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EL2/74  :  13 SQ KM

ANNUAL REPORT FOR 1984
KING RIVER DELTA PROJECT

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22 November 1984

## SUMMARY

This report covers the period 16 November 1893 to 15 November 1984.
The last four quarterly reports provide another fifteen pages
describing activities and progress.

Delays and setbacks were experienced but later in the twelve months
under review the rate of advance accelerated.

During the period processing methods were investigated in London,
results of three studies bearing on the venture arrived, and data
covering aspects of Delta chemistry were analysed.  Agreement was
reached with an optionee company;  also, a second group has been
interested in the possibility of participating.  The Department of
Mines was provided with information generated by a former licencee.

The three studies concern respectively, mineralogy of Delta sediment,
gold occurrence, and production of elemental sulphur from pyrite.

The mineralogical investigation was made by Dr D C Green of the Mines
Department, Hobart,  He examined coarser size fractions of sediment
that had been isolated and analysed by the Department's laboratory in
Launceston.  Using optical methods and electron probe Dr Green
identified several mineral species not detected hitherto.  Pyrite
grains scanned show appreciable concentrations of cobalt.

Gold levels in three different density fractions of Delta sediment
were measured by Amdel.  The maximum grade found is lower than one
Amdel encountered in an earlier test series, probably because three
separatory steps used previously were omitted.  Head grades discerned
in the two series of tests are similar however.

The review of pyrite processing was undertaken by The British Sulphur
Corporation.  Five methods of producing elemental sulphur from the
compound are described and approximate costs are given for three.  A
chlorination procedure may merit closer inspection.

Expenditure on the project for the fourth quarter of 1983 and the
first three quarters of 1984 amounts to US$35,800.  Figures for the
latter three quarters will increase after 1984 travel costs are added,
in January.

In the coming year investigation of the Delta's gold, cobalt and sulphur
resources is to continue:  so is study of extractive means.  If results
warrant this, an environmental survey leading to formulation of an
impact statement probably will be begun.

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## CONTENTS

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## APPENDICES

I                               RESEARCH


Technology

Information on equipment and processes suitable for use in treating
Delta sediment is being collected.

Apparatus which may be employed aboard dredges to separate
mechanically, as pre-concentrate, valuable higher density, generally
finer grained components from coarser, largely quartzose and chloritic
fractions is of particular interest.  Chief targets in this class
are sulphide, gold, cassiterite and barite.

Processes sought are those which may permit elemental sulphur to be
recovered from the sulphide fraction together with cobalt, copper,
silver and, possibly, iron it contains.

The two classes of mechanical apparatus offering best prospects of
treating substantial volumes of sediment quickly at low cost are screens
and cyclones.  Cyclones hold special promise for handling finer grained
fractions.

Data on several screen types are being assembled.  Screens with multi-
angled decks, a live-framed flexing variety, and a third, cleaned
during operation by air jetted upward from below  are those favoured.
Flexing and jetting each prevent blinding, raising capacities
significantly.

Four sorts of cyclone offer improved performance over conventional
types.  One has a spiral rib on the inner wall to increase discharge
rate at the downstream port.  A second is wide-angled to prevent
settling of all but highest density or coarsest fractions of feed.
The third is a water-sparged machine built in Canada:  design was
modified recently to lower risk of compaction between sparging ports.
The fourth type of cyclone,also water sparged, is a variant of the
third but does not need to be stopped periodically for removal of
concentrate;  this is discharged continuously as in standard cyclones.

Other apparatus which may be required includes magnetic separators
and flotation cells.  Separators using rare earth permanent magnets
are now available.  They have field strengths equivalent to those of
electro-magnetic type but cost less to run.  In flotation, savings
may be achieved by employing large cells.  Most leading manufacturers
now supply these.

Several companies have perfected and market non-toxic chemicals for
flotation and other recovery procedures.  One such chemical produced
in the UK and used by Renison floats wolframite, zircon and
cassiterite, the latter even where particles are no bigger than
10 microns.  Phillips Petroleum produces a harmless substitute for
sodium cyanide.

## Sulphur

Smelting of Delta sulphide is to be avoided if possible, but if such a stage is found essential a method being perfected by Chemadex of Poland appears the most attractive available. This employs a cyclonic furnace operating at 2100°C. There are several advantages. The furnace is far lighter and cheaper to build than a fluidised bed reactor. Unlike the latter it accepts charges consisting of a wide range of particle sizes including fine grained pyrite that causes difficulties in other furnaces. The high operating temperature vaporises byproduct metals, allowing them to be recovered separately, and yields clean iron cinder suitable for grinding and sale. Conventional smelting produces useless dusty cinder contaminated by the other metals. Potential revenue consequently is lost, unless expensive additional steps are taken to clean cinder and recover byproducts.

A cyclone furnace of 20 tph capacity should yield 14 tph iron oxide and about 0.5 tph non-ferrous metals. Gas streams run 11 to 16% $SO_2$. Possibly the USBM citrate process designed to recover elemental sulphur from off gases of coal-fired power generating plant would handle such a stream. Information about the process was sent to Mines' Chief Chemist last year.

One sulphur recovery process Elisna singled out which avoids the need for smelters is the Westcott. Heated pyrite is converted to ferrous chloride, using chlorine. Gaseous sulphur liberated is condensed to liquid sulphur from which a dust-free prilled solid can be obtained. The prilled form is easier and more economical to handle than powdered sulphur, and commands premium prices. Chlorine is extracted for re-use by oxidising ferrous chloride to $Fe_2O_3$.

Several leach procedures were examined.

Sherrit Gordon leaches sphalerite under pressure, at Traill, BC, Canada: 96% of the original sulphur is oxidised to elemental state.

In Spain pyrite and other sulphides are leached in water at 200°C under pressure of 30 kg/cm$^2$. Sulphide converts to ferrous sulphate thence to ferric oxide in an hour. Copper and zinc dissolve in sulphuric acid formed and are recovered via neutralisation and solvent extraction. Silver and lead are recovered by leaching ferric oxide in brine at 90°C.

In Cyprus Mines' patented process, copper sulphide is leached at atmospheric pressure with ferric chloride and/or cupric chloride. This releases sulphur which is upgraded by flotation, using lime and sodium silicate. Concentrate is leached with ammonium sulphide. After filtering, high grade rhombic sulphur is crystallised by evaporating filtrate. Ammonium sulphide is regenerated. (Appendix A).

In a novel leach method under development, elemental sulphur is recovered direct from copper sulphide through the agency of bacteria and silver. Addition of silver prevents formation of sulphate. The silver component takes no direct part in the reaction and is recyclable.

In London the subject of pyrite treatment was discussed with The British Sulphur Corporation. Later the Corporation was appointed to review applicable processes. The resultant report arrived at the end of the third quarter: see Appendix B.

Briefly, the report outlines five methods and provides costs for several. Four require initial conversion of $FeS_2$ to FeS by heating. This liberates sulphur vapour which is then condensed. Sulphur remaining in pyrrhotite produced is extracted by roasting and other steps. The fifth method described is an improved version of the Westcott, summarised above, requiring lower heat. The original version was complicated by the corrosiveness of chlorine at high temperature.

Information on new uses of sulphur also is being compiled. The elemental form is being employed increasingly as a soil additive to maximise nitrogen utilisation. Elsewhere, sulphur is used in road building as a substitute for oil-based asphalt, and in construction as sulphur cement.

Mineralogy

Coarse fractions of Delta sediment separated at Mines Department labs in Launceston were sent to Hobart, by the Chief Chemist, for mineralogical study. There, sample was split further, magnetically and in TBE. Splits were examined optically and by electron probe. The report, by Dr D C Green, is attached: see Appendix C.

Dr Green identifies eighteen mineral species. Three had not been discerned in Delta sediment before; they are bismuthinite, an aluminium phosphate running ~8% rare earths, and a rare earth phase, containing K and Si, lacking or low in Ce. Dr Green did not encounter gold, covellite, chalcocite or bornite. Pyrite contains little or no exsolved copper, but four grains scanned appear to run 2250 to 3250 ppm Co.

Gold

In 1983 Amdel was asked to investigate further the manner in which gold concentrated in Delta sediment occurs. Some months later the labs reported that all nine drums of sample held had been mislaid. As the material cannot be replaced readily they were asked to make a third and special effort to locate the drums. They did so, successfully. Results of the tests have since been received: see Appendix D.

In broad terms results duplicate those of Amdel tests described in
and attached to last year's annual report on EL 2/74.   Head grades
are similar, and in each test series gold is concentrated in the
sediment fraction of highest density.

Head grade calculated from the 1983 results is 0.17 ppm Au.   In the
recent series, heads computed from fire assay figures are 0.11 ppm and
0.19 ppm, giving a mean and average of 0.15 ppm Au.   If results of
AAS determinations on low and medium density fractions are included the
average head calculated is 0.185 ppm Au.

Levels of concentration in individual fractions differ, though, from
those of last year's tests.   All gold detected in 1983 was confined
to the densest fraction of sediment.   In recent tests it was found in
all three density fractions, ascending in grade with rising density.

This spread probably stems from differences in preparation of the
fractions.   In 1983, TBE sinks >75 microns were ground to pass mesh of
this size, dense fines were isolated, and separations in TBE and Clerici's
Solution were centrifuged.   The 1984 tests omit grinding, and removal
and analysis of fines:   only one of the heavy liquid separations involved
centrifuging;   TBE separation was carried out statically.

Apparently gold was not liberated properly in these recent tests, or it
does not separate well without being centrifuged.   Possibly both steps
are necessary, though centrifuging probably is the critical one.   The
sample split and analysed by Mines in 1983 (Report 797, Appendix E)
involved no grinding, but a cyclosizer was used to obtain concentrate
running 40 ppm Au;   this step is similar to centrifuging.

The average grade of mercury-insoluble gold in material of SG >4.3 is
0.7ppm Au.   Amdel suggests this may represent gold in solid solution
in pyrite.   Earlier tests of pyrite by Aberdare and by Mt Lyell give it
a much lower gold content.   Some insoluble gold is likely to be in
chalcopyrite which at Mt Lyell reaches 5 ppm Au:   but chalcopyrite in the
fraction discussed is insufficient to impart a grade of more than
0.05 ppm Au.   We are inclined to think that gold in Delta sediment is
mostly native and liberated but that it is covered by films of iron
compounds or other substances inhibiting solution in mercury.   This
possibility is to be investigated.

A new US leach process allegedly capable of recovering 90 to 99% of
gold from low grade even refractory ore running 0.09 to 0.18 ppm Au
is being investigated.   Leach times are said to be extremely short and
materials used non-toxic.   Costs are put at $10 pto Au recovered.

Analysis

Proportions of cobalt and sulphur in various size fractions of Delta
sediment isolated by Mines Department labs were compared.   Relevant
analyses given in Mines Report 797 were appended to our previous annual
report.   They are shown again here, attached to Appendix E.

The Co/S ratio is remarkably constant, indicating that virtually all
cobalt present in Delta sediment occurs in pyrite, the component
containing about 92% of the Delta's sulphur.   The average ratio is
equivalent to  1,100 to  1,200 ppm Co in pyrite.   The maximum grade
of 800 ppm detected by Mines in R797 illustrates the extent to which
the size fraction concerned is contaminated by minerals other than pyrite:
the corresponding sulphur content supports this interpretation.

We calculated weight percent distribution for each of ten elements in
eleven size fractions listed in Mines' Report 797:   see Appendix E.
The table indicates that the coarsest 0.3% of Delta sediment should be
worth grinding and treating mechanically to recover cassiterite it
contains.   The twenty-five percent or so of sediment in the 200- to
600-micron range may be rejected without loss of more than 4 or 5% of
the pyrite and cobalt.   The finest grained 10% of sediment also could
be removed without loss of more than another 3% of all cobalt.
Rejecting this fraction would reduce total contents of lead and bismuth
by 45% and those of arsenic and zinc by 20 to 25%.   However, about 15%
of the sediment's sulphur and 45% of its tin would be lost.   Merits
of the step need to be re-assessed once contents of valuable metals in
outer parts of the Delta, where fine grained material predominates, have
been examined in greater detail.

It is worth noting that in Cities' preliminary tests, carried out on
fine grained sediment, far higher recoveries of copper by mechanical
means were realised than the 25% achieved later, using coarser feed
from inner parts of the Delta.   Elisna considers it likely that
recoveries of gold, cassiterite, barite and pyrite/cobalt will follow
the same trend, improving offshore.   Degrees of liberation obviously
are likely to be highest in sediment of finest grain, found furthest
from the river mouth.

II                              PARTICIPATION

Negotiations begun in the second half of 1983 with the US/Australian
Cottesloe group interested in the prospect of taking over EL 2/74
and development of the project continued through the first quarter of
1984.    A series of meetings was held in the United States.

