water, and separated into an elemental sulphur fraction and an oxidic fraction, containing iron oxide, by flotation. High grade cleaner concentrate was melted and a pure elemental sulphur product obtained by hot filtration

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PROJECT SUMMARY 2-2

Flotation tailings slurry would be neutralized with limestone and lime prior to disposal in a tailings pond.

2.2 ENGINEERING STUDY

The order of magnitude capital cost for a single autoclave train pressure oxidation and sulphur recovery circuit to treat 420 t/d of pyrrhotite matte to produce 115 t/d of elemental sulphur is \$17,000,000 (U.S.) for the Indian location.

The annual operating costs for the pressure oxidation and sulphur recovery circuit are shown below.

PROJECT SUMMARY 2-3

Figure 2.1 Flowsheet Chosen for Engineering Study

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3.0 BACKGROUND

Pyrites, Phosphates and Chemicals Ltd. (PPCL) is a corporation controlled by the Government of India and is attached to the Ministry of Chemicals and Fertilizers. In addition to several phosphate deposits, PPCL is involved in the development of the Amjhore pyrite deposit in Bihar State and the Saladipura pyrite deposit in Rajasthan State (Figure 3.1). The Amjhore deposit is a sedimentary deposit containing 300 million tons of pyrites analyzing 40% sulphur, and covers an area of 124 km^2 . The deposit is approximately 0.6 m thick and the overburden is predominantly shale containing 10% sulphur in addition to carbonaceous material.

Work began in the early 1960's to exploit the Amjhore pyrite deposit for the production of sulphuric acid. In 1965 Outokumpu Oy performed some testwork using the flash smelting process to produce elemental sulphur and pyrrhotite matte. In the meantime, two sulphuric acid plants, with a total capacity of 1200 t/d, were constructed, using Bulgarian and German technology for direct roasting of pyrites. The process suffered a number of problems and at the present time one plant is shut down and the other is operating at only 30% of design capacity. The process plants are located 500 km from the mine site (Figure 3.1) and during transportation, oxidation of the fine material results in a reduction of the sulphide sulphur content to 30%. The high silica content of the pyrite (13%) has also led to a number of problems in the auxi1iary boilers.

India imports approximately 1 million t/y of sulphur with this quantity expected to double by the end of the decade. The landed price of sulphur is presently about US \$150/t, resulting in a foreign exchange drain of almost US \$150 million annually. The Indian Government has decided to offset at least 30% of the imported sulphur by recovering sulphur from the pyrite deposits. Because of the above mentioned difficulties with existing treatment plants, the Indian Government approached the United Nations Development Program (UNDP) for financial assistance to exploit the Amjhore pyrite deposit, using alternative technology. The United Nations Industrial Development Organization (UNIDO) executes the program.

PPCL has approached Outokumpu to update their pilot plant work for the design of a flash smelting plant to treat 1500 t/d of Amjhore pyrite. The Outokumpu study consists of two parts:

to update the previous study which consists of removing 55 to 60% of the sulphur in the smelter and producing granulated matte which could he roasted to produce sulphuric acid; and

to produce elemental sulphur from the roasted matte by reducing the sulphur dioxide to recover all sulphur in the elemental form.

Having read Sherritt's papers on the recovery of elemental sulphur from pyrite and zinc concentrates, PPCL decided to approach Sherritt to see if this technology could be applied to the recovery of elemental sulphur from pyrrhotite matte, with work being funded by UNIDO. At the present time, recovery of iron from the pyrite is not of interest since high purity iron ore deposits exist in the area.

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The recovery of elemental sulphur from pyrite ores has received considerable attention during the past twenty five years. The discovery of the Pyhasalmi deposit in 1958 by Outokumpu Oy led to the development of the Outokumpu process for the production of elemental sulphur from pyrite. Fine grained pyrite flotation concentrate is fed into the reaction shaft of a flash smelting furnace and suspended in the hot reducing gases created by the combustion of heavy fuel oil. Thermal decomposition results in the formation of molten pyrrhotite (FeS) particles and sulphur vapour. Pyrrhotite matte settles in the furnace hearth and is tapped and granulated in water. The combustion gases and the sulphur vapours are cooled down ard the elemental sulphur is separated from the gases. Granulated matte is roasted in a fluidized bed roaster to generate sulphur dioxide and steam. Sulphur dioxide is converted to sulphuric acid and the steam is used to generate electrical energy.

The economics of sulphur recovery from pyrite deposits as elemental sulphur or sulphuric acid are influenced by factors other than the price of sulphur. One such factor is the marketability of the iron oxide residue product, which in turn is dependent upon the purity of the material. Increasing competition from native sulphur and byproduct sulphur recovered from hydrocarbons placed the pyrites industry in a critical position in the mid 1960's. In order to increase the viability of the treatment of pyrites for sulphur recovery, it was found necessary to produce a high grade iron oxide product from the residue calcine. The Montecatini Company in Italy developed a process, based on fluosolids roasting, for the recovery of sulphuric acid and high purity iron oxide pellets. Dowa Mining Company developed the Kowa Seiko Process utilizing a chloride route for the treatment of pyrite cinders after fluosolids

BACKGROUND 3-3

roasting of pyrite to recover sulphur dioxide for sulphuric acid manufacture. Volatile non-ferrous metal chlorides were extracted from the pvrite cinder during roasting, yielding a high grade hematite pellet product.

In an attempt to improve sulphur flexibility and convert all the pyritic sulphur to elemental sulphur, Sherritt developed a process for the treatment of pyrite. The process consisted of low temperature thermal decomposition of the pyrite to elemental sulphur and artificial pyrrhotite; aqueous oxidation of the artificial pyrrhotite to hydrated iron oxide and elemental sulphur; dissolution of the hydrated iron oxide and non-ferrous metal values; purification and hydrolysis of pure basic ferric sulphate; and, processing to a final iron product. The process was designed to treat both pure and impure pyrite feedstocks. Subsequently Noranda developed a similar process, for the treatment of impure pyrite, in which a chlorination route was utilized to recover non-ferrous metals from an oxidic iron pressure leach residue, after an initial thermal decomposition of pyrite to recover approximately half of the sulphur.

In the 1970's Sherritt piloted and eventually commercialized the Sherritt Zinc Pressure Leaching Process. A major advantage of the process is that the sulphide sulphur is converted to elemental sulphur and therefore zinc production need not be tied to the constraints of sulphuric acid production. A pressure leaching plant designed to treat 190 t/d of zinc concentrate has been in operation at the Trail, British Columbia plant of Cominco since January 1981, and in August 1983 a plant designed to treat 100 t/d of zinc concentrate was commissioned at Timmins, Ontario by Kidd Creek Mines. Sherritt has considerable experience in the recovery of elemental sulphur from sulphidic ores and concentrates and has developed processes which have reached successful commercial operation.

Figure 3.1 Location of Pyrite Deposits

4.0 PROCESS DESCRIPTION AND CHEMISTRY

Alternative procedures were tested in the laboratory for the treatment of pyrrhotite matte to generate elemental sulphur. The process chosen for the engineering evaluation is given in Figure 2.1 and was based upon the optimum results from pressure oxidation test»ork. A general description of the process chemistry is given to aid in the interpretation of the results and conclusions presented in this report. The pertinent chemistry for the process steps tested, but not included in the selected flowsheet, is presented in that section of the report where the experimental data are given.

4.1 PROCESS DESCRIPTION

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> For the purposes of the Phase I study, it was assumed that the feed material for the process is a pyrrhotite matte produced from an Outokumpu smelter. The objective of the hydrometallurgical process is to convert the sulphide sulphur to elemental sulphur, to separate it from the oxidic iron solids by flotation, and to prepare pure elemental sulphur by filtration.

> Granulated matte is ground to 95% minus $44\ \mu m$ in a conventional closed circuit milling operation. Thickened solids are fed to the autoclave together with a solution recycle from the oxidation thickener overflow, and make-up sulphuric acid. The solution recycle provides a source of ferric iron for pressure oxidation and the make-up acid maintains a sulphate balance in the oxidation circuit. A small quantity of basic iron sulphates are precipitated in the pressure oxidation step and hence sulphuric acid addition is required to maintain the sulphate balance.

> The final slurry is discharged from the autoclave through a flash tank. The slurry is pumped to the primary autoclave discharge hydrocyclones to preconcentrate the elemental sulphur and sulphides in the underflow. The cyclone overflow slurry is thickened and the thickener overflow containing free sulphuric acid and iron is recycled to the autoclave. Hydrocyclone underflow, containing elemental sulphur, some iron oxides and any unreacted sulphides, is repulped in flotation circuit recycle solution to a pulp density suitable for feed to the flotation circuit.

> The flotation circuit consists of rougher, scavenger and cleaner sections with appropriate internal recycles. Flotation tailings are

PROCESS DESCRIPTION AND CHEMISTRY 4-2

added to the primary hydrocyclones overflow and thickened. Thickener underflow is treated with limestone and lime to neutralize acid and precipitate iron contained in the solution. The gypsum-iron residue is transferred to a tailings pond. Flotation concentrate is dewatered and the solution recycled to the flotation feed repulp tank. The concentrate is then melted and the molten product subjected to hot filtration to separate elemental sulphur from unoxiaized sulphides and entrained gangue. The filter cake is recycled to the grinding circuit and the molten elemental sulphur is available for sale.

4.2 PROCESS CHEMISTRY

The overall reaction which occurs during the pressure oxidation of pyrrhotite matte is intrinsically simple.

$$
FeS_{1.15} + H_2SO_4 + 0.502 \text{ --} \rightarrow FeSO_4 + H_2O + 1.155^{\circ}
$$

This reaction is, however, impractically slow in the absence of a species which will facilitate oxygen transfer. One such species is dissolved iron, and in fact the reaction is usually the sum of the reactions below.

$$
FeS_{1.15} + Fe_2(S0_4)_3 \longrightarrow 3FeS0_4 + 1.15S^{\circ}
$$

2FeS0₄ + H₂SO₄ + 0.50₂ --- > Fe₂(SO₄)₃ + H₂O

In this case, the pyrrhotite matte is the source of acid soluble iron. The presence of ferric iron in solution will also minimize the evolution of hydrogen sulphide which could result from the reaction below.

$$
FeS + H_2SO_4 \text{---} > FeSO_4 + H_2S
$$

A portion of the sulphide sulphur may be oxidized to sulphate sulphur during the pressure oxidation, as shown in the following reaction.

$$
FeS + 202 --- > FeS04
$$

Hydrolysis reactions which occur as the oxidation progresses remove iron from solution and result in the regeneration of some sulphuric acid.

$$
Fe_2(S0_4)_3 + (X + 3)H_2O \text{ --- } Fe_2O_3 \cdot xH_2O + 3H_2SO_4
$$

3Fe_2(S0_4)_3 + 14H_2O \text{ --- } 2H_3OFe_3(S0_4)_2(OH)_6 + 5H_2SO_4

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5.0 LABORATORY STUDY

Experimental work was carried out on a pyrrhotite matte prepared by smelting pyrite supplied by PPCL. This report summarizes the work carried out to convert the pyrite to a pyrrhotite matte and the results of the testwork on the pyrrhotite matte, as well as for the natural pyrrhotite from Saladipura, for the recovery of elemental sulphur.

5.1 SUMMARY

The primary objective of the laboratory study was to develop a process, based on pressure oxidation, to recover elemental sulphur from a pyrrhotite matte. Samples of lump pyrite, typically analyzing 26.2% Fe, 40.5% S and 13.6% SiO₂, were provided for the study. The pyrite was converted to a pyrrhotite matte by smelting, in the presence of an iron oxide flux, to slag off the silica content of the pyrite. No attempt was made to recover the sulphur liberated during smelting. The pyrrhotite matte was crushed and ground to 97.4% minus 44 µm.

Non oxidizing atmospheric sulphuric acid leaching of the pyrrhotite matte generated hydrogen sulphide which could be treated in a Claus plant for the recovery of elemental sulphur. Sulphuric acid could be regenerated by oxidizing the leach discharge solution in an autoclave and precipitating the iron as a jarosite by the addition of a suitable cation.

Pressure oxidation at 100°C was extensively examined. Complete oxidation of sulphide sulphur, with either air or oxygen as oxidant, required a batch retention time of 3 h. Conversion of sulphide sulphur to elemental sulphur exceeded 85%. A 32 h continuous run was carried out at 100°C with oxygen as the oxidant and a nominal retention time of 3 h. The oxidation discharge slurry was fed to a thickener and the thickener overflow, containing \sim 15 g/L Fe, 8.5 g/L Fe $^{2+}$ and 5 g/L H2SO4 was recycled to the oxidation step to provide the source of soluble iron and acid for the oxidation step. Pyrrhotite matte was treated for a period of 21 h with the conversion of sulphide sulphur to elemental sulphur in the range 70 to 80%. At a solids content of 150 g/L solution, the total heat requirements were met by the exothermic heat generated by the oxidation of the sulphide sulphur. In the next 11 h of the continuous run, natural pyrrhotite was treated.

Elemental sulphur recovery from the oxidation residues was attempted by flotation. Primary or rougher separation of the sulphur from the

bulk of the oxidic iron fraction proved successful. Using Aerofroth 73 as the frother, 95% of the elemental sulphur reported to a rougher concentrate grading -44% S°. Subsequent cleaning of the rougher concentrate to generate a high grade (>85% S°) cleaner concentrate, suitable for feed to a hot filtration step, proved unsuccessful. Little or no upgrading of the rougher concentrate was obtained, using trisodium phosphate as a depressant for iron oxide. Further testwork would be required to optimize conditions for cleaner flotation.

The 100°C oxidation route was chosen for the continuous study based or, the results of the preliminary batch testwork. Following the difficulties observed in obtaining a high grade elemental sulphur concentrate from the flotation of the 100°C oxidation residues, further batch testwork was performed at 150°C to optimize the conditions required for the recovery of a high grade elemental sulphur concentrate and obtain data for the engineering study.

Experimental work at 150°C initially indicated poor oxidation of sulphide sulphur, with the reaction apparently ceasing after $~50\%$ of the sulphide sulphur had been oxidized. Additives are required when oxidizing above the melting point of sulphur to prevent coating of unoxidized sulphidic particles by molten elemental sulphur. Optimization tests showed that greater than 85% of the sulphide sulphur could be converted to elemental sulphur at 150°C with a 1.0 h retention time, using oxygen as oxidant and with appropriate levels of additives. Standard bench scale settling tests, with feed slurry dilution to 11.9% solids using simulated thickener overflow recycle and flocculant, generated a thickener unit area requirement of $0.56 \text{ m}^2/\text{t.d.}$ Batch flotation testwork was carried out on both oxidation discharge slurry and simulated oxidation thickener underflow repulped in water. In the latter case, using Aerofroth 73 as frother, a high grade (>95% S°) cleaner concentrate was obtained and optimization of flotation conditions could yield an elemental sulphur recovery of 95%. A sample of the cleaner concentrate was subjected to melting and hot filtration to obtain a high quality elemental sulphur product.

5.2 ANALYSES

Thirteen drums of lump pyrite (<50 mm) weighing 450 kg and one drum of pyrrhotite concentrate weighing 50 kg were received from PPCL. One drum of pyrite was crushed to <1 mm in a jaw crusher and then ground to <350 pm in a plate grinder. A sample was submitted for chemical analysis and the results are shown in Table 5.1, together with the analysis

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of a sample of the pyrrhotite concentrate. Silica is the major gangue component in both samples, with the pyrrhotite concentrate containing a higher quantity of gangue material than the lump pyrite. A sample of the pyrrhotite concentrate was wet screened at 44 μ m and contained 62.9% greater than 44 pin material.

6.3 SMELTING TESTWORK

Small scale roasting and smelting testwork was carried out to determine the preferred method for converting the pyrite into a pyrrhotite matte. Roasting in a hydrogen atmosphere indicated that the labile sulphur could easily be driven off at 700°C to yield an artificial pyrrhotite matte with a sulphurriron molar ratio of 1.14:1. Previous testwork has shown that delabi1ization of pyrite under such conditions yields an extremely reactive artificial pyrrhotite product and it was considered that the reactivity may not be typical of a pyrrhotite matte produced ny a flash smelting process.

Small scale smelting tests carried out in an electric muffle furnace under an air atmosphere demonstrated the feasibility of producing a pyrrhotite matte with a sulphur: iron molar ratio of $\sim 1.15:1$. The presence of silica in the pyrite also indicated the need to slag off the silica by the addition of a suitable flux, such as iron oxide, FeO. Facilities for the large scale smelting of the pyrite were not available at Sherritt. Enquiries were made to other metaIlurgical companies and research centres in an attempt to locate a suitably sized furnace for the production of ~ 100 kg of pyrrhotite matte. Finally, agreement was reached with Falconbridge Nickel Mines to smelt the pyrite in their 50 kVA electric furnace.

The pyrite (303 kg) was shipped to the Falconbridge Research Laboratory in the form of 50 mm lumps (235 kg), <12 mm crusher product (29 kg) and <355 pm pulverizer product (39 kg). The objective was to smelt the pyrite in the presence of an iron oxide flux to produce pyrrhotite matte and a fayalite (2Fe0.Si02) slag. No attempt was to be made to recover the sulphur released during the smelting step. At the Falconbridge laboratory 125 kg of lump pyrite was crushed to <12 mm and smelted to produce approximately 100 kg of pyrrhotite matte which was cooled in crucibles and crushed to <12 mm for shipment to Sherritt. The memorandum on the testwork, provided by Falconbridge, is presented in Section 7.0. Chemical analysis of the pyrrhotite matte is given in Table 5.2.

5.4 BATCH TESTWORK

The batch testwork program was designed to identify the optimum processing route for the recovery of elemental sulphur from the pyrrhotite matte. Prior to commencing the testwork, the crushed pyrrhotite matte was milled in open circuit for 1.0 h, in two 50 kg charges, in a 60 cm dia x 90 cm rubber lined ball mi 11. The ball mill discharge was thickened and stored as a 70% solids slurry. Screen analysis and chemical content of the solids are given in Table 5.2.

5.4.1 Non Oxidizing Atmospheric Acid Leach of Pyrrhotite Matte

In the non oxidizing sulphuric acid leac^t of pyrrhotite matte, sulphide sulphur is converted to hydrogen sulphide and the iron dissolves as the ferrous species.

$Fes + H_2SO_4$ ---> $FesO_4 + H_2S$

Hydrogen sulphide gas could be treated in a Claus plant for the recovery of elemental sulphur. Sulphuric acid could be regenerated by oxidizing the leach discharge solution in an autoclave and precipitating the iron as a jarosite by the addition of a suitable cation. A simplified flowsheet is given in Figure 5.1.

Two single stage batch leach tests were performed to assess the effect of acid: iron stoichiometry on sulphide sulphur conversion. The acid was added at room temperature (24°C) and the slurry temperature increased to \sim 34°C at which point the reaction commenced vigorously with the generation of a large quantity of froth. After all of the acid had been added, the temperature reached 37 to 40°C and the initial reaction subsided. At this stage heating commenced. To minimize the circulating acid load and improve efficiency, the leach should be carried out in a two stage countercurrent mode. Results of the testwork are given in Table 5.3. Conversions of sulphide sulphur to hydrogen sulphide are calculated by difference from the sulphur balance. Approximately 80% of the sulphide was converted to hydrogen sulphide in both tests.

X-ray diffraction analysis of the two residues indicated the presence of some unreacted pyrrhotite from test 1 but none in the test 2 residue. Elemental sulphur was also shown to be present in the test 2 residue.

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5.4.2 Pressure Oxidation Below the Melting Point of Sulphur

In the 1960's, a considerable amount of work was done to investigate the recovery ot elemental sulphur from pyrrhotite feed materials. Initial attempts to perform the oxidation at temperatures above the melting point ot sulphur proved unsuccessful. The molten elemental sulphur tended to coat unreacted sulphide particles and inhibit further reaction. Subsequently additives were discovered which prevented this coating action and allowed reactions to proceed to completion, however the early work concentrated on oxidation temperatures below the melting point of sulphur and it was decided to investigate the behaviour of the pyrrhotite matte at such temperatures. Initial tests were conducted at 11U°C with subsequent tests at 100°C. The lower temperature is more realistic since the exothermic nature of the reaction could lead to temperature excursions above the melting point of sulphur. Variables examined were additive dosage, retention time, pulp density, oxidant and oxygen partial pressure.

Laboratory autoclaves used for batch oxidation are vertical cylinders, typically 2.5 L in working volume. The batch oxidation test procedure in the laboratory was generally as follows. Concentrate and additives were weighed and charged into the empty autoclave and the solution volume was adjusted to 2 L with water. The autoclave was sealed and the required oxygen partial pressure applied and maintained in the head space. Agitation and heating were started. During heating, the autoclave gases were vented to remove inerts. When the temperature was \sim 15°C below the desired operating temperature, 0.5 L solution containing the required sulphuric acid and iron concentrations, was pumped into the autoclave. Once the desired operating temperature was reached, sparging was commenced, the pressure adjusted and timing began. Upon completion of the run, the slurry charge was either cooled under agitation or flash discharged into an agitated flash tank to simulate the discharge from a continuous operation. After cooling under agitation the autoclave was depressurized and discharged.