Cottesloe was furnished with data on past surveys of the Delta, with
information on current testwork, and proposed extensions of it.
Rough estimates concerning anticipated development costs and returns
likely to eventuate from mining also were provided.

Cottesloe subsequently elected to enter the venture and has been
granted an option.    While tests continue the licence remains in
Elisna's name, but Cottesloe may exercise its option as soon as
results considered satisfactory are received.    Plans to set up a
pilot plant await the outcome of tests in progress.

In conjunction with Elisna the optionee has since approached a
Victorian group which, earlier, had expressed enthusiasm about the
possibility of joining the venture.    This organisation recently
completed preliminary examination of some technical records bearing
on the Delta and as a result has reiterated willingness to proceed.
Representatives are to meet with officers of Elisna and the optionee
group in Melbourne late in November and early in December to devise
terms under which the third party might participate.

III                              REPORTING

Over the past twelve months an annual report and four quarterly
reports have been prepared for the Department of Mines.

Six other reports relating to the activities of an earlier licencee,
Cities Service, were copied and donated to the Department.
Material copied totals some 350 pages:  details follow.

Robertson Research (Australia) Pty Ltd, 12 September 1975
    Memorandum No. 822.  Sizing of Drill Samples, Macquarie Harbour
    Project.
    Prepared for Australian Cities Service Inc., 151 Macquarie Street,
    Sydney NSW 2000.  Project 756/9807/6B.

_____ 19 September 1975,
    Memorandum No. 825.  As above.

Lakefield Research of Canada Limited,   9 February 1976,
    The Recovery of Sulphides from a Slag Sample submitted by
    Cities Service International Inc.
    Progress Report No. 1.

_____ 12 May 1976,
    The Recovery of Sulphides from an ACS Feed Sample submitted
    by Cities Service International Inc.
    Progress Report No. 4.

Cities International Minerals Co.,      11 October 1976,
    Tasmania Copper Project:  Phase III - Final Report.

_____ 13 June 1977,
    Tasmania Pyrite Project (2pp).

Elisna also had duplicated and then contributed a plan.    Particulars
are:

Cities Service International Inc.,        7 August 1975
    Drillhole Location Map, Macquarie Harbour, Tasmania.
    Scale, 1:10,000.   Re-drawn 22 October 1975.

IV                          ADMINISTRATION


An application for renewal of Exploration Licence EL 2/74 was lodged. Term
of the licence was extended to 28 December 1984.

Accounts for 1983 were drawn up, audited  and approved.    Interim
figures for part of 1984 also have been prepared.

Annual returns for Elisna Pty Ltd and for Aberdare Incorporated
have been submitted.

Elisna's Annual General Meeting and a directors' meeting were held.

Policy discussions and preparation for fieldwork took further
time.

In the US records were sorted and moved to storage.

V                             EXPENDITURE

Twenty-eight man-weeks' time was devoted to the project over the fourth quarter of 1983 and first three quarters of 1984. Details are given in the four quarterly returns.

Expenditure for this period amounts to US$35,800 approximately, or about A$42,950. The figure in US dollars is made up of sub-totals below:-

| | |
|---|---:|
| Travel | 1,299 |
| Field expenses | 1,058 |
| Technical services | 27,967 |
| Management fee | 2,000 |
| Communications | 283 |
| Charters, rents | 3,175 |
| Miscellaneous | 18 |

Amounts shown exclude most travel costs and field expenses of 1984. These will not be available until early next year, after 1984 figures have been split, pro rata, between projects involved.

Expenditure on the enterprise by Elisna/Aberdare for the period 1.1.79 through 31.12.83 amounts to US$134,670.

The latter figure does not include additional expenditure by Union Oil/Molycorp, a group which took over the exploration licence and work commitment for part of that five-year interval.

Expenditure by Union, by Aberdare/Holb prior to 1.1.79, and by Cities Service amounts to an additional $650,000.

VI                          PROGRAMME

If current plans of the US/Australian optionee corporation and a
Victorian venture group keen on participating proceed, a Tasmanian
company will be established to handle the project and Aberdare
will then request that the exploration licence be transferred to
the new company.   It is anticipated that the company will be
operational by mid-year approximately.   Until then Aberdare will
continue investigations in progress.

Three components of King Delta mineral-bearing sediment are being
examined, specifically gold, cobalt and sulphur.   Fourth, several
analytical methods are being compared so that grades of elements in
which Delta sediment is enriched may be refined, and related reserve
estimates tightened.

Ways and concentrations in which gold occurs in various parts of
the Delta are under study, with an eye to discovering what fraction
of the metal exists in native state and how much of this gold is
liberated.   Grinding tests are being run, and more sampling and
assaying of finer grained sediment from outer parts of the Delta
is planned.   Later, additional measurements of the gold's
solubility in mercury may be made.

The extent to which acid probably forming in drummed sample
dissolves cobalt present in the sulphidic component of Delta sediment
is being examined.   In another experiment sediment from deep water
is to be tested, allowing distribution and grade of its cobalt to
be determined.   So far, data of this nature are available for
relatively coarse grained, shallow-water cobaltiferous sediment
only.

Principal tests to be run on cobalt during 1985 will be those
directed at leach methods.   Processes employing water or brine,
or weak acid generated direct from sulphide in the sediment are of
particular interest.   Behaviour of solvents found more effective
may be studied further, subsequently, at temperatures and pressures
above atmospheric levels.

In connection with sulphur, Aberdare anticipates having its
consultants review prospects of selling the elemental form, produced
locally, in Australia and New Zealand.

Analytical methods under comparison are XRF, AAS, ICP and high
quality wet chemical.   Head grades of Ag, Ba, Co, Cu and Sn in
Delta sediment are being measured by each of the latter two
techniques and by one or other of the first two.

If research results continue to indicate that cleaning and
redistribution of Delta sediment is feasible technically and

justifiable in terms of economics, an environmental study probably
will be commissioned and begun, permitting an impact statement
to be completed and submitted in 1986.

Expenditure on the Delta project in the coming year cannot be
predicted accurately until intentions of the Victorian group
wishing to join the enterprise become clearer.   However, it is
expected that at least $15,000 will be spent, that is, a sum far
in excess of the minimum required officially.

APPENDIX A

# United States Patent [19]

**Narain**

[11] **4,138,248**

[45] **Feb. 6, 1979**

[54] **RECOVERY OF ELEMENTAL SULFUR AND METAL VALUES FROM TAILINGS FROM COPPER RECOVERY PROCESSES**

[75] Inventor: **Kartik A. Narain,** Tucson, Ariz.

[73] Assignee: **Cyprus Metallurgical Processes Corporation,** Los Angeles, Calif.

[21] Appl. No.: **894,515**

[22] Filed: **Apr. 10, 1978**

[51] Int. Cl.² .................... C22B 15/08; C22B 11/08; C22B 34/34

[52] U.S. Cl. ........................................ 75/101 R; 75/2; 75/104; 75/117; 75/118 R; 75/121; 423/26; 423/29; 423/38; 423/53; 423/567 A

[58] Field of Search ................ 75/2, 104, 117, 118 R, 75/121, 101 R; 423/26, 29, 38, 53, 567 A
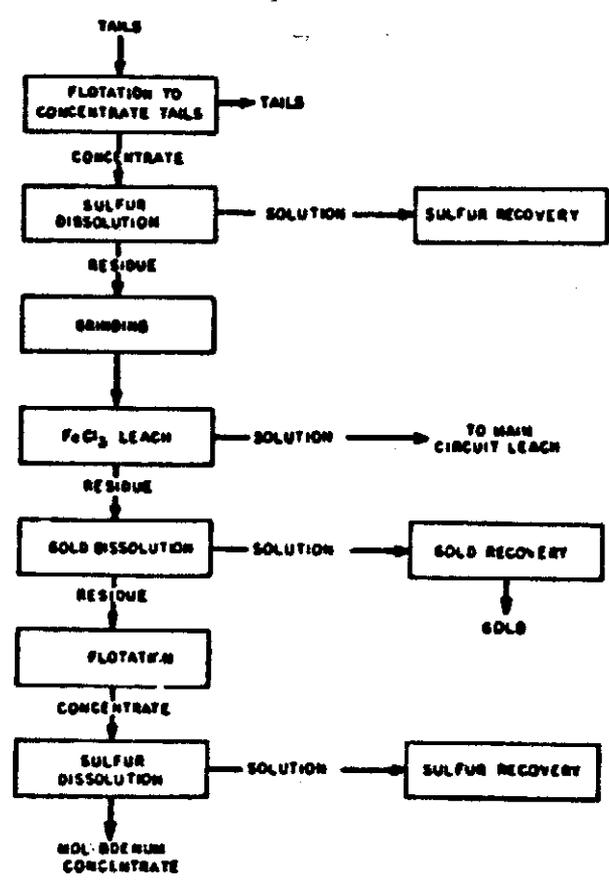
[56] **References Cited**

**U.S. PATENT DOCUMENTS**

| | | | |
|---|---|---|---|
| 2,658,827 | 11/1953 | Rizo-Patron | 75/2 |
| 3,645,455 | 2/1972 | Castillo | 75/2 X |
| 3,785,944 | 1/1974 | Atwood et al. | 75/104 X |
| 3,798,026 | 3/1974 | Milner et al. | 423/38 X |
| 3,816,105 | 6/1974 | McKay et al. | 75/117 X |
| 3,834,893 | 9/1974 | Queneau et al. | 75/2 |
| 3,879,272 | 4/1975 | Atwood et al. | 423/141 X |
| 3,923,616 | 12/1975 | Atadan et al. | 75/104 X |
| 3,972,711 | 8/1976 | Goens et al. | 75/117 |
| 4,013,457 | 3/1977 | Goens et al. | 75/104 |
| 4,039,324 | 8/1977 | Stephens et al. | 75/72 |

*Primary Examiner*—G. Ozaki
*Attorney, Agent, or Firm*—Sheridan, Ross, Fields & McIntosh