An initial test was carried out at 110°C with a one hour retention time. Solids content of the feed slurry was 300 g/L of slurry and the pressure oxidation solution contained 20 g/L sulphuric acid. No additives were used and the oxygen partial pressure was maintained at 345 kPa. Results of the test are shown in Table 5.4. The sulphide conversion to elemental sulphur was 76%. Unreacted sulphidic sulphur was present in the residue indicating that the retention time was insufficient to allow the reaction to go to completion. Approximately 4% of

the sulphide sulphur reported to the residue as sulphate sulphur and the increase in sulphate concentration in solution was equivalent to $\sim 3.5\%$ of the sulphidic sulphur in the matte.

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The above oxidation test was repeated with the addition of a surface active agent to the slurry to improve the rate of oxidation of the artificial pyrrhotite. The oxidation discharge slurry was subjected to flotation prior to liquid-solid separation. The results (Table 5.4) show that the quantity of unoxidized sulphide present in the flotation concentrate was 22.1% and that again $~\sim 4\%$ of the sulphide sulphur reported to the residues as sulphate sulphur. Increase in solution sulphate concentration amounted to $~5\%$ of the matte sulphur. The sulphide conversion to elemental sulphur was approximately 63%. The apparent decrease in conversion of sulphidic sulphur to elemental sulphur is due to a poorer sulphur balance across the run. Flotation proved effective in separating elemental sulphur (96% recovery) but the grade of the flotation concentrate (43.1% S°) is considerably lower than that required for feed to hot filtration. No attempt was made to clean the flotation concentrate.

The choice of oxidant for pressure oxidation is dependent upon a number of factors. The use of air rather than oxygen allows for a higher pulp density and hence greater solids throughput to maintain the heat balance, and also allows for the removal of more water from the circuit if required. A series of tests were carried out to assess the pressure oxidation performance with both oxygen and air at different retention times. Tests with oxygen were carried out at a solids content of 150 g/L solution and an oxygen partial pressure of 345 kPa. For the air runs, the solids content was increased to 200 g/L whilst the oxygen partial pressure was decreased to 205 kPa. In an attempt to simulate a solution recycle, the feed solution to the oxidation step contained 19.1 g/L H₂SO₄, 12.6 g/L Fe²⁺ and 5.6 g/L Fe³⁺. A surface active agent was added to all of the runs.

Results for oxidation with oxygen are presented in Table 5.5 and Figure 5.2. Tht effect of retention time on oxidation of the sulphide sulphur is clearly shown in the results. The residue sulphide sulphur content of the residue decreased from 27.7% after 0.5 h, to 5.1% after 2.0 h and complete oxidation of the sulphide sulphur was achieved after 3.0 h. Consequently, conversion of sulphide sulphur to elemental sulphur increased with increasing retention time, but that increase was offset by the increase in oxidation of sulphide sulphur to sulphate. The sulphide conversion to elemental sulphur was 88.5% after 3 h reten-

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tion time. Solution sulphate concentration remained almost constant for each test, but the ratio of $Fe^{3+} : Fe^{2+}$ increased from 0.7 to 3.2 as the retention time increased from 0.5 to 3.0 h.

Oxidation with air was carried out for identical retention times and the results are shown in Table 5.6 and Figure 5.2. After a retention time of 3.0 h, the conversion of sulphide sulphur to elemental sulphur was virtually identical: 88.5% with oxygen and 85.9% air as oxidant. Total iron in solution after 3.0 h was the same with both oxygen and air, but the $Fe^{3+}:Fe^{2+}$ ratio was 0.6:1 for air as compared to 3.2:1 for oxygen. Oxidation of sulphide sulphur to sulphate was apparently similar in both cases.

5.4.3 Pressure Oxidation Above the Melting Point of Sulphur

Several pressure oxidation tests were carried out above the melting point of sulphur with the objective of optimizing the conditions for the conversion of sulphide sulphur to elemental sulphur and the hydrolysis of the iron. Recovery of elemental sulphur from the oxidation residue was also evaluated. Variables examined during the study were oxygen partial pressure, retention time, pulp density, acid concentration and additives. Results are presented in Tables 5.7 to 5.12.

5.4.3.1 Effect of Retention Time

Results presented in Table 5.7 indicate that although better conversions of sulphide sulphur to elemental sulphur were achieved with a 1.0 h retention time, the oxidation residue contained $\sim8.6\%$ sulphide sulphur, equivalent to $\sim 30\%$ of the sulphide sulphur present in pyrrhotite matte. Only 50% of the sulphide sulphur was converted to elemental sulphur. Oxygen consumption was monitored and demand ceased after $~40$ min at which time the oxygen feed rate equalled the vent rate. Since the reaction demanded no oxygen after 40 min but the oxidation was incomplete at that time, it is concluded that a separate effect was controlling the oxidation efficiency. At least 13% of sulphide sulphur present in the matte was oxidized to sulphate sulphur after a retention time of 1.0 h, the majority of the increased sulphate being present in the solution at the end of the leach. The conditions for the 1.0 h retention time test were used as a base case for all subsequent tests.

5.4.3.2 Effect of Oxygen Partial Pressure

Oxidation of sulphide sulphur was slower at 690 kPa oxygen partial

pressure than at 345 kPa (Table 5.8). The reason for this is not easily explained since increasing the oxygen partial pressure usually results in more favourable oxidizing conditions and hence improved sulphide sulphur oxidation. Very coarse sulphidic pellets were observed in the oxidation residue slurry which was cooled under agitation, indicating enhanced coating of unoxidized sulphides with elemental sulphur. The increase in sulphate concentration in solution was equivalent to \sim 10% of the matte sulphide sulphur in both cases, and sulphate was also present in the oxidation residues.

5.4.3.3 Effect of Pulp Density

The lower pulp density feed yielded a slight increase in oxidation of sulphide sulphur but little increase in elemental sulphur yield due to a greater portion of the sulphide sulphur being oxidized to sulphate, as shown in Table 5.9. Again the majority of the sulphate was present in the final oxidation solution. Heat balance in the autoclave will dictate the feed pulp density for a commercial installation. As in previous tests, oxidation of sulphide sulphur was incomplete but oxygen demand ceased prior to the end of the pressure oxidation retention time.

5.4.3.4 Effect of Initial Acidity

The effect of initial acidity on the oxidation of pyrrhotite matte was investigated at three levels of initial acidity, 5, 20 and 50 g/L (Table 5.10). Oxidation of sulphide sulphur improved with increasing initial acidity whilst oxidation through to sulphate decreased. Approximately 15% of the sulphide sulphur was oxidized to sulphate at the lowest initial acidity whereas with 50 g/L acid in the initial solution, only 8% of the sulphide sulphur was oxidized through to sulphate. Therefore, a high recycle of sulphate in solution should be employed to minimize oxidation of sulphide sulphur to sulphate and hence maximize conversion to elemental sulphur. Again, the oxidation of sulphide sulphur ceased prior to completion of the run. The maximum conversion of sulphide sulphur to elemental sulphur was 60% (at 50 g/L initial acid).

5.4.3.5 Effect of Additives

In the previously discussed tests at 150°C, oxidation slurries were cooled under agitation; the sulphidic fraction of the residue was extremely coarse and easily separated by screening. Experience in the oxidation of sulphide materials in the sulphate system has shown that the size of the sulphidic pellets formed when a leach slurry is cooled under agitation is dependent upon additives levels. The fact that

oxygen demand ceased before complete oxidation of the unoxidized sulphur was achieved, indicated the possibility of premature coating of the unleached sulphide particles by elemental sulphur. It was therefore decided to increase the dosage of additive to improve sulphide oxidation.

Results are given in Table 5.11. The final slurry was flash discharged from the autoclave, to simulate discharge from a continuous operation, and the cooled slurry (40°C) was subjected to flotation for elemental sulphur recovery. Approximately 84% of the sulpr'je sulphur was converted to elemental sulphur and sulphide sulphur oxidation exceeded 94%. Flotation separation of the elemental sulphur from the iron oxide fraction yielded 73% recovery of the elemental sulphur to the cleaner concentrate which graded 88.7% S°. The elemental sulphur loss to the rougher tailings was high at \sim 18% but optimization of the circuit, including the addition of frother to the scavenger circuit, should improve elemental sulphur recovery.

An identical test was carried out and the oxidation discharge slurry was filtered and repulped in water prior to flotation (Table 5.12). This was done to simulate a thickening operation prior to flotation as shown in Figure 2.1. The pH of the flotation feed slurry was 2.0 and reagents (50 g/t Aerofroth 73) were required to produce a stable froth. Flotation was successful and a high grade (>95% S°) cleaner concentrate was obtained. Again further optimization of the rougher and scavenger circuits would be required to maximize elemental sulphur recovery. In each of the above tests, the quantity of sulphate sulphur present in the residue was essentially equivalent to the decrease in sulphate content of the solution, indicating little oxidation of sulphide sulphur to sulphate.

A 50 g sample of the cleaner concentrate $($ >95% S°) was melted in an oven and subjected to hot filtration. Melting was easily achieved at 140°C and 49.5 g of pure elemental sulphur were recovered after filtration and granulation of the filtrate in water. The filter cake contained iron oxide. Chemical analysis of the elemental sulphur (Table 5.13) confirmed a high quality product.

To obtain data for the design of a thickener to separate the oxidation discharge solution, which is recycled to the oxidation step, from the final oxidation residue prior to flotation, a further test was conducted (Table 5.12 test conditions) and the flashed discharge slurry subjected to standard bench scale settling tests. All tests were con-

ducted by a standard procedure using 1.0 L graduated cylinders. The tests were done at 70°C, by placing the cylinders in a thermostatically controlled water bath. Settling rates were extremely slow without flocculant addition. The pulp density of the autoclave discharge was \sim 1300 g/L, equivalent to a solids content of 18.6%. Optimum solids content for thickening is <10% and hence a sample of discharge slurry was diluted with discharge solution to give a solids content of 11.9%. The settling test data, with a flocculant addition of 170 g/t is presented in Table 5.14. A four hour underflow reading was arbitarily chosen for the unit area calculation but the test was continued for 24 h. The thickener unit area was calculated to be $0.56 \text{ m}^2/\text{t.d.}$

5.4.4 Miscellaneous Testwork

Natural pyrrhotite was ground for 1.0 h in a steel ball mill at 77% solids. The ground product was 87.4% less than $44 \mu m$. To assess the oxidation characteristics of this material, a charge of 200 g/L was oxidized for 2.0 h at 100°C with an air sparge and oxygen partial pressure of 205 kPa (Table 5.15). Approximately 86% of the sulphide sulphur was oxidized and conversion to elemental sulphur was \sim 79%. An identical test with pyrrhotite matte (Table 5.6) yielded 76% oxidation of sulphide sulphur and 69% conversion to elemental sulphur. It was therefore concluded that natural pyrrhotite could be successfully treated in an identical manner to pyrrhotite matte.