[57] **ABSTRACT**

A process for the recovery of copper, molybdenum, gold and elemental sulfur in tailings from hydrometallurgical processing of copper sulfide ores, the process comprising concentrating the tailings containing elemental sulfur and copper, gold and molybdenum to a small bulk volume by froth flotation to reject barren gangue including jarosite, if present, and other impurities, separating the liquids and solids in the float concentrate, leaching the resulting residue with a solvent for sulfur followed by liquid-solids separation and recovering elemental sulfur from the liquid, leaching the residue from the sulfur solvent leach with ferric chloride to selectively dissolve copper and iron therein followed by liquid-solids separation and recovering copper from the liquid or sending it back to the hydrometallurgical circuit, leaching the residue from the ferric chloride leach with cyanide to selectively solubilize gold followed by liquid-solids separation and recovering of solubilized gold from the liquid, recovering molybdenum ore from the residue from the cyanide leach by froth flotation, and recovering molybdenum from the molybdenum ore. The process is particularly applicable to tailings resulting from the treatment of chalcopyrite by hydrometallurgical processes for the recovery of copper.
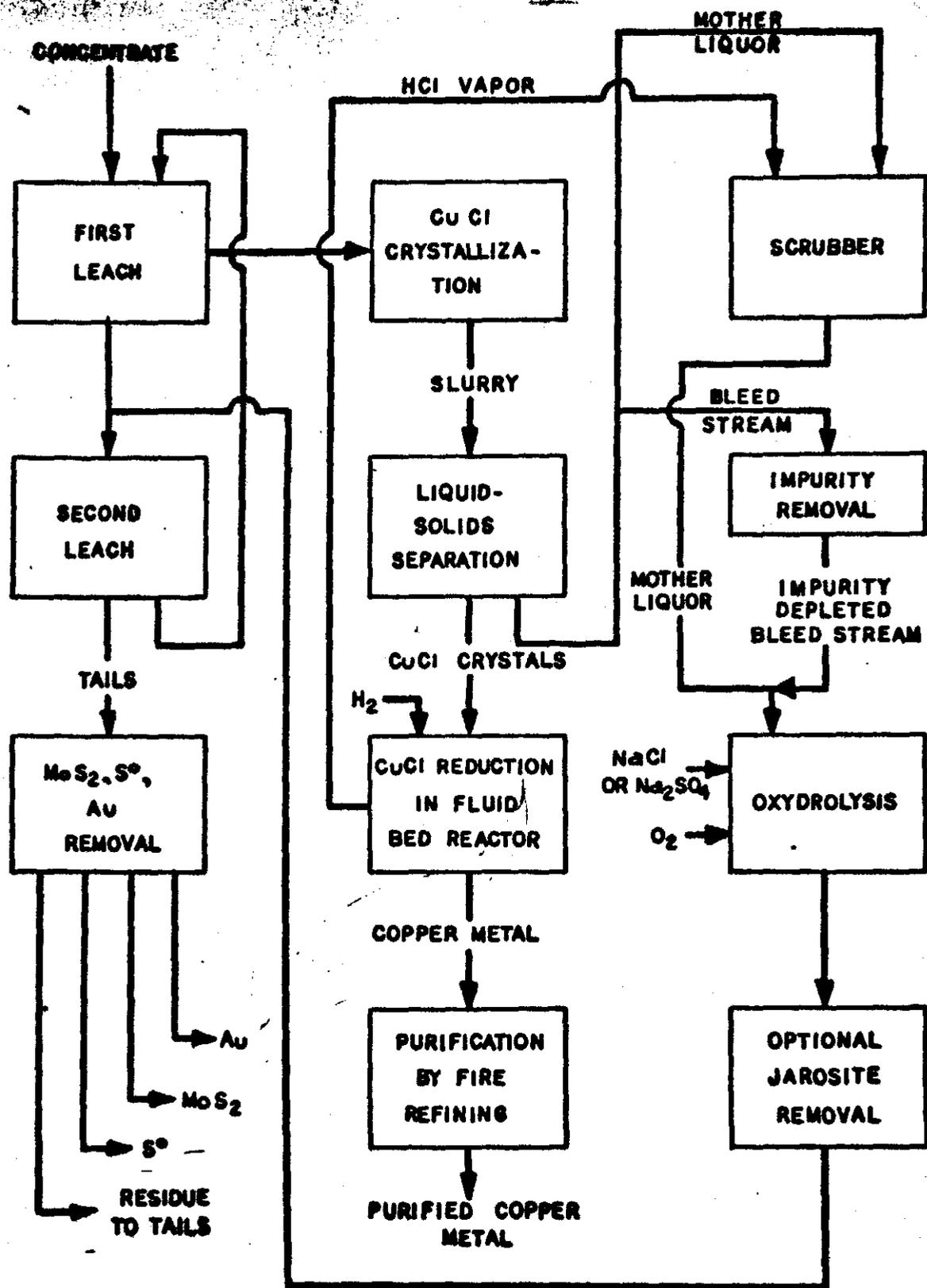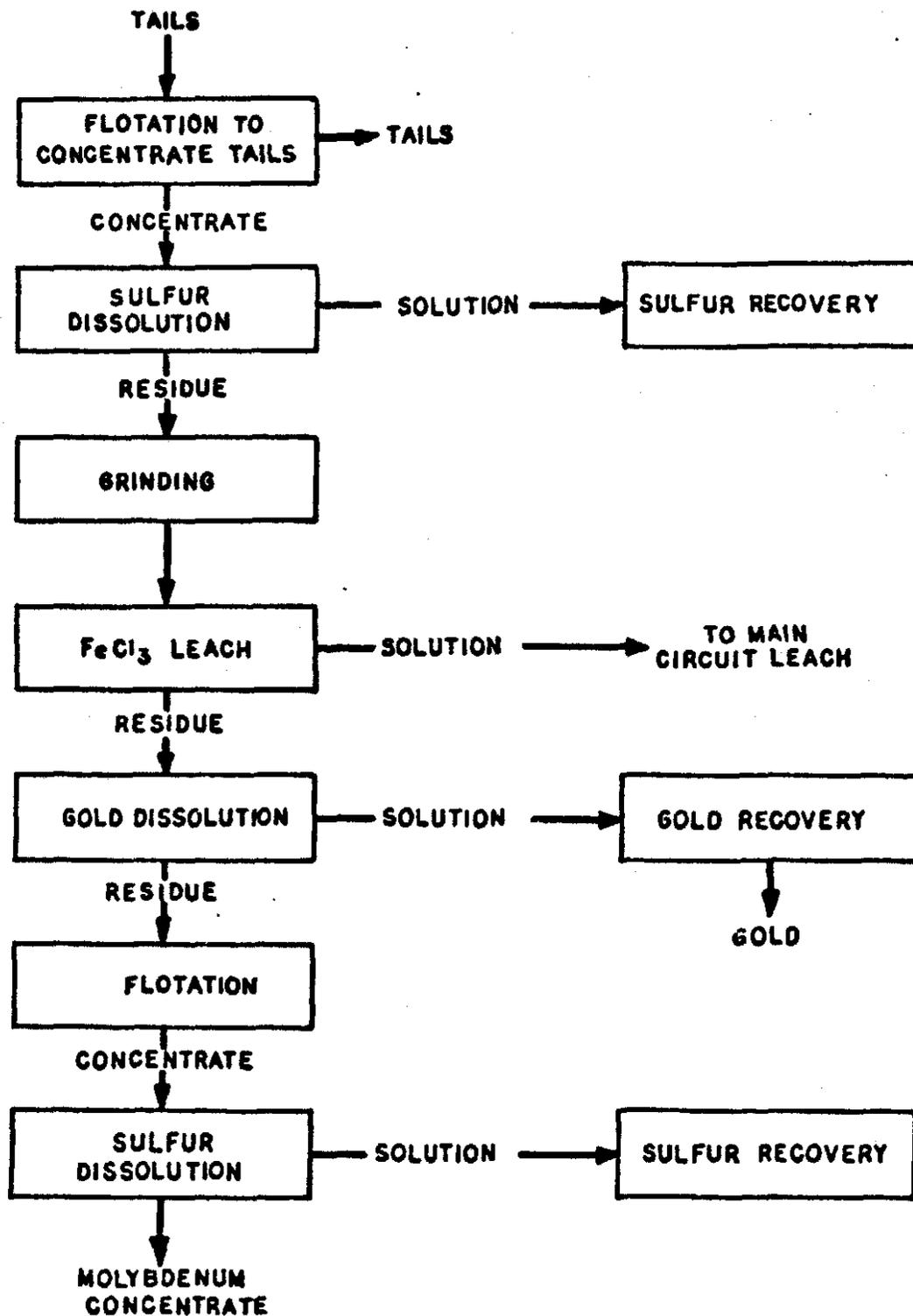
**23 Claims, 2 Drawing Figures**

266017

CONCENTRATE

HCl VAPOR

MOTHER LIQUOR

FIRST LEACH

Cu Cl CRYSTALLIZATION

SCRUBBER

SECOND LEACH

SLURRY

BLEED STREAM

LIQUID-SOLIDS SEPARATION

IMPURITY REMOVAL

TAILS

$CuCl$ CRYSTALS

MOTHER LIQUOR

IMPURITY DEPLETED BLEED STREAM

$MoS_2, S^o, Au$ REMOVAL

$H_2$

CuCl REDUCTION IN FLUID BED REACTOR

$NaCl$ OR $Na_2SO_4$

$O_2$

OXYDROLYSIS

COPPER METAL

Au

$MoS_2$

$S^o$

RESIDUE TO TAILS

PURIFICATION BY FIRE REFINING

OPTIONAL JAROSITE REMOVAL

PURIFIED COPPER METAL

FIG I

A2

266018

TAILS

↓

┌─────────────────────┐
│ FLOTATION TO        │ → TAILS
│ CONCENTRATE TAILS   │
└─────────────────────┘

CONCENTRATE

↓

┌─────────────────────┐                    ┌─────────────────────┐
│ SULFUR              │ → SOLUTION →       │ SULFUR RECOVERY     │
│ DISSOLUTION         │                    └─────────────────────┘
└─────────────────────┘

RESIDUE

↓

┌─────────────────────┐
│ GRINDING            │
└─────────────────────┘

↓

┌─────────────────────┐                    TO MAIN
│ FeCl₃ LEACH         │ → SOLUTION →       CIRCUIT LEACH
└─────────────────────┘

RESIDUE

↓

┌─────────────────────┐                    ┌─────────────────────┐
│ GOLD DISSOLUTION    │ → SOLUTION →       │ GOLD RECOVERY       │
└─────────────────────┘                    └─────────────────────┘
                                                    ↓
RESIDUE                                           GOLD

↓

┌─────────────────────┐
│ FLOTATION           │
└─────────────────────┘

CONCENTRATE

↓

┌─────────────────────┐                    ┌─────────────────────┐
│ SULFUR              │ → SOLUTION →       │ SULFUR RECOVERY     │
│ DISSOLUTION         │                    └─────────────────────┘
└─────────────────────┘

↓

MOLYBDENUM
CONCENTRATE

FIG 2

A3

4,138,248

**1**

# RECOVERY OF ELEMENTAL SULFUR AND METAL VALUES FROM TAILINGS FROM COPPER RECOVERY PROCESSES

## BACKGROUND OF THE INVENTION

The invention is related to hydrometallurgical processes for the recovery of copper from its ores, particularly, sulfide ores, in which the ore concentrate is leached with ferric chloride and/or cupric chloride to solubilize the copper as the chloride and produce elemental sulfur. This type process is illustrated by those described in U.S. Pat. Nos. 3,785,944; 3,798,026; 3,879,272; 3,972,711; 4,013,457; 4,039,324. The disclosure of some of these patents includes chemical equations illustrating the reactions occurring when chalcopyrite is leached with ferric chloride and cupric chloride to solubilize the copper and produce elemental sulfur. Some of the patents further describe how copper is recovered from the formed cuprous chloride by crystallization followed by recovery of copper from the crystallized cuprous chloride. The prior art discloses various other methods for the recovery of copper from the leach solution resulting from the leaching of copper ores and concentrates with ferric chloride and/or cupric chloride.

Copper sulfide ores, in particular, contain materials which are insoluble in ferric chloride and cupric chloride leachants and are usually discarded in the tails from hydrometallurgical leaching with these leachants. These materials may include valuable substances, such as, the elemental sulfur formed in the leaching reactions as well as gold and molybdenum values. They also may contain impurity-like materials, such as, pyrite, jarosite and others. If the pyrite contains gold it is not rejected in the flotation step. Some of the copper sulfide mineral which is embedded in the mineral grains is not dissolved by the leachant as the leachant does not come into direct contact with the copper mineral and this undissolved mineral is contained in the tailings.

As the processes for recovery of copper from its sulfide ores which are acceptable under environmental regulations are quite competitive, it is important from an economic standpoint to have available effective procedures which are compatible with the copper recovery processes for recovering saleable elemental sulfur and metal values from the tailings. Such a process should be one that is adaptable to pilot plant production in a continuous operation and no such process is known to be available today. A major difficulty has been that the relatively small amounts of metal values in the ore other than copper have been contained in large bulk volumes of gangue after concentrating the copper ore and it was not possible to economically process this large bulk of material to recover the relatively small amounts of metal values. This was particularly true in prior processes in which sulfur was removed from the ore by pyrometallurgical processes. Difficulty has been encountered in separating elemental sulfur in the presence of copper and molybdenum in the concentrates. A further difficulty has been encounted in recovering molybdenum in the presence of copper which is not contaminated by the copper to the point where the molybdenum is unsaleable, and at the same time achieve high recovery of molybdenum. Any molybdenum left in the tails ordinarily could not be recovered. If gold is present it will also contaminate the molybdenum.

**2**

Accordingly it is the object of this invention to provide a process for the recovery from tailings resulting from the hydrometallurgical processing of copper ores, of elemental sulfur, copper, gold and molybdenum in one continuous operation in which the tailings from which the sulfur and metal values are recovered are first reduced to a relatively small bulk volume.

It is another object of this invention to provide a process for the recovery of a higher percentage of the copper from the tailings resulting from the hydrometallurgical processing of copper sulfide ores.

It is a further object of this invention to provide a process for the recovery from tailings from the hydrometallurgical processing of copper sulfide ores, of molybdenum which is not contaminated with copper, or gold, if present, to the extent that the molybdenum does not meet the purity standards for a saleable product.

## SUMMARY OF THE INVENTION

A process for the recovery from tailings from the hydrometallurgical treatment of copper ores, of elemental sulfur, copper, gold and molybdenum in which sulfur and the metals are selectively separated in a required sequence with specific reagents which comprises (a) subjecting the tailings to froth flotation to recover elemental sulfur, copper, gold and molybdenum values in a float concentrate containing a relatively small portion of the original tailings and rejecting a relatively large portion of the tailings containing barren gangue; (b) performing a liquid-solids separation on the float concentrate; (c) leaching the residue of step (b) with a solvent for sulfur; (d) performing a liquid-solids separation on the slurry of step (c); (e) recovering sulfur from the liquid of step (d); (f) grinding the residue of step (d) to expose the copper minerals; (g) leaching the ground residue of step (f) with ferric chloride to selectively dissolve copper and iron therein; (h) performing a liquid-solids separation on the slurry of step (g); (i) returning the filtrate of step (h) containing solubilized copper to the original leach for copper recovery; (j) leaching the residue of step (h) with cyanide to solubilize gold and recovering gold from the resulting solution; (k) subjecting the residue of step (j) to froth flotation and recovering the float concentrate containing molybdenum values and elemental sulfur formed in the ferric chloride leach; (l) leaching the float concentrate of step (k) with a solvent for sulfur to solubilize the elemental sulfur followed by liquid-solids separation and recovery of sulfur from the solution, and (m) recovering molybdenum from the residue of step (l).

The tails will ordinarily contain pyrite. If gold is present with the pyrite the pyrite is not rejected with the barren gangue. Of course, if there is no gold present the gold recovery step is omitted. Jarosite will be present in the barren gangue unless it was optionally removed as shown in the flow sheet of FIG. 1. The sulfur removal step after gold recovery is mainly for the purpose of upgrading the product molybdenum for marketing. It is optional depending upon the amount of copper sulfide reporting to the tails and, therefore, the amount of sulfur produced by the ferric chloride leach.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow sheet of a process for the hydrometallurgical recovery of copper incorporating the process of the present invention, and

FIG. 2 is a flow sheet of the process of the invention as applied to tailings resulting from the ore leaching step

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in hydrometallurgical processes like that illustrated in FIG. 1.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention will now be described with reference to the accompanying drawings and the illustrative examples which follow.

The results set forth in the examples below were obtained on the tailings resulting from the hydrometallurgical processing of chalcopyrite for the recovery of copper, however, the process is not limited to these particular tailings as it is applicable to tailings obtained from the hydrometallurgical treatment of other copper sulfide ores. The process is not limited in its applications to tailings alone as it obviously can be used on ore concentrates generally. The term "tailings" as used herein includes concentrates.

Referring to FIG. 1, it is seen that the chalcopyrite concentrate is subjected to two leaches resulting in the tails which contain some unsolubilized copper, gold, molybdenite, elemental sulfur, and other undissolved materials which latter make up the bulk of the tails and are rejected in the flotation step. The copper will be contained in undissolved chalcopyrite not contacted by the leaching agent.

The leaching illustrated in the flow sheet was performed with ferric chloride and cupric chloride and follows the procedure set forth in some of the above referred-to patents. Briefly, the process comprises leaching copper sulfide ores and concentrates with ferric chloride and/or cupric chloride to produce a leach solution comprising cuprous chloride, cupric chloride, ferrous chloride, soluble metal impurities, and insoluble materials which latter go to the tailings, separating by crystallization at least a portion of the cuprous chloride in the leach solution resulting in cuprous chloride crystals and a mother liquor, separating the cuprous chloride crystals from the mother liquor, reducing the crystallized cuprous chloride to product copper, controlling the impurity level of the mother liquor with the use of a bleed stream, subjecting the resulting mother liquor to oxydrolysis with oxygen to regenerate the leachants, cupric chloride and ferric chloride and precipitate iron, filtering, and returning the filtrate to the second leach. Jarosite may optionally be removed from the filtrate as shown.

Obviously, the application of the process of the invention is not restricted to tails resulting from the above or any other specific procedure for the recovery of copper from sulfide ores.

The composition of the tails from chalcopyrite leaching as described above presents a special problem in that the tails contain elemental sulfur which must be removed first to prevent its interference with the recovery of copper, gold and molybdenum. The copper contained in the tails will contaminate the molybdenum if not effectively removed before molybdenum recovery. Gold must also be removed before molybdenum recovery or it will contaminate the molybdenum. As copper is soluble in sodium cyanide the copper removal step must precede the gold removal step. Accordingly, it will be seen that the order of steps performed with the reagents used is critical for the production of substantially pure gold and molybdenum products. The present process is a cooperative adjunct to processes like those disclosed in the above-mentioned patents because it provides for recovery of copper which would other-

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wise be lost from the tails, and which is removed from the tails in a solution which is compatible with the main leach circuit for recovery of copper to which the solution is returned. Also, the process of the patents produces elemental sulfur and the present process is directed to recovery of this element from tails where it exists with copper, gold, and molybdenum.

Reference will now be made to the Figures in describing the process of the invention. As will be seen, tailings from the second leaching step of the original or main chalcopyrite leach containing pyrite and possibly jarosite are subjected to flotation. As shown in FIG. 1, jarosite may optionally be removed from the recycle stream from the oxydrolysis before it is returned to second leach. The flotation is a pre-concentration stage which is used to reduce the bulk of the tailings to be processed for the recovery of elemental sulfur and metal values. The flotation circuit consists of two stages of flotation with the use of conventional flotation agents whereby the barren gangue including any jarosite present and most of the pyrite is rejected provided the latter does not contain gold. The float concentrate was found to constitute only 27.5 percent by weight of the tailings and consistently contained 93 percent of the copper, 84 percent of the molybdenum and 99 percent of the sulfur in the tails. This substantial reduction in tailings to be processed for the recovery of elemental sulfur and metal values is a very advantageous result of the invention from an economic standpoint. The rejected iron bearing compounds may be either acidified to produce a material suitable as a soil nutrient or disposed of as waste material. The process is operative without this flotation step but would obviously be more expensive because of the additional material which would have to be handled.

The elemental sulfur is next recovered from the float concentrate. The order of performance of this step is important because if elemental sulfur is present during the recovery steps for copper, gold and molybdenum it will cause serious problems from a physical standpoint. The float concentrate is filtered to remove water and the residue leached for fifteen minutes preferably with ammonium sulfide to form ammonium polysulfide in accordance with the following reaction:

$$xS + (NH_4)_2S \rightarrow (NH_4)_2S_{x+1}$$

Preferred ammonium sulfide requirements appear to be about one pound of ammonium sulfide per pound of sulfur. The pulp is leached, filtered and washed thoroughly. The filtrate is then sent to an evaporator where ammonium polysulfide is decomposed according to the following equation by heating at 95° C.:

$$(NH_4)_2S_x + 1 \xrightarrow{Heat} H_2S + 2NH_3 + xS.$$

This temperature is not critical. Sulfur is crystallized out and ammonium sulfide is regenerated by scrubbing the gases given off with water and sent back to the ammonium sulfide treatment step. Because of this regeneration of ammonium sulfide, the net ammonium sulfide loss in the process is less than about five percent. The sulfur precipitate consists of pure (99.8 percent) rhombic crystals, the major impurity being iron.

Other solvents than ammonium sulfide may be used for the dissolution of sulfur, such as, sodium sulfide, perchloroethylene and carbon disulfide. Of course, ammonium sulfide is the preferred solvent as it can be regenerated for reuse.

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Since approximately two percent of the copper fed to the leach circuit as chalcopyrite remains in the tails because it has not been contacted with the leachant, it is important from an economic standpoint to recover the copper values in the tailings from which elemental sulfur has been separated. The order of performance of this step is important because unless copper is removed before molybdenum is recovered the copper will contaminate the molybdenum to the point where it is not saleable for important commercial usages, such as, alloying with steel. Copper must be removed before the gold recovery step as it is soluble in sodium cyanide, the solvent used for gold recovery.

The residue from the ammonium sulfide leach amounts to only about six percent of the total weight of the tailings, further illustrating the effectiveness of the invention in reducing the amount of tailings which must be processed for recovery of the metal values. The residue is ground to about 95 percent being −325 mesh in a ball mill closed circuit with a cyclone to expose substantially all of the remaining copper ore in the concentrate. The ground solids are then subjected to ferric chloride leach for about three hours at 105° C, after which the pulp is filtered and the filtrate containing the solubilized copper and iron as chlorides is sent back to the main hydrometallurgical leach circuit. The ferric chloride leaching temperature used is not critical.

As the flow sheet of FIG. 2 indicates, gold, if present, is next recovered. The residue from the ferric chloride leach is leached with sodium cyanide as is conventional for the selective solubilization of the gold from the molybdenum and a liquid-solids separation performed on the resulting slurry. The gold is recovered from its cyanide solution by conventional techniques. Other cyanides may be used for solubilizing gold, such as, some of the other alkalies metal cyanides; however, sodium cyanide is preferred for economic reasons.

Molybdenum is next recovered as shown in the flow sheet. The residue from the cyanide leach is filtered and washed. Wash water, being very small in quantity, is recycled to the cyanide leach. The residue is repulped and cleaned three times. The recleaned concentrate from this float circuit is again leached with ammonium sulfide to remove elemental sulfur formed in the ferric chloride leach, and sulfur recovered and ammonium sulfide regenerated as explained above. The water washed residue from which elemental sulfur, gold, and copper have been removed contains 50-70 percent of the original molybdenum in the concentrate and assays 25-45 percent molybdenum and one percent copper. Molybdenum can be recovered from the residue by known procedures.

Tests have shown that procedure based on the above described flow sheet results in recovery from the tailings of up to 90 percent copper, 50 percent molybdenum (80 percent recovery predicted by recycling), and over 95 percent of the elemental sulfur.

The process is illustrated by the following example in which the procedure outlined in the flow sheet of FIG. 2 was followed. The sample used contained no appreciable amount of gold.

### EXAMPLE 1

The tails had the following assayed composition:
Cu – 0.52%
Mo – 0.21%
S° – 21.0%

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The tails were subjected to two flotation steps using as flotation agents calcium oxide, sodium silicate and sodium cyanide. After flotation and elimination of the rejected residue or tails from the flotation concentrate, the latter had the following assayed composition:
Cu – 1.76%
Mo – 0.65%
S° – 76.3%

The discarded tails or residue from the flotation had the following assayed composition:
Cu – 0.060%
Mo – 0.058%
S° – 0%

After filtering the float concentrate, the residue was leached with 45 percent ammonium sulfide solution using about one pound of ammonium sulfide per pound of sulfur to solubilize the elemental sulfur and form ammonium polysulfide. The formed slurry was filtered and the filtrate evaporated at 90° C for two hours to crystallize out sulfur. The gases were scrubbed with water to recover ammonium sulfide which was recycled to the ammonium sulfide leaching step. The recovered sulfur crystals assayed 99.8 percent sulfur; 98 percent of the original elemental sulfur was recovered.

The residue from the ammonium sulfide leach was ground in a ball mill until 95 percent of the solids were about −325 mesh. The ground residue was leached with concentrated ferric chloride for three hours at 105° C and the formed slurry filtered. The filtrate was sent back to the main leach. It had the following assay:
Cu – 0.23%
Mo – 2.87%
S° – 21.06%

indicating that 90.3 percent of the total copper in the tails had been dissolved and sent back to the main leach for recovery.

The residue from the ferric chloride leach was again subjected to flotation with the same flotation agents as used above. The float concentrate was recovered and found by assay to have the following composition:
Cu – 0.48%
Mo – 7.11%
S° – 72.05%

The elemental sulfur was formed in the ferric chloride leach, and it is necessary to remove it before recovering molybdenum. The elemental sulfur was removed by the ammonium sulfide treatment, recovered by the procedure described above, and ammonium sulfide regenerated and returned to the ammonium sulfide leaching step. After a liquid-solids separation the residue was thoroughly washed and recleaned and had the following assayed percentage composition:
Cu – 1.64%
Mo – 24.4%
S° – 2.5%

50.4 percent of the molybdenum in the original tails was recovered. Molybdenum having the required purity for alloying with steel is recovered from the concentrate.

In order to illustrate the process applied to a gold containing concentrate the process was run on two concentrates containing gold, i.e., a "Magma" concentrate and an "Eldorado" concentrate and the results of the gold recovery step are given in the following tables:

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### Table 1

| Concentrate | Gold concentration after FeCl₃ and/or CuCl₂ mass leach |
|---|---|
| Magma | 0.051 troy oz./ton |
| Eldorado | 0.933 troy oz./ton |

Gold distribution after cyanide leach was as follows:

### Table 2

| | Gold Assay | Gold Distribution |
|---|---|---|
| **Magma Concentrate** | | |
| Filtrate | 0.48 ppm | 92% |
| Residue | 1.4 ppm | 8% |
| **Eldorado Concentrate** | | |
| Filtrate | 7.15 ppm | 93% |
| Residue | 22.5 ppm | 7% |

From the above description it is seen that a process has been provided for recovering copper, gold, molybdenum and elemental sulfur from the tailings resulting from hydrometallurgical processing of copper sulfide ores. The process provides for processing the minimum amount of tailings. It can be adapted to continuous operation. The order of performance of the steps with the reagents is important in order to prevent the interference by elemental sulfur with the recovery of copper, gold, and molybdenum, and in order to provide for effective selection separation of the various metals so that contamination of recovered metals is prevented. The process is cooperatively related to the main copper ore leaching step because this latter step always produces elemental sulfur and because ferric chloride leach solutions containing the copper recovered from the tails in the process of the invention is adaptable for introduction in to the main copper ore leach step of the copper recovery process, thus making return of the leach solution to the main leaching step for recovery of copper feasible. The high percentage recoveries of sulfur, copper, molybdenum and gold obtained from the tails illustrates the economic effectiveness of the process.