A further test was performed in which a 50:50 mixture of pyrrhotite matte and natural pyrrhotite was subjected to the same conditions (Table 5.16). Approximately 75% of the sulphide sulphur was oxidized with a 71% conversion to elemental sulphur.

5.5 CONTINUOUS TESTWORK

Analysis of the preliminary batch testwork data indicated that complete oxidation of sulphide sulphur could be achieved at 100°C whereas at 150°C complete oxidation could only be achieved by using additives. It was therefore decided to carry out the continuous oxidation at 100°C in order to generate data for the engineering study.

5.5.1 Flowsheet Description and Operation

The equipment flowsheet for the continuous pressure oxidation is shown in Figure 5.3. Ground pyrrhotite matte, having a specific gravity of 4.78, was repulped in water to give a feed slurry containing 70%

solids by weight (pulp density 2240 g/L). Slurry was transferred to the slurry feed tank on a batch basis and surfactant was added. Slurry was fed to the autoclave at a nominal rate of S.2 mL/min, or 0.49 kg/h of pyrrhotite matte.

A synthetic oxidation thickener overflow solution was prepared containing 19 g/L Fe $^{2+}$, 4.6 g/L Fe $^{3+}$ and 12.7 g/L H2SO $_4$. This solution was used to fill the autoclave, thickener and provide feed solution for the first six hours of operation. Solution was continuously pumped into the autoclave at a rate of 50.4 mL/min, thus giving a solids content in the feed slurry of 150 g matte/L total solution.

The combined slurry and solution flow rate gave a retention time in the autoclave of 3.0 h. Oxygen was sparged into each compartment with a total mass flow of 0.44 kg/kg matte. The stoichiometric oxygen requirement for the matte, based upon the following overall reaction,

$$
2FeS_x + 1.50_2 + yH_20 --- \text{Fe}_2O_3 \cdot yH_2O + 2xS^{\circ}
$$

is 0.25 kg/kg matte, hence the oxygen feed rate provided a 76% excess. The equivalent volumetric flow rates were 1.33, 0.67, 0.33 and 0.33 L/min to cells one, two, three, and four, respectively. Cell temperatures were controlled at 100°C and a total autoclave pressure of 275 kPa was maintained with a continuous vent of excess oxygen.

Slurry discharged from the autoclave at \sim 55 mL/min and transferred to the oxidation thickener feed tank. Flocculant was added to the slurry at a rate of 100 g/t pyrrhotite matte. The flocculant was prepared at a concentration of 0.5 g/L and further diluted with a oxidation thickener overflow solution recycle to 0.037 g/L. The diluted flocculant stream was then equally divided between the incomming slurry and the thickener feed well. The flow rate of oxidation thickener overflow recycle was controlled to give a thickener feed slurry containing \sim 7.5% solids by weight. The thickener was operated at \sim 35°C and was equipped with a slow turning rake The thickener overflowed continuously and overflow was recycled to the oxidation step. Thickener underflow was pumped to storage at a rate which maximized underflow pulp density while maintaining a constant mud level in the thickener.

5.5.2 Continuous Pressure Oxidation

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Continuous pressure oxidation was carried out in a 10 L volume autoclave which consists of four pressure vessels (cells) arranged in

cascade, appropriate agitators were installed in each cell which can be independently heated and cooled. Pyrrhotite matte slurry at 70% solids and solution were pumped separately into the first cell. Oxygen was introduced into each autoclave cell. The autoclave discharge was automatically controlled to match the feed rate and maintain a constant level in the autoclave.

At the start of the run, the cells were filled with solution as described in Section 5.5.1 and oxygen was sparged into the slurry in each cell at the required flow rates. Heating was commenced and when the temperature reached 90°C, feed and discharge systems were put into operation. The temperature was then gradually increased to 100°C. Shutdown involved cooling of the autoclave while maintaining agitation and oxygen supply.

Analyses of samples taken from individual compartments gave a measure of the rate of sulphide oxidation across the autoclave. Sampling at three hour intervals was carried out at six sample points across the oxidation circuit, namely feed solution, the four individual cell slurries and discharge slurry. Disch.rge samples were also taken every hour for control purposes.

The scope of the laboratory program included a continuous pressure oxidation test of 20 to 24 h duration. Pyrrhotite matte was fed to the autoclave for 21 h and then the feed was changed to natural pyrrhotite. The Saladipura deposit contains ~40% pyrrhotite which could be easily separated from the pyrite by magnetic separation. It was therefore felt that useful information could be obtained by treating natural pyrrhotite for a period of time in the continuous autoclave under the same conditions as used for the pyrrhotite matte.

The target pressure oxidation parameters are presented below.

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Table 5.17 represents the pressure oxidation operating log for the treatment of pyrrhotite matte and natural pyrrhotite. In general, the target parameters were easily maintained. The feed rate of solids, equivalent to 150 g matte/L solution, was chosen such that the heat generated in the chemical reactions would provide the heat required to maintain a temperature of 100°C, thus giving an autogeneous reaction with respect to heat requirements.

Under steady operating conditions, the vent rate was ~ 0.9 L/min from a feed of 2.67 L/min. Oxygen consumption was therefore ~1.8 L/min or 0.29 kg/kg matte. A small quantity of gas, discharged with the slurry, is not measured in the vent gas flow rate. Therefore, the actual oxygen utilization was very close to the stoichiometric requirement of 0.25 kg/kg matte.

Results from the continuous oxidation of both pyrrhotite matte and natural pyrrhotite are presented in Tables 5.18 to 5.24 and Figures 5.4 to 5.12. Conversion of sulphide sulphur to elemental sulphur and sulphate and the unreacted sulphide content were determined by a material balance method. The weight of solids/L of slurry for each sample taken was determined from a knowledge of the volume of the sample and the dry weight of solids in the sample. Elemental sulphur, sulphide sulphur and sulphate sulphur contents per litre of slurry for each sample could then be calculated from the analyses of the solids. These values were then related to the solids in the combined feed slurry. The method produces variation in results due to the long retention time and is clearly very susceptible to sampling errors. The results presented should therefore not be considered as absolute values but rather indicative of a range within which the true values will lie.

Solution analyses for feed, cell and discharge samples are presented in Tables 5.18 and 5.19 and Figures 5.4 to 5.12. The sample number refers to the location of the sample. F is the feed sample, Cl through C4 are the cell samples and DX is the discharge sample. Synthetic feed solution was pumped into the autoclave for the first six hours of operation after which time oxidation thickener overflow was recycled. The large volume of the thickener (45 L) compared to the total volume of slurry processed during the run (100 L) meant that equilibrium concentrations were not reached between oxidation discharge solution (Figure 5.12) and feed solution (Figure 5.7) during the run. Furthermore, the feed solution sulphuric acid concentration should have been maintained at a constant level to balance the sulphate leaving the circuit in the solution associated with the thickener underflow and also as precipitated basic iron sulphate.

Sulphuric acid was rapidly consumed in cell 1 (Figures 5.4 and 5.8), while ferrous iron concentration increased and the total iron concentration remained tairly constant. In cells 2, 3 and 4, the ferrous iron concentration decreased (Figure 5.5) as oxidation of ferrous to ferric iron occurred and the total iron concentration (Figure 5.6) decreased as ferric iron was precipitated as either goethite or hydrated iron oxide. Precipitation of the iron was accompanied by a slight increase in acid concentration (Figure 5.4) in cells 2, 3 and 4.

Residue analyses for cell and discharge samples are shown in Tables 5.20 to 5.24, together with conversion data. The solids weight gain across the oxidation step was in the range 30 to 40%, based on the sample volumes and dry solids weights. The rate of conversion of sulphide sulphur to elemental sulphur, and hence the optimum retention time, can be determined from the profile samples. Median values for each cell and hourly discharge samples are presented below for the treatment of pyrrhotite matte.

Values for cell 3 and 4 indicate that optimum conversion has been achieved in cell 3, or after a retention time of 2.25 h. However the discharge samples show a considerably higher median conversion. In Tables 5.20 and 5.21 it can be seen that the solids content of the discharge slurries are considerably greater than for the cell 4 slurries and this would account for the apparent increase in conversion of sulphide sulphur to elemental sulphur. Cell samples are taken from dip pipes located near the bottom of the cell. Sulphur is readily flotable in a sparged slurry and hence cell samples would tend to yield lower solids content than the discharge sample which contains the whole contents of the autoclave discharge. It is therefore assumed that the discharge samples are more representative of the total slurry than the cell samples, especially cell 4 where the highest concentration of elemental sulphur wi11 exist.

The median value for percent unreacted sulphide sulphur in the discharge samples was 6.2%, thus indicating that a slightly longer retention time would be required to obtain complete oxidation of the sulphide sulphur. The flow rates of feed slurry and solution were set to give a retention time of 3.0 h based upon the static autoclave volume of 10 L. In practice, the dynamic volume is ~8 L and therefore the true retention time for the oxidation step was ~ 2.4 h. Batch retention times to achieve complete sulphide oxidation were 3.0 h.

When the feed was changed to natural pyrrhotite, difficulties were experienced in controlling the slurry feed rate for the first two hours of operation, resulting in wide fluctuations in solution analyses. As the oxidation progressed, the oxidation of sulphide sulphur decreased, with -40% of the sulphide reporting to the discharge residue, and only $\sim50\%$ of the sulphide sulphur being recovered as elemental sulphur. Cell and discharge solution analyses (Figures 5.8 to 5.12) show that the ratio of ferrous iron:total iron increased almost to unity, indicating a lack of ferric iron to perform the oxygen transfer function and maintain the oxidation reaction. The natural pyrrhotite was fed at a rate of \sim 215 g/L of solution to maintain the same total iron feed to the system and hence the same oxygen stoichiometry. Batch oxidation tests showed that the behaviour of natural pyrrhotite was almost identical to that of pyrrhotite matte in a 10U°C test. It is expected that if the acidity in the feed solution had been maintained at 12 to 15 g/L, to balance the sulphate loss with the residues, the oxidation of sulphide sulphur would have exceeded 90%, with a corresponding increase in elemental sulphur recovery.

The sulphate sulphur present in the residues after treatment of the pyrrhotite matte corresponded to $\sim 18\%$ of the sulphide sulphur in the matte, and \sim 14% for the treatment of natural pyrrhotite. A portion of this sulphate originated in the feed solution, since the sulphate content of the solution decreased from feed to discharge.

5.5.3 Liquid-Solid Separation

Continuous thickening of the autoclave discharge slurry was carried out in a 45 L volume Plexiglas thickener, equipped with a slow speed rake. At the start of the run the thickener was filled with synthetic overflow solution and flocculated slurry was then fed to the thickener. The mud level was allowed to rise to a depth of 25 to 30 cm before underflow was continuously pumped at a rate to maintain that level.

The oxidation thickener operating log is presented in Table 5.25. Flocculant was added at a dosage of 100 y/t of solids. A stock solution was prepared at 0.5 g/L and the required feed rate was 2 mL/min. Underflow solid specific gravity was 2.95. Under steady operating conditions, thickener underflows containing in excess of 50% solids could be anticipated. No attempt was made to optimize the flocculant requirements because of the short duration of the testwork.

5.5.4 Elemental Sulphur Recovery

Recovery of elemental sulphur from the oxidation thickener underflow was attempted by both flotation and pelletization. The final stage of elemental sulphur recovery is hot filtration. Recovery of elemental sulphur by hot filtration is extremely sensitive to the elemental sulphur grade of the feed. Therefore the objective of the recovery route was to maximize both the recovery and the grade or elemental sulphur in the final concentrate.

5.5.4.1 Flotation Testwork

Flotation testwork was carried out in a 2 L batch flotation cell equipped with a mechanical paddle for the removal of froth and an electronic level controller. Flotation tests were carried out on oxidation thickener underflow obtained from the treatment of pyrrhotite matte. Sufficient thickener underflow was diluted with water to a volume of 2 L to give a solids content of ~ 100 g/L slurry, 10% solids. All tests were performed under ambient conditions and at a constant impeller speed of 1200 rpm. Flotation concentrate samples were removed after 0.25, 0.5, 1, 2, 4, and 8 min to enable flotation rate curves to be plotted. The objectives of the tests were to optimize elemental sulphur recovery and depress flotation of iron oxide. Results are presented in Tables 5.26 to 5.83 and Figures 5.13 to 5.19.

Elemental sulphur floats readi ly in an agitated and aerated flotation cell and therefore flotation was attempted without reagent addition (Table 5.26). Subsequently three different frothers were tested at a typical frother addition of 50 g/t (Tables 5.27 to 5.29). The results of these tests are presented in Figure 5.13 and show that Aerofroth 73 has a marked advantage over the other frothers tested, in terms of elemental sulphur recovery. After a retention time of four minutes, \sim 95% of the elemental sulphur had been recovered to a rougher concentrate grading $42.4%$ S°.

The effect of washing the oxidation residue to remove soluble metal salts, on the flotation behaviour of elemental sulphur and iron oxide, was investigated (Table 5.30). The results, shown in Figures b.14 and 5.15, indicate that both elemental sulphur and iron oxide flotation are suppressed and therefore no advantage is gained by thoroughly washing the oxidation residue prior to flotation.

Further testwork to suppress the flotation of iron oxide involved the use of trisodium phosphate, a reagent used commercially for depressing iron oxide slimes. Typical dosages are 250 to 1000 g/t and these levels were tested with both Aerofroth 73 (Table 5.31) and Pine Oil (Tables 5.32 and 5.33) as the frother. The addition of 1000 g/t trisodium phosphate together with 50 g/t Aerofroth 73 produced a slight improvement in the depression of iron oxide (Figure 5.17) but elemental sulphur flotation was also depressed. The addition of various levels of trisodium phosphate together with 50 g/t Pine Oil also failed to depress iron oxide flotation to any significant extent (Figures 5.18 to 5.19). The difficulty of separating elemental sulphur from iron oxides in residues from leaches conducted below the melting point of sulphur is probably due to the intimate association of the two phases.

A continuous flotation test was carried out on oxidation thickener underflow repulped with water to give a feed slurry containing -200 g/L solids. The circuit consisted of three rougher cells, three cleaner cells and six scavenger cells. Each cell had a working volume of 300 mL and fresh feed was pumped to the circuit at a rate of 100 mL/ min. The flowsheet is shown schematically in Figure 5.20. Reagents, 50 g/t Aerofroth 73 and 1000 g/t trisodium phosphate, were added to the rougher circuit feed tank. Rougher concentrate was fed to the cleaner circuit and the final cleaner concentrate product was withdrawn from the first two cells, with the concentrate from the third cell being recycled to cleaner circuit feed. Cleaner tailings were fed to the front of the rougher circuit. Rougher tailings were treated in the six cell scavenger circuit, concentrates from the first three cells being recycled to the rougher circuit. Concentrate from the final three cells was recycled to the front of the scavenger circuit. After two hours of steady operation, a sample of cleaner concentrate analyzed 44.3% S°. Although sulphur recovery across the circuit appeared to be satisfactory, flotation of iron oxide remained a problem. A sample of cleaner concentrate was subjected to a batch flotation rate run and the results are presented in Table 5.34. No upgrading of the concentrate was achieved and the cumulative weight distribution was identical to the cumulative elemental sulphur distribution.

To obtain high recoveries of elemental sulphur in a hot filtration operation, the feed to the step (flotation cleaner concentrate) must have a grade in excess of 85% S°. Therefore for a viable process based on pressure oxidation of pyrrhotite matte below the melting point of sulphur, it would be necessary to perform further testwork to optimize conditions and reagents for the depression of iron oxide. This testwork was not within the scope of the Phase I study.

5.5.4.2 Pelletization

Three tests were performed in an attempt to pelletize the elemental sulphur content of the oxidation residue by heating the oxidation thickener underflow slurry above the melting point of sulphur. In the first test, 2.5 L of oxidation thickener underflow, pulp density 1436 g/L, 40% solids, was heated in an autoclave to 130°C under agitation and the temperature was maintained for fifteen minutes. The autoclave was then cooled under agitation and the slurry screened at $150 \mu m$. No elemental sulphur pellets were observed. The test was repeated at a temperature of 150°C for thirty minutes and again no pellets were obtained.

Previous testwork in this area has shown that pelletization of elemental sulphur is difficult with slurries containing less than 25% S°. The elemental sulphur content of the slurry was therefore doubled to ~35% S° by adding 250 g of elemental sulphur. The test was then performed at 130°C for fifteen minutes and again no pellets were formed. Further testwork would be required to fully investigate pelletization, with slurry pulp density and additives addition being considered as major parameters.

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Table 5.2 Chemical and Screen Analysis of Lump Pyrrhotite Matte

Chemical Analysis

Screen Analyses (Milled Matte)

Table 5.3 Non Oxidizing Acid Leach of Pyrrhotite Matte

Test 1 120 g/L H_2SO_4 , H_2SO_4 : Fe molar ratio = 1.22:1

				Analysis $(\% , g/L)$		$ Distribution(\%) $	% $S = -\rangle$		
$\textsf{Fraction}[\texttt{L}, \texttt{g}]$		$Fe2+$	Fe	S°		H_2 50al	Fe		H ₂ S
Head	119			57.2 <0.01	29.1		100	109	
Solution	1.275	58.7				23.5	93.6	5.8	
Residue	15.0			29.2 5.8	31.9		6,4	13.8	80.4

Test 2 200 g/L H_2SO_4 , H_2SO_4 : Fe molar ratio = 2.04:1

			Analysis $(\% , g/L)$			$ Distriolution (\%) $	% $S = -\rangle$		
\lvert Fraction \lvert L,g		$Fe2+$	Fe	S° S		H_2SO_4	Fe		H ₂ S
Head	119		57.2		29.1		100	100	
$\textcolor{orange}{\textbf{\small{Solution}}} \textcolor{orange}{\textbf{\small{[1.275}}}$		61.2				104	97.9	11.3	
Residue	15.0		18.6	21.4	41.6		2.1	9.1	79.6

Table 5.4 Pressure Oxidation of Pyrrhotite Matte Below the Melting Point of Sulphur: Effect of Additive

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Table 5.5 Pressure Oxidation of Pyrrhotite №tte Below the Melting Point of Sulphur: Effect of Retention Time During Leaching with Oxygen

Charge Temperature Retention Time Oxygen Pressure 345 kPa Total Pressure 345 kPa 375 g (150 g/L) pyrrhotite matte as a 70% solids slurry, solution to give a total slurry volume of 2.5 L containing 19.1 g/L H₂SO₄, 12.6 g/L Fe²⁺, 5.6 g/L Fe³⁺, and surfactant additive : 100° C Variable

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Table 5.6 Pressure Oxidation of Pyrrhotite Matte Below the Melting Point of Sulphur: Effect of Retention Time During Leaching with Air

Table 5.7 Pressure Oxidation of Pyrrhotite Hatte Above the Melting Point of Sulphur: Effect of Retention Time

Total Pressure 825 kPa

Charge Temperature Retention Time Variable Oxygen Pressure 345 kPa 750 g (300 g/L) pyrrhotite matte as a 70% solids slurry, solution to give a total slurry volume of 2.5 L containing 50 g $(20 g/L)$ H₂SO₄ and additives $: 150^{\circ}$ C

Time						Analysis $(\%,\ g/L)$	Distribution(%)				
(h)	Fraction L, q		$ Fe^{2+} $	Fe ₁		S° S(SO ₄ =) S		H_2SO_4	Fe	$S =$	$\left \begin{smallmatrix} 2 & 2 \ 2 & 5 \end{smallmatrix} \right $
0.5	Head	$ 750\rangle$		57.2 \leq 01		0.17	29.1		100	100	
	Solution 2.345 7.2			16.4				11.4	18.0		
	Residue:										
	$+150 \mu m$	1299.61	$\overline{}$	$39,9$ [23.6]		0,24	59.2		27.9	48.9	32.6
	$-150 \mu m$	448.2	$\overline{}$		51,810,67	1.04	3.49	\bullet	54.1	3.7	1.4
1.0	Head	$ 750\rangle$	$\qquad \qquad -$		$57.2 \zeta, 01 $	0.17	29.1		100	100	
	Solution 2.345 8.4			16.5	$\overline{}$		\bullet	11.2	12.4		
	Residue	753.5	\overline{a}		49.9 [14.3]	0.83	23.7		87.6	29.8	49.7

Table 5.8 Pressure Oxidation of Pyrrhotite Matte Above the Melting Point of **Sulphur: Effect of Oxygen Partial Pressure**

Charge Temperature Retention Time Oxygen Pressure Variable Total Pressure — : Variable 750 g (300 g/L) pyrrhotite matte as a 70% solids slurry, solution to give a total slurry volume of 2.5 L containing 50 g $(20 g/L)$ H₂SO₄ and additives $: 150^{\circ}$ C $: 1.0 h$