An advantage of the process is that it eliminates the necessity of having a molybdenum flotation circuit in the mine concentrator as the process provides for recovery of the molybdenum which remains in the concentrate. It is well known that recovery of the molybdenum in the flotation circuit in the mine concentrator requires the recovery of molybdenum in the presence of copper at all copper mills and this is very difficult to do and results in losing a substantial portion of molybdenum values in meeting the copper content limit of the recovered molybdenum.

I claim:

1. A process for recovering copper, molybdenum and elemental sulfur from copper sulfide ore concentrates or tailings containing copper, molybdenum, elemental sulfur, pyrite and other impurities which comprises:
   a. subjecting the concentrate or tailings to froth flotation to collect elemental sulfur, copper and molybdenum values in a float concentrate and reject the remainder of the tailings;
   b. performing a liquid-solids separation on the float concentrate of step (a);
   c. leaching the residue of step (b) with a solvent for sulfur to dissolve elemental sulfur;
   d. performing a liquid-solids separation on the slurry of step (c);
   e. recovering elemental sulfur from the filtrate of step (d);

f. leaching the residue of step (d) with ferric chloride to selectively dissolve copper therein;
   g. performing a liquid-solids separation on the slurry of step (f)
   h. recovering copper from the filtrate of step (g); and
   i. recovering molybdenum from the residue of step (g).

2. The process of claim 1 in which in step (c) the solvent for sulfur is ammonium sulfide.

3. The process of claim 2 in which in step (e) the filtrate of step (d) is evaporated to recover elemental sulfur and regenerate ammonium sulfide.

4. The process of claim 1 in which in step (h) the copper is recovered from the ferric chloride leach solution by sending the solution to the leaching step of a hydrometallurgical circuit for the recovery of copper from its sulfide ores in which the ore is leached with ferric chloride and/or cupric chloride to produce a leach solution comprising cuprous chloride, cupric chloride and ferrous chloride.

5. The process of claim 1 in which the concentrate of step (a) contains gold and before step (i) the residue of step (g) is leached with cyanide to solubilize gold before the residue is sent to step (i) and gold recovered from the cyanide solution.

6. In the process for recovering copper from copper sulfide ore concentrates in which the concentrate is leached in a main leach step to produce a leach slurry comprising cuprous chloride, cupric chloride, and ferrous chloride in solution which latter is separated from the residue or tailings containing undissolved materials such as molybdenite, and elemental sulfur, some copper, and impurities and the solution further processed to recover copper, the improvement by which the elemental sulfur, copper and molybdenum in the tailings are selectively separated and recovered, comprising:
   a. subjecting the tailings to froth flotation to collect the elemental sulfur, and copper and molybdenum values in a float concentrate and reject pyrite, jarosite, if present, and other impurities;
   b. performing a liquid-solids separation on said float concentrate;
   c. leaching the residue of step (b) with a sulfur solvent to dissolve elemental sulfur;
   d. performing a liquid-solids separation on the slurry of step (c);
   e recovering elemental sulfur from the filtrate of step (d)
   f leaching the residue of step (d) with ferric chloride to selectively dissolve copper therein;
   g performing a liquid-solids separation on the slurry of step (f);
   h recovering copper from the filtrate of step (g);
   i subjecting the residue of step (g) to froth flotation and recovering the float concentrate containing elemental sulfur and molybdenum values;
   j leaching the float concentrate of step (i) with a sulfur solvent to solubilize elemental sulfur produced by the ferric chloride leach followed by liquid-solids separation and recovery of sulfur from the solution; and
   k recovering molybdenum from the residue of step (j).

7. The improved process of claim 6 in which in step (c) the sulfur solvent is ammonium sulfide.

8. The improved process of claim 7 in which in step (e) the filtrate of step (d) is evaporated to recover elemental sulfur and regenerate ammonium sulfide.

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9. The improved process of claim 8 in which in step (e) the filtrate is evaporated at a temperature of at least about 95° C.

10. The improved process of claim 6 in which in step (h) the copper is recovered from the ferric chloride leach solution by recycling the latter to said main leach for recovery of copper.

11. The improved process of claim 6 in which the concentrate of step (a) contains gold and before step (i) the residue of step (g) is leached with cyanide to solubilize gold before the residue is sent to step (i) and gold recovered from the cyanide solution.

12. The improved process of claim 6 in which in step (f) the residue is ground to about 95 percent being about −325 mesh to expose interlocked copper sulfide ore before it is leached with ferric chloride.

13. In the process for recovering copper from copper sulfide concentrates in which the concentrate is leached in a main leach circuit to produce a leach solution comprising cuprous chloride, cupric chloride, ferrous chloride and soluble metal impurities, the solution further processed for copper recovery, the improvement by which elemental sulfur, copper and molybdenum in the tailings from the main leach are selectively separated and recovered which comprises the following:

a. recovering elemental sulfur from the tailings by solubilizing the sulfur with a solvent for sulfur followed by recovering elemental sulfur from the solution;

b. recovering copper from the residue from the sulfur solvent leach of step (a) by leaching the sulfur depleted residue with ferric chloride to selectively solubilize copper; and

c. recovering molybdenum from the residue from the ferric chloride leach of step (b).

14. The process of claim 13 in which the recovered solubilized copper is returned to the main leach circuit for recovery of elemental copper.

15. The process of claim 13 performed continuously with the main leach.

16. The process of claim 13 in which in step (a) the sulfur solvent is ammonium sulfide.

17. The process of claim 16 in which ammonium sulfide is used in an amount by weight equal to about the amount of sulfur in the tails.

18. The process of claim 16 in which elemental sulfur is recovered from the sulfur solution by evaporation and ammonium sulfide is regenerated by dissolving the offgases in water.

19. The process of claim 13 in which the tailings of step (a) contain gold and before step (c) the residue of step (b) is leached with cyanide to solubilize gold before the residue is sent to step (c) and gold recovered from the cyanide solution.

20. The process of claim 13 in which prior to step (a) the tailings are concentrated by froth flotation to reject impurities such as pyrite and jarosite.

21. In a hydrometallurgical process for recovering copper from copper sulfide ore concentrates in which

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the concentrate is leached in a main leach step with ferric chloride and/or cupric chloride to produce a leach slurry comprising cuprous chloride, cupric chloride and ferrous chloride in solution which latter is separated from the residue or tailings containing undissolved materials such as gold, molybdenite, elemental sulfur, some copper, and impurities, and the solution further processed to recover copper, the improvement by which the tailings are concentrated into a small bulk containing substantially all of the materials to be recovered and the elemental sulfur, gold, copper, and molybdenum in the concentrated tailings are selectively separated and recovered, comprising the following steps performed in the recited order:

a. concentrating said tailings by subjecting them to froth flotation to collect the elemental sulfur and copper, gold and molybdenum values in a float concentrate having a greatly reduced solids volume and to reject jarosite if present, and other impurities in a barren gangue;

b. performing a liquids-solids separation on said float concentrate;

c. leaching the residue of step (b) with a sulfur solvent to dissolve elemental sulfur;

d. performing a liquid-solids separation on the slurry of step (c);

e. recovering elemental sulfur from the filtrate of step (d);

f. leaching the residue of step (d) with ferric chloride to selectively dissolve copper therein;

g. performing a liquid-solids separation on the slurry of step (f);

h. recycling the filtrate of step (g) to said main leach step for copper recovery;

i. leaching the residue of step (g) with cyanide to solubilize gold therein;

j. performing a liquid-solids separation on the slurry of step (i);

k. recovering gold from the solution of step (j);

l. subjecting the residue of step (j) to froth flotation and recovering the float concentrate containing molybdenum values, and elemental sulfur produced by the ferric chloride leach;

m. leaching the float concentrate of step (l) with a sulfur solvent to solubilize the elemental sulfur produced by the ferric chloride leach of step (f);

n. performing a liquid-solids separation on the slurry of step (m);

o. recovering sulfur from the filtrate of step (n); and

p. recovering molybdenum from the residue of step (n).

22. The improved process of claim 21 in which the sulfur solvent of step (c) is ammonium sulfide.

23. The improved process of claim 22 in which elemental sulfur is recovered from the sulfur solution by evaporation and ammonium sulfide regenerated by contacting the off-gases with water.

* * * * *

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APPENDIX B

# Consultancy Studies

CD84-1032

The Production of Elemental Sulpuhr
from Pyrites:

A Process Appraisal

Prepared for:

Aberdare Incorporated
Princetown, NJ, USA.

AUGUST 1984

## The British Sulphur Corporation Limited

266026

# CONTENTS

## List of diagrams

1.    **INTRODUCTION**

The object of this report is to summarize technically and, where possible, economically processes which could be employed to enable the production of elemental sulphur from pyrites.

The types of processes discussed tend to split into two groups:

1.    Dedicated processes for recovering sulphur from pyrites, some of which have been commercially proven in full scale operation, and others which have never reached beyond the pilot or bench-scale stage.

2.    Processes which are currently employed to produce elemental metals with by-product sulphur from metal minerals other than pyrites which could possibly be applicable to pyrites by the addition of (an) extra process step(s).

In all cases, the absence of a detailed mineralogical analysis of the Aberdare pyrite prevents detailed comparisons and techno-economic recommendations. This report, therefore, can only be of a general nature and is intended to inform and guide rather than state any definite conclusions regarding the exploitation of the pyritic deposit in question.

From the data provided the following assumptions have been made regarding the available pyrite to be processed:

1.    Production: 300,000 m.t.p.a.

2.    Cobalt content of pyrite: 0.11 - 0.22%.

The economics of the various processes, where available, are for the most part extremely outdated, in the cases where economics have been given the originally calculated or achieved costs have been updated to give an estimated present day equivalent.

## 2. SUMMARY AND CONCLUSIONS

Recovering elemental sulphur from pyrite is an extremely expensive and technically complex process. Research and development occurs from time to time when sulphur prices rise, as they are doing at the present time, but at the moment there is no commercially operating process which can be demonstrated for the purpose of this report. Only one of the examples in this report has seen commercial operation: the Outokumpu process in Finland, but even this process was never operated in order to maximise elemental sulphur production - only around 50% of the sulphur was recovered in elemental form.

If a plant producing elemental sulphur from pyrite were to be constructed, the only real option regarding process route would involve thermal decomposition of pyrite to liberate elemental sulphur and iron monosulphide (pyrrhotite). The monosulphide could be further treated in a number of ways to maximise sulphur production.

Hydrometallurgical treatment of sulphide ores is practised exlcusively for the production of valuable metals with elemental sulphur being produced as a by-product. It is not forseeable that this process would ever be used specifically for recovering such a relatively low value product as sulphur.

The process could be applicable to recovering cobalt as the primary product and sulphur as the secondary product but would require ores containing fairly high quantities of cobalt (greater than 2%), and a correspondingly high cobalt price, to justify the investment required. The direct treatment of pyrite to liberate elemental sulphur from the iron disulphide is not possible without first thermally treating the pyrite to produce an iron monosulphide.

Three possible thermal treatment processes have been discussed here: Outokumpu, Sherrit-Gordon and Dorr Oliver. In addition a possible hydrometallurgical route has been discussed which at present is commercially applied to the treatment of zinc sulphides. A novel, patented process for the production of elemental sulphur through the chlorination of pyrite has also been described. Where possible, estimates for the capital and production costs of the processes have been prepared and are summarized in the accompaying table.

It should be noted that all these costs are based on calculations performed pre 1970s energy crisis. Present day costs of equipment, fuels and utilities etc. have been used as far as possible but any accurate costings would require a complete appraisal of each process to be performed on the basis of a specific present day case.

Cobalt recovery from residues resulting from the thermal process route for pyrite treatment has been practised in the past. This, however, is no longer seen as commercially viable compared with direct ore smelting. In any case the cobalt must again be in sufficient concentration in the ore to justify exploitation, the figure of 2% Co in the ore concentrate is again considered a reasonable minimum.

## Summary of Capital and Production Costs

| Process | Type | Processing Capacity S.T.P.A. pyrite | Approximate Capital Cost US $ million | Production Cost Per Ton Sulphur |
|---|---|---|---|---|
| Outokumpu | Thermal | 300,000 | 86 | 100 (approx) |
| Sherritt Gordon | Thermal and Aqueous Oxidation | 500,000 | 100 [1] 70 [2] | 110.00[2] |
|  |  | 300,000 | 52 |  |
| Dorr Oliver | Thermal | 270,000 | 50 | 108.00 |
|  |  | 300,000 | 53 |  |
| Adapted Sherritt | Thermal and Hydrometallurgical | 300,000 | 40 | no accurate figure available, but expected to be greater than 100 |

[1] Figures are calculated on the basis of the original process which was intended to recovery sulphur and also process the resulting iron compounds.