Press kPa 0 ₂		Total Fraction L, g					Analysis $(\frac{6}{6}, \frac{9}{L})$ $\left \overline{Fe^{2+}} \right $ Fe S° S(SO ₄ =) S		$H_{2}SO_{4}$	$ Distribution(\%) $ Fe	$S =$	χ S = -25°
345	825	Head: Solution $2.345/8.4$ Residue	750 753.5	\blacksquare $\overline{}$	$ 16.5 $ –	57.2 \leq 01 [49.9 14.3]	0.17 0.83	29.1 23.7	11.2 \sim	100 12.4 87.6	100 29.8	49.7
690	1170	Head Solution $[2, 345]9.2$ Residue: +150 առ $-150~\mu m$	$ 750\rangle$ 281 435	$\overline{}$ $\ddot{ }$ $\overline{}$	[15.7] $ 61.8 \le 1$	$[57,2] \le 01$ [42.1 26.8]	0.17 1.14 1.06	29.1 58.1 4,30	17.0 ~ 2.1 $\overline{}$	100 9.7 27.6 62.7	100 39.1 6.5	34.7 $\langle .2$

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Table 5.9 Pressure Oxidation of Pyrrhotite Matte Above the Melting Point of Sulphur: Effect of Pulp Density

Charge ieniperatii re $Retention Time$ \therefore 1.0 h Oxygen Pressure 345 kPa Variable g pyrrhotite matte as as a /0% solids slurry, solution to give a total slurry volume of 2.5 L containing 50 g (20 g/L) H2SO4 and additives : 150° C

Total Pressure 325 kPa

Table 5.10 Pressure Oxidation of Pyrrhotite Matte Above the Melting Point of Sulphur: Initial Acidity

Charge

750 g (300 g/L) pyrrhotite matte as as a 70% solids slurry, solution to give a total slurry volume of 2.5 L containing variable g H2SO4 and additives

Table 5.11 Pressure Oxidation of Pyrrhotite Matte Above the Melting Point **of Sulphur: Optimization Test**

375 g (151) y/L) pyrrhotite matte as as a 70% solids slurry, Charge solution to give a total solution volume of 2.5 L contrining 2.6 g/L Fe²⁺, 22 g/L Fe, 20.4 g/L H₂S0₄ and additive 150°C Tempe rature $\ddot{\mathbb{C}}$ 1.0 h Rétention Time 345 kPa Oxygen Pressure 825 kPa Total Pressure Leach, flash discharge Conditions $\mathbb{R}^{\mathbb{Z}^n}$

Table 5.12 Pressure Oxidation of Pyrrhotite Matte Above the Melting Point of Sulphur: Optimization Test

Charge Temperature Retention Time Oxygen Pressure 345 kPa Total Pressure Conditions 375 g (150 g/L) pyrrhotite matte as as a 70% solids slurry, solution to give a total solution volume of 2.5 L containing 2.6 g/L Fe²⁺, 22 g/L Fe, 20.4 g/L H₂SO₄ and additive $: 150^{\circ}$ C $: 1.0 h$ 325 kPa Leach, flash discharge

Conditions:

Flotation: Leach residue washed and repulped, 1200 rpin. 40°C, 50 g/t Aerofroth 73

Table 5.13 Elemental Sulphur Recovery from Flotation Concentrate

Conditions: Cleaner flotation concentrate (95.4% S°) melted at 14U°C

Melt filtered

Filtrate granulated in water

Sulphur Product:

Table 5.14 Settling Test Data for 150°C Oxidation Discharge Slurry

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Calculated Values (Kunch Method):

Table 5.15 Pressure Oxidation of Natural Pyrrhotite Below the Melting Point of Sulphur

Charge : 500 g (200 g/L) natural pyrrhotite (87.4% <44 pm), 2.5 L solution containing 18.6 g/L H₂SO₄, 12.5 g/L Fe²⁺, 5.2 g/L Fe³⁺ and surfactant additive

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Table 5.16 Pressure Oxidation of a 50:50 Mixture of Pyrrhotite Matte and Natural Pyrrhotite Below the Melting Point of Sulphur

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Run		Solution Analysis (g/L)				Run		Solution Analysis (g/L)			
Time (h) Sample Fe^{2+}			Fe	S^{\star}	H_2SU_4	$ Time(h) $ Sample $ Fe^{2+} $			Fe	S^{\star}	H_2S0_4
3	F.	19.0	23.6	19.0	12.7	14	DΧ	9.2	15.0	12.3	6.2
	C ₁	22.2	23.1	14.7	3.5	15	F.	17.2	24.3	18.3	7.2
	C ₂	20.8	24.3	16.3	4.2		C ₁	21.8	23.5	15.3	4.1
	C ₃	17.2	20.4	14.3	5.1		C2	17.2	20.5	14.3	4.9
	(4)	16.2	20.6	15.1	6.3		$\mathbb C$	13.0	18.0	13.4	5.1
	DХ	17.2	21.6	15.1	4.3		C4	9.3	15.2	12.2	5.4
$\overline{4}$	ĐΧ	11.5	18.4	14.0	4.4		DX.				
5	ĐΧ	9.4	15.8	12.6	5.2	16	DX.	8.7	15.2	i2.3	5.3
$\boldsymbol{6}$	$\mathsf F$	18.9	24.0	19.4	12.6	17	$\mathsf{D}\mathsf{X}$	8.8	14.7	11.8	5.1
	C ₁	22.5	23.5	15.1	4.2	$18\,$	F	15.1	22.0	16.5	5.7
	(2)	17.0	18.5	12.8	5.3		C1	18.9	20.6	13.3	4.5
	C ₃	11.8	18.5	14.5	5.9		C2	15.8	18.5	13.1	5.2
	C ₄	9.1	15.8	13.2	6.7		C3	12.3	17.6	13.5	5.7
	ĐΧ	8.7	16.1	13.0	5.0		C ₄	9.0	15.6	12.8	5.9
\overline{I}	DΧ	8.7	16.1	13.0	5.0		IJΧ	8.9	15.0	12.1	5.3
8	IJΧ	8.7	16.0	12.9	5.1	19	ĐΧ	8.7	14.9	12.2	5.6
$\overline{9}$	F.	18.6	24.1	19.3	11.9	20	DX	8.7	13.0	10.4	5.3
	C ₁	21.6	23.8	15.9	4,4	21	F.	14.8	21.6	16.1	5.3
	C ₂	16.1	20.8	15.2	5.8		C1	19.3	20.1	13.1	4.1
	C3	11.0	19.6	15.7	6.1		C2	15.0	17.0	11.9	4.9
	C ₄	8.5	16.4	13.9	6.8		C ₃	11.6	15.2	11.5	5.3
	ÐХ	8.5	15.9	13.0	5.4		C ₄	8.7	13.0	10.7	6.1
10	ĐΧ	8.0	15.9	13.3	5.9		ĐΧ	8.8	13.5	10.9	5.4
11	DХ	8,4	17.3	14.1	4.9	22	DX	8.4	13.3	10.7	5.2
12	F	18.2	22.9	17.9	10.5	23	$\mathfrak{f})\mathfrak{X}$	8.4	13.7	11.3	5.8
	C ₁	21.9	21.9	14.2	4.9	24	F	13.8	20.6	15.2	4.5
	C ₂	17.4	21.1	14.9	5.3		Ω	14.5	[14.5]	9.4	3.9
	C ₃	13.3	18.6	14.1	5.8		C2	14.4	[15.3]	10.6	4.9
	C ₄	9.5	17.5	14.4	6.2		C3	3,4	7.9	6.8	2.9
	ĐΧ	9.0	13.7	10.8	4.9		C ₄	6.8	10.7	9.6	7.3
13	DΧ	8.6	18.4	15.1	5.2		${\sf D}{\sf X}$	6.8	9.2	8.0	6.2

Table 5.18 Continuous Pressure Oxidation of Pyrrhotite Matte: Solution Analyses

* Calculated

Run			Solution Analysis (g/L)			Run		Solution Analysis (g/L)				
Time (h) $\lceil \text{Sample} \rceil$ Fe ²⁺			Fe	S^{\star}	H ₂ S0 ₄	$ Time(h) $ Sample $ $		Fe^{2+}	Fe	S^{\star}	H_2 SO ₄	
25	DX.	6,4	11.4	9.6	4.9	30	C2	11.4	13.1	9.3	4.0	
26	ЫX	8.7	[12.6]	9.6	3.8		C ₃	10, 2	10.9	7.8	4.1	
27	F	11.9	12.7	8.6	3.4		C ₄	\S .	9.2	6.6	4.0	
	Ω	13.5	[13.6]	8.8	2.9		DХ	ϵ .7	9.0	6.2	2.9	
	C ₂	12.7	18.0	12,9	3.3	31	DX.	9.7	13.2	9.5	2.9	
	C ₃	10.9	10.9	7.5	3.7	32 [°]	F	11.9	17.8	13.1	3.6	
	C ₄	9,7	10.8	7.8	3.8		C ₁	12.3	14.9	10.5	3.7	
	DХ	9.2	13.5	9.9	2.9		C2	11.7	11.9	8.0	3.5	
28	DX.	9.0	9.7	6.7	2.7		C3	10.2	11.2	8.0	3.9	
29	DХ	9.0	9.2	6.3	2.8		C ₄	8.7	11.5	8,5	3.3	
30	F	11.8	18.3	13.6	3.9		DX	8.7	10.6	7.6	3.1	
	C ₁	12.8	15.6	11.0	3.7							

Table 5.19 Continuous Pressure Oxidation of Natural Pyrrtiotite: Solution Analyses

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Table 5.21 Continuous Pressure Oxidation of Pyrrhotite Matte: Profile Samples Analytical and Conversion Data

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Table 5.23 Continuous Pressure Oxidation of Pyrrhotite Matte: Discharge Samples Analytical and Conversion Data

* Transition period between feeds, some difficulty in controlling slurry feed rate

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Table 5.25 Oxidation Thickener Operating Log

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Table 5.26 Batch Flotation Test: Ho Reagent Addition

Conditions: 330 mL thickener underflow, PD 1455 g/L, diluted to 2 L with water

- 20°C ~ 10
- : 1200 rpm

Reagents : None

* Calculated

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Table 5.27 Batch Flotation Test: Effect of Dowfroth 200

Conditions:

- \therefore 20 \degree C
- 1200 rpm \mathcal{L}^{\pm}

Reagents 50 g/t Dowfroth 200

* Calculated

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Table 5.28 Batch Flotation Test: Effect of Pine Oil

* Calculated

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Table 5.29 Batch Flotation Test: Effect of Aerofroth 73

Conditions:

330 mL thickener underflow, PD 1455 g/L, bulked to 2 L with water

- 20 °C $\frac{1}{2}$
- 1200 rpm \mathbb{Z}^+

Reagents : 50 g/t Aerofroth 73

* Calculated

Table 5.30 Batch Flotation Test: Effect of Residue Washing

Conditions: 330 mL thickener underflow, filtered, washed and repulped with water to 2 L volume

- : 20°C
- 1200 rpm $\mathbb{R}^{n \times n}$

Reagents 50 g/t Aerofroth 73

* Calculated

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Table 5.31 Batch Flotation Test: Effect of Depressant

Conditions:

400 mL thickener underflow, PD 1405 g/L, oulked to 2 L with water

- 20°C
- \mathbb{C}^{\times}
- 12U0 rpm \mathbb{R}^2

Reagents : 50 g/t Aerofroth 73

1000 g/t Trisodium Phosphate

* Calculated

Table 5.32 Batch Flotation Test: Effect of Depressant

: 1200 rpm

Reagents : 50 g/t Pine Oil

250 g/t Trisodium Phosphate

* Calculated

Table 5.33 Batch Flotation Test: Effect of Depressant

Conditions: 400 mL thickener underflow, PD 1405 g/L, bulked to 2 L with water : 20°C

1200 rpm

 $\ddot{\ddot{\xi}}$ Reagents : 50 g/t Pine Oil

1000 g/t Trisodium Phosphate

* Calculated

Table 5*34 Batch Flotation Test on Continuous Flotation Cleaner Concentrate

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1000 g/t Trisodium Phosphate

* Calculated

Figure 5.1 Non Oxidizing Acid Leach of Pyrrhotite Matte

FIGURE 5.2 CONVERSION OF SULPHIDE SULPHUR TO ELEMENTAL SULPHUR WITH OXYGEN AND AIR AS OXIDANT

O OXYGEN

□ AIR

Figure 5.3 Equipment Flowsheet for the Continuous Pressure Oxidation of Pyrrhotite Matte

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FIGURE 5.9 CELL TWO SOLUTION ANALYSES.

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IRON \bullet \Box FERROUS IRON \Diamond SULPHURIC ACID

FIGURE 5.11 CELL FOUR SOLUTION ANALYSES.

EFFECT OF FROTHER TYPE.

- 50 g/t AEROFROTH 73 \circ
- 50 g/t PINE OIL \Box
- \Diamond 50 g/t DOWFROTH 200
- Δ NO FROTHER

FIGURE 5.14 FLOTATION OF MATTE OXIDATION RESIDUE: EFFECT OF WASHING RESIDUE ON SULPHUR RECOV-ERY WITH 50 g/t AEROFROTH 73 AS FROTHER.

UNDERFLOW WASHED PRIOR TO FLOTATION \Box

UNDERFLOW AS RECEIVED \circ

FIGURE 5.15 FLOTATION OF MATTE OXIDATION RESIDUE : EFFECT OF WASHING RESIDUE ON IRON RECOV-ERY WITH 50 g/t AEROFROTH 73 AS FROTHER.

O UNDERFLOW AS RECEIVED

□ UNDERFLOW WASHED PRIOR TO FLOTATION

FIGURE 5.16 FLOTATION OF MATTE OXIDATION RESIDUE : EFFECT OF DEPRESSANT ADDITION ON SULPHUR RE-COVERY WITH 50 g/t AEROFROTH 73 AS FROTHER.

- \circ NO DEPRESSANT
- 1000 g/t TRISODIUM PHOSPHATE \Box

FIGURE 5.17 FLOTATION OF MATTE OXIDATION RESIDUE : EFFECT OF DEPRESSANT ADDITION ON IRON RE-COVERY WITH 50 g/t AEROFROTH 73 AS FROTHER.

- NO DEPRESSANT \circ
- 1000 g/t TRISODIUM PHOSPHATE \Box

' FIGURE 5.18 FLOTATION OF MATTE OXIDATION RESIDUE : . EFFECT OF DEPRESSANT ADDITION ON SULPHUR I RECOVERY WITH 50 g/t PINE OIL AS FROTHER.

O NO OEPRESSANT

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- **j □ 250 g/t TRISODIUM PHOSPHATE**
- **O 1000 g/t TRISODIUM PHOSPHATE**

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FIGURE 5.19 FLOTATION OF MATTE OXIDATION RESIDUE « EFFECT OF DEPRESSANT ADDITION ON IRON RECOVERY WITH 50 g/t PINE OIL AS FROTHER.

- **O NO DEPRESSANT**
- **□ 250 g/t TRISODIUM PHOSPHATE**
- \diamondsuit 1000 g/t TRISODIUM PHOSPHATE

Figure 5.20 Continuous Flotation Circuit

6.0 ENGINEERING STUDY

Based on the results of the laboratory studies and information supplied by the client, a preliminary cost estimate was done. The capital cost for a pressure oxidation and sulphur recovery circuit capable of treating 420 t/d of artificial pyrrhotite to produce 115 t/d of sulphur i> estimated at S17 million (U.S.) with estimated annual operating costs of \$3.1 million (U.S.).

Natural pyrrhotite from the Saladipura deposit could also be used as feed to the Sherritt process. Capital and operating cost would be similar if natural pyrrhotite was used as feed in place of the artificial pyrrhotite.

6.1 Project Description

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Pyrites, Phosphates, and Chemicals Ltd. of India (PPCL) own and mine the Amjhore pyrite deposit located in Bihar State, India. PPCL are considering mining 1600 t/d of Amjhore pyrite to produce elemental sulphur and artificial pyrrhotite matte through a conventional pyrometallurgical smelting process. This matte could be further treated to recover elemental sulphur in Sherritt's aqueous oxidation process. Sherritt's process would convert the pyrrhotite to elemental sulphur and iron oxide.

The pyrrhotite matte was assumed to have a composition of 57% iron and 29% sulphur. A single autoclave train was used as the design basis for the pressure oxidation and sulphur recovery circuit. The single train would be capable of processing 420 t/d of matte, which would produce 115 t/d of elemental sulphur.

The battery limits of the pressure ovidation and sulphur recovery circuit and the streams entering and leaving the battery limits, are described overleaf.

6.2 PROCESS DESCRIPTION

Drawing 09901-66-04-001 depicts the Process Flowsheet for the PPCL pressure oxidation and sulphur recovery circuit.

Granulated pyrrhotite matte is delivered from the smelter and reclaimed onto a conveyor from the matte storage area. The matte is metered into the ball mill with a weigh belt. The ball mill discharge is pumped to the primary hydrocyclones in which the oversize is separated as underflow and is recycled to the ball mill. The overflow product is sent to the secondary hydrocyclones in which the slurry is thickened to the required pulp density. The ground matte product from the secondary hydrocyclones underflow reports to the ground matte storage tanks, which provides a surge volume.

The ground matte slurry is pumped from the storage tank to the metering tank and then into the pressure oxidation autoclave using an air displacement slurry transfer pump. Slurry recycled from the autoclave discharge hydrocyclones and solution from the tailings thickener are also fed into the autoclave to maintain the autoclave heat balance. The oxidation, achieved using pure oxygen, is carried out in a lead and brick lined autoclave which is 3.66 m diameter by 14.6 m. The vessel is divided into four compartments each of which is agitated, Slurry from the autoclave is discharged to the flash tank.

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 $\label{eq:10} \begin{array}{ll} \mathcal{D}^{\mathcal{A}}_{\mathbf{A}} & \mbox{and} \quad \mathcal{D}^{\mathcal{A}}_{\mathbf{A}} = \mathcal{D}^{\mathcal{A}}_{\mathbf{A}} \left(\mathcal{D}^{\mathcal{A}}_{\mathbf{A}} \left(\mathcal{D}^{\mathcal{A}}_{\mathbf{A}} \right) \right) \times \mathcal{D}^{\mathcal{A}}_{\mathbf{A}} \\ & \mbox{if} \quad \mathcal{D}^{\mathcal{A}}_{\mathbf{A}} = \mathcal{D}^{\mathcal{A}}_{\mathbf{A}} \left(\mathcal{D}^$

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Steam produced at the flash tank is vented, and the flashed slurry is drained to a seal tank. Slurry from the seal tank is pumped to the primary autoclave discharge hydrocyclones which are used to preconcentrate the elemental sulphur and sulphides in the underflow, which is sent to the flotation circuit. Flotation tailings are added to the primary hydrocyclones overflow which are sent to the secondary hydrocyclones. The remaining elemental sulphur and sulphides report to the secondary hydrocyclones underflow and are recycled to the autoclave. The secondary hydrocyclones overflow, containing the iron oxide residue, is sent to the tailings thickener, the thickener overflow is partially recycled to the autoclave. The thickener underflow, and overflow which is not recycled to the autoclave, are sent to the tailings neutralization section.

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The tailings are initially neutralized with a limestone slurry in two agitated tanks. Slurry from the first tank overflows to the second larger reaction tank which ensures adequate retention time for the complete reaction of the limestone. The slurry then reports to two agitated tanks in series into which lime slurry is added to neutralize any sulphate remaining in solution. The neutralized slurry overflows to the tailings pump tank from which it is pumped to the tailings pond. In the tailings pond the solids are settled out from the solution which is then available for use within the process.

Underflow from the primary autoclave hydrocyclones reports to the flotation conditioning tank. In the conditioning tank the slurry is adjusted to the required pulp density, recycle streams and the flotation reagent are added. The slurry overflows from the conditioning tank to a constant head tank which feeds the flotation circuit. The flotation circuit consists of rougher, cleaner and scavenger cells. Feed to the flotation circuit reports to the rougher cells, the rougher concentrate then reports to the cleaner cells while the tailings report to the scavenger cells. Scavenger concentrate is recycled to the flotation conditioning tank and the scavenger tailings are pumped to the secondary autoclave hydrocyclones. Tailings from the cleaner cells are also recycled to the flotation conditioning tank. The cleaner concentrate is the flotation product which is collected in the filter feed tank.

The cleaner concentrate is dewatered and washed on a vacuum belt filter. The filtrate from the oelt filter is recycled to the flotation conditioning tank. The filter cake is conveyed to the dirty sulphur pit via the sulphur melting cyclone. Molten sulphur from the pit is

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circulated through the melting cyclone to supply tne heat required to melt the sulphur contained in the incoming filter cake. The dirty molten sulphur is filtered using a pressure leaf filter. The product sulphur passes through the filter and reports to the clean sulphur pit. The product sulphur is stored in the Jean sulphur pit. Filter cake produced at the pressure leaf filter is discharged periodically and is broken up in a pug mill and is then pulverized in a hammer mill. The filter cake, which contains unreacted sulphides and entrained sulphur, is recycled to the matte stroage area for reprocessing in the pressure oxidation section.