[2] Figures are adjusted to remove costs of iron processing and present a cost in terms of sulphur production alone.

3.    PROCESS DESCRIPTIONS

3.1    The Thermal Route

3.1.1    The Outokumpu Process

This process was installed at Kokkola on the west coast of Finland in 1963 and was designed to exploit the massive deposit of pyrite ore discovered near Pyhasalmi in central Finland. The deposit indicated 17,000,000 tonnes assaying 0.85% copper, 2.8% zinc, 33.0% iron and 37.0% sulphur. The process was designed to treat 360,000 t.p.a. pyrite flotation concentrate but at the height of its production, in 1967, the plant was processing 480,000 t.p.a. Of pyrite flotation concentrate to produce:

1.    113,500 t.p.a. sulphur in the form of prills or liquid sulphur (99.99% S).

2.    107,000 t.p.a. sulphur in $SO_2$ gas (8.2% $SO_2$ in gas).

3.    325,000 t.p.a. coarse iron oxide calcine, (67.0% Fe and 0.2% S) for high grade iron blast furnace feed.

4.    Cogenerated electric power of 42 MW nominal allowing plant self sufficiency and electric power export revenue.

The process was originally developed to make copper and zinc recovery from the deposit more economically viable by deriving revenue from the pyrite. The European pyrite market at the time was weak and this meant that the pyrite would have to be processed in Finland rather than sold directly.

The plant was shut down in 1977 due to the increasing abundance and relative cheapness of brimstone sulphur and the rising cost of energy in the form of fuel oil for the smelting operation.

The Outokumpu process involves drying of the concentrate and blowing into the top of a flash smelting furnace to decompose pyrite to form elemental sulphur vapour and a liquid iron sulphide matte.

The sulphur vapours and combustion gases are cooled, cleaned and then treated in catalysers for best recovery in the last sulphur condensing step. The liquid matte is continuously tapped from the bottom of the furnace, granulated with water and then roasted to produce $SO_2$ gas and $Fe_2O_3$ calcine. The $SO_2$ gas was sold to a neighbouring sulphuric acid producer.

The key process steps are:

1.  Flash smelting          -    $2 FeS_2 + heat = 2FeS + S_2$

2.  Catalyser 1.           -    $2CO + SO_2 = \frac{1}{2} S_2 + 2CO_2$

                                $COS + H_2O = H_2S + CO_2$

3.  Catalyser 2.           -    $4H_2S + 2SO_2 = S_6 + 4H_2O$

4.  Sulphide matte roasting    -    $2FeS + 3\frac{1}{2} O_2 = Fe_2O_3 + 2SO_2$

Descriptions of the operation of these steps are briefly presented below.

1.  Flash Smelting

    After drying in a rotary kiln, using fuel oil as the heat source, the pyrite, at a temperature of about $120^{\circ}C$, is blown into the furnace along with $340^{\circ}C$ preheated combustion air which may be oxygen enriched. The quantity of air must be kept stoichiometrically correct to avoid formation of $SO_2$. The molten matte collects in the bottom of the furnace while the gases sweep over the molten pool to the exhaust flue. The temperature of the furnace gas is about $1,250^{\circ}C$ while the matte is about $50-100^{\circ}C$ lower than this. The matte is continuously tapped from the furnace, granulated with jets of water and then stockpiled before roasting. The hot gases, including sulphur vapour, pass through a boiler where steam is raised at about 70 bar and $285^{\circ}C$. The gases leaving the boiler are at a temperature of around $350^{\circ}C$ and pass through an electrostatic precipitator which removes all the dust which is carried over.

2.  Catalysis

    A reheater raises the gases from the electrostatic precipitator to around $400^{\circ}C$ before introduction into the first catalyser where the concentration of elemental sulphur is increased according to the reactions in 2. above. After cooling in a low pressure steam boiler the exhaust gases from the high temperature catalyser enter the low temperature catalyser where sulphur is recovered by catalytic reaction of $H_2S$ and $SO_2$ at a temperature of about $260^{\circ}C$. The catalysts material is alumina soft concrete.

Condensation of the sulphur takes place in a low pressure boiler and the melt is then sprayed into a cooling tower where contact with hot furnace gases condenses out further sulphur. The molten sulphur then flows to a collection tank. The cooled furnace gases are emitted to atmosphere after wash-water scrubbing.

3.   Roasting

The granulated matte is reclaimed from stockpiles and roasted at a temperature in excess of $1,000^{\circ}C$ to produce $SO_2$ and a calcine containing 67.0% iron and 0.2% sulphur.

Outokumpu later installed a cobalt recovery plant to process the resulting cobalt containing calcine. The cobalt recovery plant is still in operation but all the pyrite is now directly roasted to produce the calcine, there being no longer an elemental sulpur removal step. The cobalt content of the pyrite is around 2% and is recovered via smelting.

Technically the pyrite smelter operation worked well and was only closed down because of the unfavourable economics which occurred during the 1970's.

The Outokumpu process was always operated to jointly produce $SO_2$ and sulphur as there was a market for the $SO_2$ produced, they do claim, however, that the process can be adapted for maximising the production of elemental sulphur.

3.1.2   The Sherritt Gordon Process

Sherritt-Gordon of Alberta, Canada developed a process in the mid 1960s for the production of iron and sulphur from pyrites. Unlike Outokumpu the process never achieved commercial operation for much the same reasons that forced the Outokumpu process plant to be closed down, i.e. lack of sound economics.

At the 'front-end' the process is similar to Outokumpu, requiring a thermal treatment step to drive off and recover labile sulphur leaving an iron monosulphide. The process then varies by the required aim of maximising the elemental sulphur production through aqueous oxidation of the monosulphide to produce elemental sulphur and hydrated iron oxide. There are four main process steps, as follows:

1.   Low temperature thermal decomposition of the pyrite to elemental sulphur and iron monosulphide.

2.  Aqueous oxidation of the iron monosulphide to hydrated iron oxide and elemental sulphur.

3.  Dissolution of the hydrated iron oxide and non-ferrous metal values, purification and hydrolysis of pure basic ferric sulphate.

4.  Processing to a final iron product.

The process has been theoretically applied to two different pyrite bases:

-   'clean' or relatively pure pyrite to produce sponge iron and elemental sulphur ( in this case step 3 above would be omitted).

-   'dirty' or impure pyrite containing assorted non-ferrous metal impurities to produce high purity sponge iron or high purity iron powder in addition to elemental sulphur and concentrates containing non-ferrous metals.

For the purposes of this report the treatment of 'dirty' pyrite will be considered both technically and, later, economically.

An outline of the main process steps involved in the process is given below.

1.  Thermal Decomposition (Figures 1 & 2)

Pyrite concentrates are dried in a fluid-bed dryer. The dried pyrite is then combined with unreacted sulphides from the aqueous oxidation step, and fed to the thermal decomposition reactor. The endothermic heat of reaction (525 BTU/lb pyrite) is provided by direct combustion of fuel oil in the fluid bed. The oxygen requirement has to be carefully controlled, as in the Outokumpu process, to avoid formation of $SO_2$. Operation of the reactor at 1,300-1,500 $^oF$ (700-815$^oC$) and a retention time of 30 minutes is sufficient to produce an iron monosulphide with a sulphur/iron molar ratio of approximately 1 to 1.15 which is adequate for the subsequent process steps. The solids are discharged from the reactor and then slurried in a quench tank with a recycle solution before feeding to the aqueous oxidation autoclave.

The combustion gases leaving the reactor contain elemental sulphur together with small quantities of $H_2S$, $SO_2$ and carbonyl sulphide, COS. These gases pass through dust cyclones, a waste heat boiler, an electrostatic precipitator and

then a sulphur recovery unit consisting of a catalytic converter for the conversion by reaction of $H_2S$ and $SO_2$ to produce elemental sulphur, and a sulphur condenser generating low pressure steam.

2.    Aqueous Oxidation (Figure 3 & 4)

This step is an oxidation reaction converting iron monosulphide to hydrated iron oxide and elemental sulphur according to the reaction: $2FeS + 3H_2O + 1\frac{1}{2}O_2 = 2Fe(OH)_3 + 2S^{\circ}$. The exothermic reaction (-1,525 BTU/lb FeS) is carried out in an autoclave, constructed of acid resistant materials, similar to autoclaves used in acid leaching processes. Iron monosulphide from the thermal decomposition reactor is repulped in recycle solution from the liquid-solids separation step, following hydrolysis, then pumped into the autoclave using a suitable high pressure slurry pump. Air is added at a pressure of approximately 800 PSIG to enable oxidation to take place. An alternative to high pressure air might be pure oxygen or oxygen enriched air.

A gas turbine is used to compress the air and this also provides the process steam requirements through the use of a waste heat boiler on the turbine exhaust.

The exothermic heat of reaction is removed by cooling coils installed in the autoclave.

Exhaust gases depleted in oxygen leaving the autoclave are water-scrubbed and then vented.

3.    Iron Dissolution and Hydrolysis of Basic Ferric Sulphate

The discharge solution from the aqueous acidation autoclave is first flashed to atmospheric pressure and then diluted to approximately 200g. per litre solids by the addition of recycle solution from the hydrolysis step before being charged directly to the iron dissolution vessel. The slurry is contacted with $SO_2$ from the calcination step which is absorbed to totally dissolve the iron as ferrous sulphate. The elemental sulphur, pyrite, pyrrhotite, precious metals and lead sulphate remain unattacked.

Following iron dissolution the slurry is filtered, the residue then heated abve the melting point of sulphur, flash cooled to form pellets of elemental sulphur, and screened to recover the sulphur pellets. The elemental sulphur pellets are then treated in the sulphur recovery circuit consisting of agitation, hot

water heating at 300°F (150°C), and then pressure filtering to recover approximately 95% of the elemental sulphur present as pure product. The hot filtration residue consisting of unreacted pyrite unreacted pyrrhotite and some sulphur is milled and then returned to the thermal decomposition step.

The filtrate from the slurry filter consists of a solution containing approximately 100g per litre of dissolved iron together with any nickel, cobalt, copper or zinc. The non ferrous metals can be stripped as a bulk precipitate or selectively precipitated.

The remaining solution now passes to the hydrolysis step which is carried out at 400°F (200°C).

Air is added to convert ferrous to ferric iron and a mixture of hydrated iron oxide and basic ferric sulphate is precipitated and filtered. The filtrate recycles to the iron dissolution step and/or the aqueous oxidation step. The residue passes to the iron processing step.

4.    Iron Processing

The basic ferric sulphate/hydrated iron oxide mixture from the treatment of impure pyrite is very pure and can be treated by calcination to drive off the remaining sulphur as $SO_2$ and $SO_3$ for recycling to the iron dissolution step. The calcine may also be reduced to a high-purity iron powder.

While appearing a sound process on paper and achieving good laboratory results, the Sherrit-Gordon process has not been a source of great joy to the company. There are very large technical difficulties in adopting the process to full scale operation and up to the present day, the economics have not justified work to remove the technical difficulties. A large 'dirty' pyrite deposit in Spain has been fairly recently studied in terms of applicability to this process but it was discovered that, to achieve reasonable project economics, the plant would be required to process between 1 and 1½ million tonnes of pyrite per annum. It was thus decided that there were too many technical risks on a plant of too huge a scale to justify going ahead.
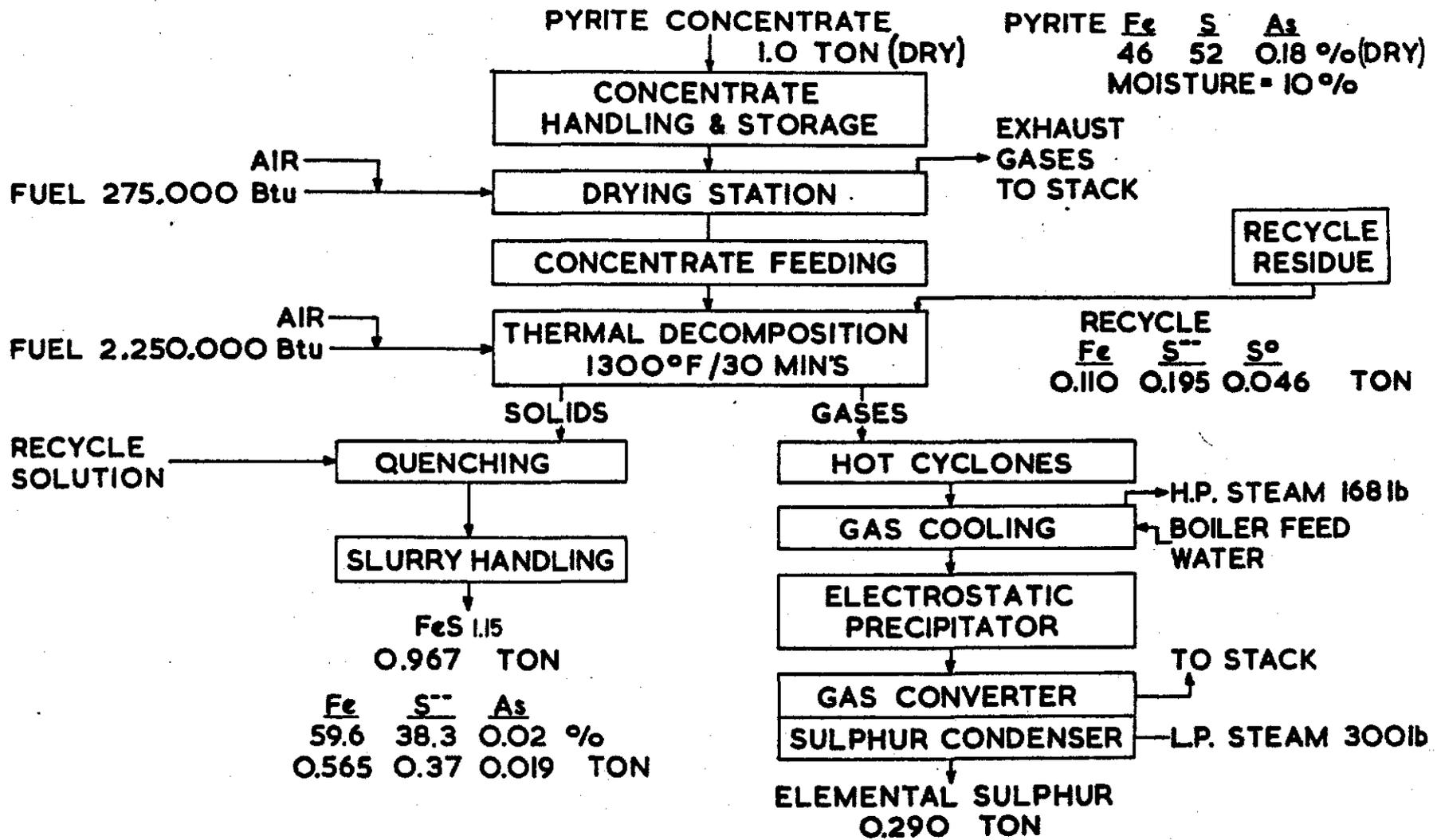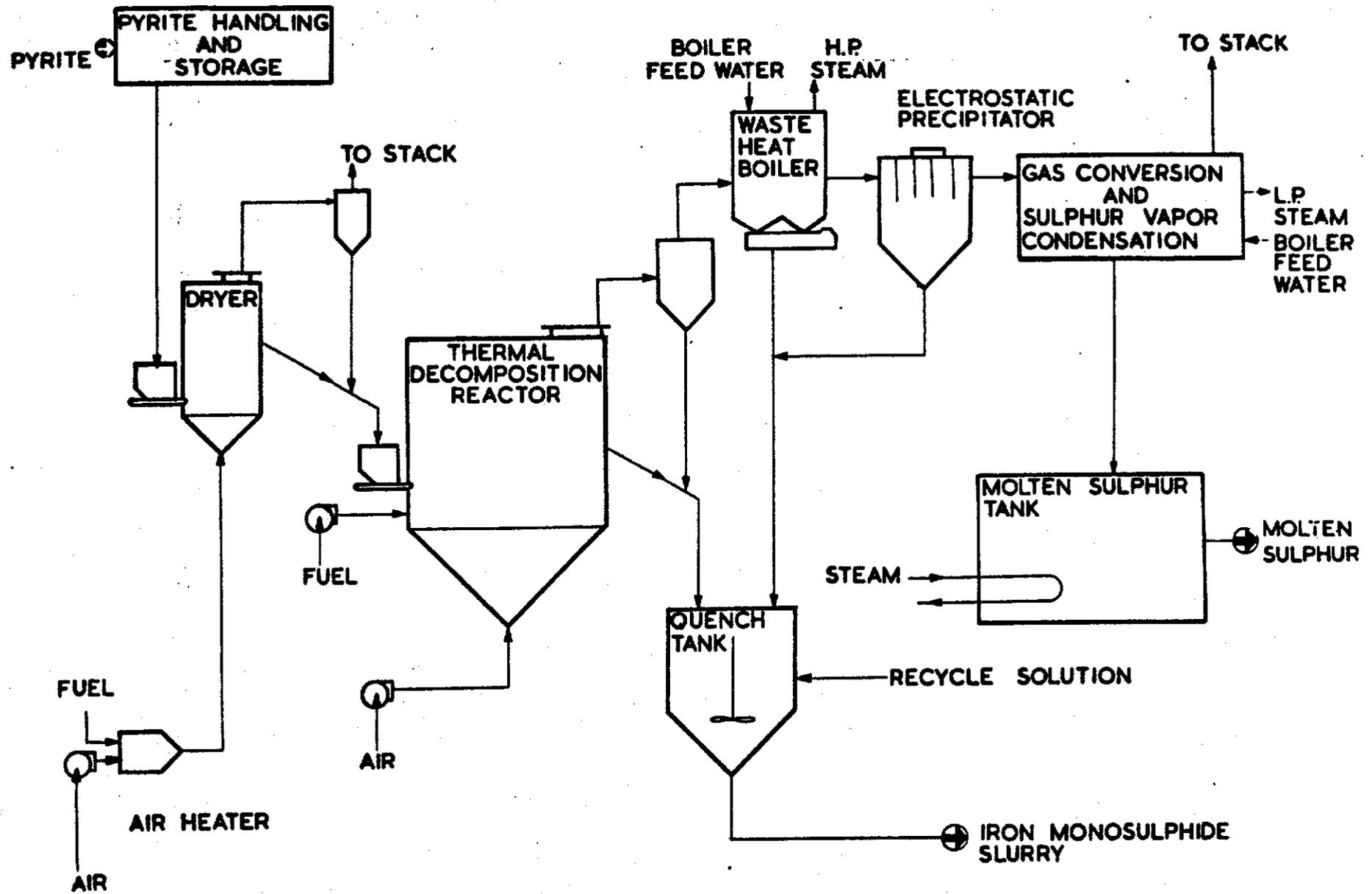
PYRITE CONCENTRATE
1.0 TON (DRY)

PYRITE | Fe | S | As
46 | 52 | 0.18 %(DRY)
MOISTURE = 10%

```
                    ┌──────────────────────────┐
                    │      CONCENTRATE          │
                    │   HANDLING & STORAGE      │
                    └──────────────────────────┘
AIR ─┐                           │              EXHAUST
     │              ┌────────────────────────┐  GASES
FUEL 275.000 Btu ──→│    DRYING STATION      │→ TO STACK
                    └────────────────────────┘
                    ┌────────────────────────┐      ┌──────────┐
                    │  CONCENTRATE FEEDING    │      │ RECYCLE  │
                    └────────────────────────┘      │ RESIDUE  │
AIR ─┐                           │                  └──────────┘
     │              ┌────────────────────────┐  RECYCLE
FUEL 2.250.000 Btu →│  THERMAL DECOMPOSITION  │
                    │    1300°F / 30 MIN'S    │
                    └────────────────────────┘
```

RECYCLE
Fe | S⁻⁻ | S°
0.110  0.195  0.046   TON

| SOLIDS | | GASES |

RECYCLE
SOLUTION ──→ QUENCHING

HOT CYCLONES

GAS COOLING ← H.P. STEAM 168 lb
← BOILER FEED WATER

SLURRY HANDLING

ELECTROSTATIC
PRECIPITATOR

FeS 1.15
0.967   TON

| Fe | S⁻⁻ | As |
|----|-----|----|
| 59.6 | 38.3 | 0.02 % |
| 0.565 | 0.37 | 0.019 TON |

GAS CONVERTER → TO STACK

SULPHUR CONDENSER ── L.P. STEAM 300 lb

ELEMENTAL SULPHUR
0.290   TON

FIGURE-1

LOW TEMPERATURE
THERMAL DECOMPOSITION

PROCESS FLOW DIAGRAM

FIGURE — 2
LOW TEMPERATURE
THERMAL DECOMPOSITION
SCHEMATIC EQUIPMENT FLOW DIAGRAM

DIRTY PYRITE
1.0 TON (DRY)

ELEMENTAL SULPHUR
0.288 TON ◄─── | LOW TEMPERATURE THERMAL DECOMPOSITION | ◄─── RECYCLE RESIDUE

RECYCLE SOLUTION
320 IG ───► | SLURRY PREPARATION 600 GPL SOLIDS |

| SLURRY PUMPING |

COOLING WATER ───► | AQUEOUS OXIDATION 230°F, 150 PSI O₂, 1.5 HOUR | ◄─── SURFACTANT
◄─── AIR 65.000 SCF

RECYCLE SOLUTION
530 IG ───► | SLURRY ADJUSTMENT |

| IRON DISSOLUTION 200°F, 20 PSI, 1.0 HOUR | ◄─── (SO₂ + SO₃) GAS RECYCLE

FILTRATE ◄─── | FILTRATION | ───► RESIDUE

0.03 TON Fe ◄─── | METAL STRIPPING |
0.015 TON S° ◄───

| SULPHUR GRANULATION | ◄─── STEAM

| FILTRATION | ───► MIXED SULPHIDES

| Cu | Zn | Ni | Co |
|------|------|------|------|
| 5.27 | 39.6 | 0.55 | 0.92 lb |