Final sulphur product is delivered to the battery limits of the plant in molten form in a pipeline.

6.3 PROCESS FLOWSHEET

The process flowsheet, drawing number 09901-66-04-001, is shown at the end of this section. The equipment for the pressure oxidation and sulphur recovery circuit is listed on the flowsheet. The equipment sizing was based on a single autoclave train capable of processing 420 t/d of matte which would produce 155 t/d of elemental sulphur.

A preliminary plant layout, Figure 6.1, is also included.

6.4 CAPITAL COST ESTIMATE

6.4.1 Results

The following table contains the summary of the capital cost estimates of the PPCL pressure oxidation and sulphur recovery circuit. The capital costs are based on a single autoclave train, which would produce 115 t/d of elemental sulphur.

6.4.2 Rasis

The basis of the capital cost estimate has been reviewed with PPCL to reflect the Indian conditions.

Due to the preliminary nature of the engineering and laboratory work carried out, this capital cost estimate is an order of magnitude estimate with an accuracy of no better than ±30%.

Preliminary material and energy balances were used to estimate the equipment sizes for the complete plant.

The costs tabulated are based on fourth quarter of 1983 for an Indian location and do not include escalation. Costs for the Indian ^cation were oased on information supplied by PPCL.

An exchange rate of 10 Rs equals \$1 (U.S.) was used.

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The installed equipment costs include actual equipment installation which covers equipment erection, concrete pads, access steel, insulation and paint which were estimated using a modular estimating technique based on equipment complexity, materials and size. Piping costs were estimated using the modular estimating technique which is based on material cost and the complexity of the piping around a specific piece of equipment. Instrumentation costs were estimated using the modular estimating technique based on an instrument loop count and the complexity of the instrumentation needed fur the class cf process equipment. Electrical motor hookup costs were also estimated using the modular estimating technique. An allowance was made for control wiring and power supply within the motor control centres.

The oxygen plant would produce 100 t/d of 98% pure oxygen. Oxygen plant costs were based on a quotation for a turnkey plant supplied by PPCL for the Indian location. Utilities include power distribution, pipe racks and pipe on rack. Utilities were estimated using a combination of modular estimating and factoring.

Offsites include the process effluent collection system.

Indirects include freight, insurance, duty and sales tax. Project insurance was estimated as a percentage of the total project cost. Engineering cost was estimated at 104 of all non turnkey direct cost items. For all turnkey items 5* engineering was allowed. Project contingency was estimated at ¿8* of total project cost excluding engineering and licensing fee.

6.4.3 Limitations

The following items are not included in the capital cost estimate:

- preproduction costs and working canital;
- interest during construction;
- escalation;
- land aquisition costs;
- stonm water collection system and treatment;
- construction camp costs;
- tailings pund;
- delivery of utilities to the battery limits;
- project indirects other than labour related;
- contractors fee;
- procèss area development;
ENGINEERING STUDY 6-7

power distribution to the MCC;

- mobiles; and
- buildings.

Allowance for the distribution of the utilities within the battery limits has been included.

Items such as an adminstration building, water treatment facilities, utilities plant, instrument air, steam , water, tailings pond, and laboratories are not included in the estimate.

The structure around the process plant has not been included as the type of structure would be determined by local standards.

6.5 OPERATING COST ESTIMATE

6.5.1 Results

Operating requirements and operating costs for the proposed single stage autoclave pressure oxidation and sulphur recovery circuit to produce 115 t/d of elemental sulphur are tabulated overleaf. Major requirements are for sulphuric acid, electric power, autoclave additive reagent, and maintenance. Oxygen to the process is supplied from a turnkey oxygen plant, so oxygen production costs are included in the overall utilities, labour and maintenance charges.

ENGINEERING STUDY 6-8

ANNUAL OPERATING REQUIREMENTS AND OPERATING COSTS

* Electric Power consumed by oxygen plant = 13 700 Mwh/y.

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6.5.2 Basis

Consumption of operating materials were developed from process requirements nased on the material and energy balances and historical data.

Operating costs were estimated using data supplied by PPCL to establish unit prices for labour and materials. When costs for various items were not specified, in house data were used.

An exchange rate of lORs equal SI (U.S.) was used.

Operating labour requirements were developed from historical data and assumes U.S. Gulf Coast productivities. Operating labour would include five floor operators per shift, one control room operator per shift, two labourers and one day supervisor.

Maintenance material and labour requirements were based on an appropriate percentage of installed equipment cost, depending upon the plant section. Maintenance costs do not include supervisory or general personnel.

6.5.3 Limitations

Local taxes, insurance and overheads have been excluded.

Mo allov;ance has been included for pumping or maintenance costs associated with the delivery of the tailings pond return water to the process.

6.6 BASIS FOR ECOMOMICS

6.6.1 Preproduction Expense - Startup Cost and Working Capital

PPCL requested that Sherritt provide the basis required to evaluate the economics of the process. The preproduction expense, start up costs and the working capital for the process plant are shown overleaf.

ENGINEERING STUDY 6-10

- Preproduction expense includes mini pilot plant test work and writing of operating manuals.
- Start Up costs include operator training, cost of a start-up team, one month of maintenance costs, and one week of materials and supplies costs.
- *** Working capital includes spares, in process inventory and 30 days of total operating costs less 30 days operating supplies and utilities.

6.6.2 Additional Revenues

The proposed circuit would produce a significant amount of flashed steam that could be recovered. If the flashed steam is recovered, the project could be credited with an additional \$320 000 (U.S.) per year.

The iron oxide tailings produced may have a potential use in the cement industry. The tailings, if sold, could produce additional revenues of \$4.2 million (U.S.) per year.

6.7 USE OF SALADIPURA PYRRHOTITE

Saladipura natural pyrrhotite was tested in the lab and was found to behave in a similar way as the artificial pyrrhotite matte. It is therefore expected that Saladipura pyrrhotite could be treated in a circuit similar to the one described in this report. The unit capital and operating costs for treating Saladipura pyrrhotite, based on sulphur produced, would be expected to be the same or perhaps somewhat lower than for the artificial pyrrhotite, depending upon the sulphur content of the Saladipura pyrrhotite.

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FALCONBRIDGE MEMORANDUM 7-1

7.0 FALCONdRIDGE MEMORANDUM

Following is a copy of the memorandum provided by Falcombridge on the smelting of lump pyrite. It is included in this report for completeness sake.

sherrftt

FALCONBRIDGE NICKEL MINES LIMITED

INTER OFFICE MEMORANDUM

PROJECT No.

MFMO TO: I. Masters/G.L. Bolton

FROM: R.E. Ranford

DATE: June 16, 1983

SUBJECT: Electric Furnace Smelting of Lump Pyrite

KEYWORDS: (in title)

COPIES TO: RAB, AIO, File²

Introduction and Summary

As per your request, approx. 125 kg of lump pyrite was crushed to $-1/2$ " and smelted in a 50 kVA electric arc furnace with various fluxes to produce approx. 100 kg of iron sulphide matte. The matte was cooled in salamander crucibles and easily crushed to $-1/2$ " for shipment.

Since the pyrite was very high in silica, 13.6%, a large amount of iron oxide, 37% of the pyrite, was required to produce a fluid s'ag. Due to the furnace conditions, some of the iron oxide was reduced to the iron sulphide matte increasing the yield of matte: pyrite to 82.7% and decreasing the sulphur loss to 26.5% of the pyrite sulphur. The slag product was 31.6% of the pyrite smelted.

The power consumption after correcting for some delays was 1456 kWh/1000 kg, pyrite. This is a reasonable value considering the size of the furnace.

Material and Procedures and Observations

The 2" lump pyrite from Sherritt Gordon was crushed to $-1/2$ " prior to feeding to the furnace. Three other fluxes were used: Dofasco bydrolyzer iron oxide calcine, S5837, and Northern Pigments red iron oxide, and technical grade CaO powder. The pyrite had the analysis shown below:

TABLE 1: Chemical Analysis of Pyrite L83-274

 wt . $%$

Cu Co Fe S $\mathrm{Si}\,0_{2}$ Cr₂O₃ CaO MgO A1₂O- $0.02 \quad 0.04 \quad 36.2 \quad 40.5$ 13.56 $0.18 \quad 0.11 \quad 0.35 \quad 0.94$

The furnace is a 50 kVA Birlefo Lindbcrg electric arc furnace supplied by a 4 tap transformer . An auxiliary saturable core reactor was used to control current at deep electrode immmrsions.

The furnace was operated at the highest voltage, 140 volts, open#circit. At the maximum power, approx. 35 kW, the current was 380 amperes and about 100 volts.

The arc. furnace was preheated by striking an arc on a carbon block placed on the hearth of the furnace. This was done for about 45 minutes using 15-20 kW until some of the residual "skull" material began to melt, at which point, the block was removed and the 1 1/2 graphite electrodes were immersed in the pool. After the remaining skull started to melt in, pyrite was fed with a "scoop" in through the lid. The power input was 22-26 kW for 112 minutes.

The pyrite charge was $14.3 \text{ kg}/31.5$ lbs to this point and all the matte and slag was tapped out.

During this initial period, it was obvious that the slag was very poor, ''gummy", viscous and solid against the back wall opposite the pouring spout. To improve the fluidity, 3.4 kg of various iron oxides were added toward the end of the 112 minutes. Since this made an obvious improvement in the slag, iron oxide was added through the subsequent batches as seen in Table II.

Charging and tapping continued until there was approx. 100 kg of matte product contained in 7 taps. The "charging" and "tapping" times are also shown in Table I 1.

During "tapping", most of the matte and slag was tapped from the furnace over the furnace lip. **A** small pool of matte was left to avoid the use of the "block" for the next batch.

Results and Conclusions

The smelting results are summarized in Table III. As seen here, the very high yield of matte/pyrite, 82.7% versus the expected 33% is quite interesting. Although there were no sulphur assays done, XRF analysis on the matte indicates mainly FeS with no metallics. This means that there must have been less sulphur loss from the furnace and some iron reduction from the oxide as seen in the iron distribution shown in Table III.

The low air entrainment due to the high sulphur evolution rate and the intense reducing conditions around the graphite electrodes probably both contribute to the iron reduction to the matte.

The need for iron oxide to give a more fluid slag arises from the very high silica in the pyrite and the lack of other oxides to flux the silica. A lime i lux would be effective also, but the slag/matte temperatures would then be much higher leading, to rapid matte penetration of the refractory.

The power consumption of 145b kWh per 1000 kg pyrite is quite reasonable considering the small size of the furnace. Some of the power is consumed in reducing the iron oxide to the matte.

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TABLE II: Charging and Smelting of Pyrite in 50 kVA Arc Furnace

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TABLE 111: General Summary of Smelting Test Results