| SCREENING | ───► S° PELLETS

STEAM
850.000 Btu ───► | SOLUTION HEATING |

| SULPHUR MELTER | ◄─── STEAM

AIR
13.700 SCF ───► | HYDROLYSIS 400°F, 20 PSI O₂, 1.0 HOUR |

| HOT FILTRATION |

RESIDUE

| Pb | Insol | Ag. |
|------|-------|------------|
| 26.6 | 36 | lb, 1.64 oz |

| FILTRATION |

MOLTEN
SULPHUR
0.173 TON

| RECYCLE SOLUTION |

| PELLETIZATION |

FUEL
800.000 Btu ───► | INDURATION & CALCINATION | ───► (SO₂ + SO₃) GAS RECYCLE

IRON ORE

HYDROGEN
0.026 TON ───► | IRON ORE REDUCTION |

HIGH PURITY IRON
0.420 TON, Fe = 0.419 TON

FIGURE-3

AQUEOUS OXIDATION OF
DIRTY IRON MONOSULPHIDE
PROCESS FLOW SHEET

B15

266039

13

IRON MONOSULPHIDE SLURRY

SLURRY PUMP

SLURRY PREPARATION TANK

AQUEOUS OXIDATION PRESSURE AUTOCLAVE

COOLING WATER

AIR

AIR COMPRESSOR

RECYCLE SOLUTION STORAGE TANK

FLASH TANK

GASES & VAPORS

SLURRY HOLDING TANK

RECYCLE SOLUTION TANK

IRON DISSOLUTION TOWER

(SO$_2$ + SO$_3$) GAS

SLURRY TANK

FILTER

TO RESIDUE TANK

VACUUM

TO FLARE

MIXED SULPHIDE PRECIPITATION REACTOR

Fe

S°

REACTOR

FILTER

TO METAL FREE SOLUTION TANK

MIXED SULPHIDES OF Cu, Zn, Co, Ni

FIGURE-4

AQUEOUS OXIDATION OF DIRTY IRON MONOSULPHIDE

SCHEMATIC EQUIPMENT FLOW DIAGRAM
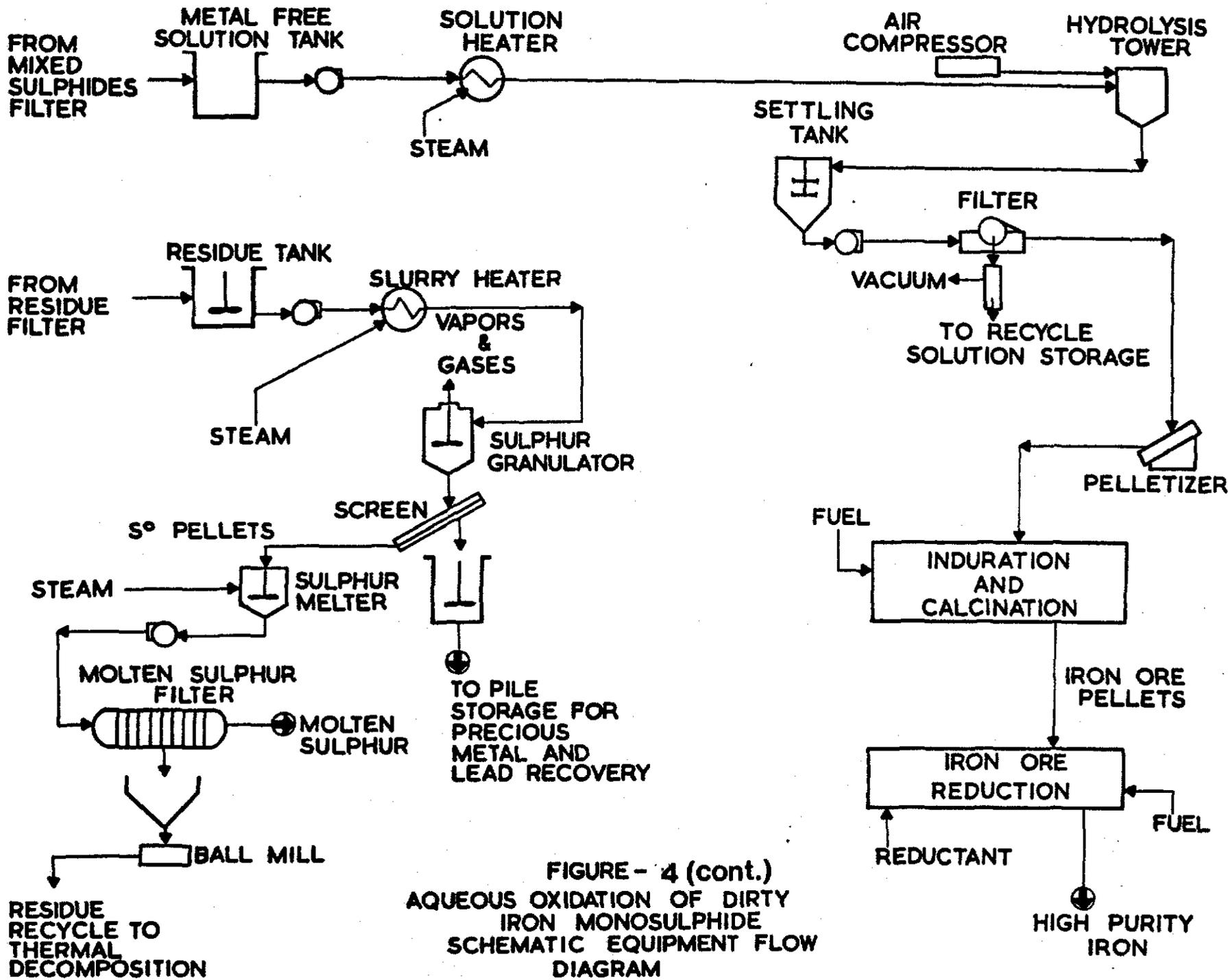
FIGURE - 4 (cont.)
AQUEOUS OXIDATION OF DIRTY
IRON MONOSULPHIDE
SCHEMATIC EQUIPMENT FLOW
DIAGRAM

### 3.1.3.    The Dorr-Oliver Process

Another process which was researched during the mid to late 1960's involving the thermal decomposition of pyrite is the Dorr-Oliver Fluo Solid System Process. Originally conceived to operate in a similar manner to the Outokumpu Process, whereby only 40% maximum recovery of elemental sulphur is achieved, the remaining sulphur being destined for sulphuric acid manufacture via $SO_2$, a 100% elemental sulphur process was considered. The process involves using two reactors for pyrite treatment. In the first reactor the pyrite is heated by the combustion of fuel in air at a temperature of around $700^{\circ}C$ in order to drive off the labile sulphur and form pyrrhotite exactly as has been described before in the Sherrit Gordon process. In addition to this, however, the hot $SO_2$ gases produced by roasting the pyrrhotite in the second reactor are passed through a cyclone and up through the fluid bed of the first reactor. The $SO_2$ gas is reacted with hydrocarbon fuel in the upper section of the first reactor resulting in the oxidation of the hydrocarbon and the production of sulphur mainly as sulphur gas but partially as $H_2S$ and remaining $SO_2$. The process (Figure 5) then follows similar lines to the two previously described processes involving gas cooling, electrical precipitation and catalytic conversion of $H_2S$ and $SO_2$ to elemental sulphur.

Although 100% recovery of sulphur is theoretically possible, in reality this will proably be unachievable through thermodynamic limitations and losses of fine pyrite occurring in the cyclones. A more realistic recovery figure would be nearer 85%.

The overall reactions occuring in the process are as follows:

Reactor 1.    $FeS_2 + Fuel + SO_2 = S_2 \text{ (gas)} + H_2S + SO_2 +$
$\qquad\qquad\qquad\qquad Combustion\ gases + FeS_{1.2}$

Reactor 2.    $FeS_{1.2} + O_2 = Fe_3O_4 + SO_2$

Converter.    $H_2S + SO_2 = H_2O + S_2 \text{ (gas)}.$
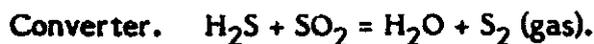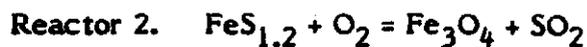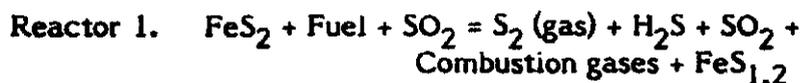
The obvious economic constraint on this process is the cost of the hydrocarbon fuel required to convert $SO_2$ to sulphur. The process would require an extremely low fuel cost and a situation where recovery of sulphur directly from sour natural gases or flue gases using the Claus catalytic recovery process was not possible (e.g. the only source of cheap fuel being on extremely sweet natural gas).
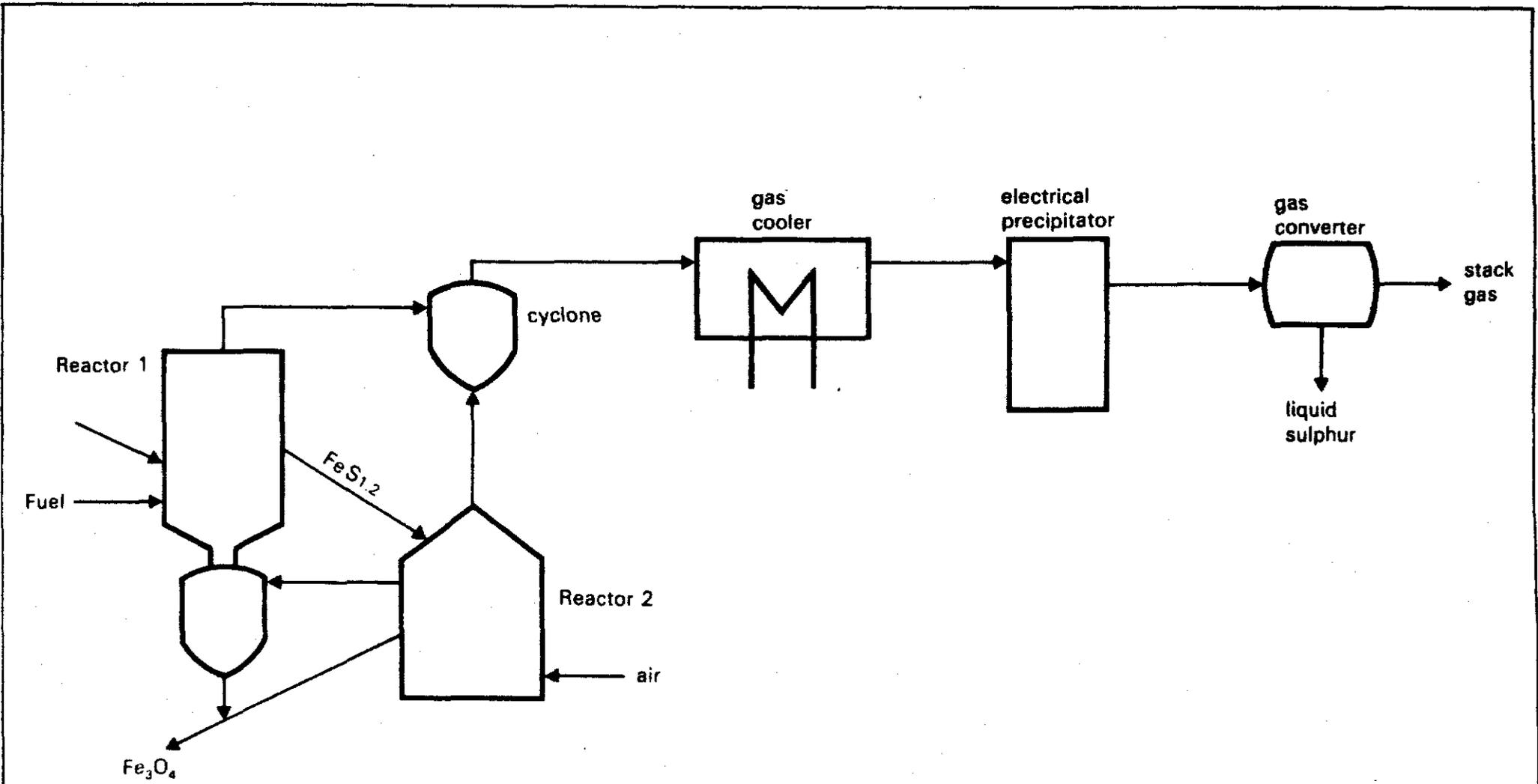
Fig. 5: Dorr Oliver Process for 100% Sulphur Recovery from Pyrite

3.2.    **The Hydrometallurgical Route**

Hydrometallurgy as applied to metal minerals has been developed for the metal refining industries where the required products are high value metals. The basic difference between hydrometallurgy and pyrometallurgy is the chemical, rather than thermal, oxidation of sulphide ores.

The main reason for the increasing development and use of this type of process is the increasing environmental concern regarding sulphur oxide emissions from thermal processes. These emissions from metal recovery operations are responsible to a large degree for atmospheric pollution leading to undesirable phenomena such as acid rain.

Hydrometallurgy avoids the production of sulphur oxide gases by essentially completely converting the sulphide to elemental sulphur. The resulting sulphur is either stockpiled or sold as a supplementaty product of the metal recovery process.

The only previously 'clean' method of sulphur oxide disposal was to utilise the gases in the production of sulphuric acid. This is only suitable when there is a local market for this product, which is very often not the case in many countries. Where restrictions on emissions are strenously applied, therefore, the operational flexibility of the metal refiner is severly limited. The use of hydrometallurgy thus permits continuous independent operation of high value metal production from sulphide ores.

Hydrometallurgical treatment of sulphide ores was developed mainly to avoid the roasting step of, for example, the standard roast-leach-electrowin process for producing metallic zinc. Sherritt Gordon have had considerable success with their zinc sulphide leaching process which involves direct leaching using recycled electrolyte, from the electrowinning step of the zinc production process, which is normally ferric sulphate produced by direct acid leaching of non-pyrite iron containing minerals in the concentrate, (Figure 6).

The reactions occuring in the zinc leaching process are shown below.

$$ZnS + Fe_2 (SO_4)_3 = ZnSO_4 + 2FeSO_4 + S^o$$
$$2 FeSO_4 + H_2SO_4 + 0.5O_2 = Fe (SO_4)_3 + H_2O.$$
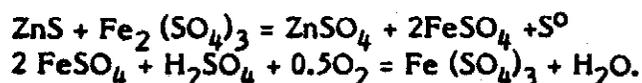
Pyrite cannot be directly pressure leached with the expectation of recovering elemental sulphur. Any pyrite contained in zinc sulphide ores passes through the process virtually unattacked.

To recover sulphur from pyrite using this process would require the production of the iron monosulphide, pyrrhotite using a thermal decomposition step as described in section 3.1 of this report.

The direct leaching of the cobalt compounds contained in the pyrite would, on the other hand, be possible.

The importance of metal values to the process was investigated with specific regard to cobalt in the period 1979-81. At this time the cobalt price was about C$20-25/lb and the recovery of this material made the process quite attractive. The cobalt price subsequently slumped, however, ruling out any further development. It is reckoned that in order to justify the process economically a cobalt price of greater than C$15/lb must be maintained (c.f. present day $8-12/lb).

Other, technical difficulties were encountered during the research, not least of which was the difficulty in making a good flotation concentrate. Cobalt tends to be very finely diffused throughout pyrite (the ore under study contained about 2% cobalt compared with zinc sulphide ores containing up to 50% zinc).

A reasonable concentrate was achieved however and the process was successful achieving a cobalt/nickel product suitable for refining. Any cobalt and elemental sulphur production facility using this process and based on pyrite with a cobalt content similar to the Aberdare deposit would, in addition to the necessarily high cobalt price, require a vast throughput of ore to achieve even a reasonable level of saleable production.
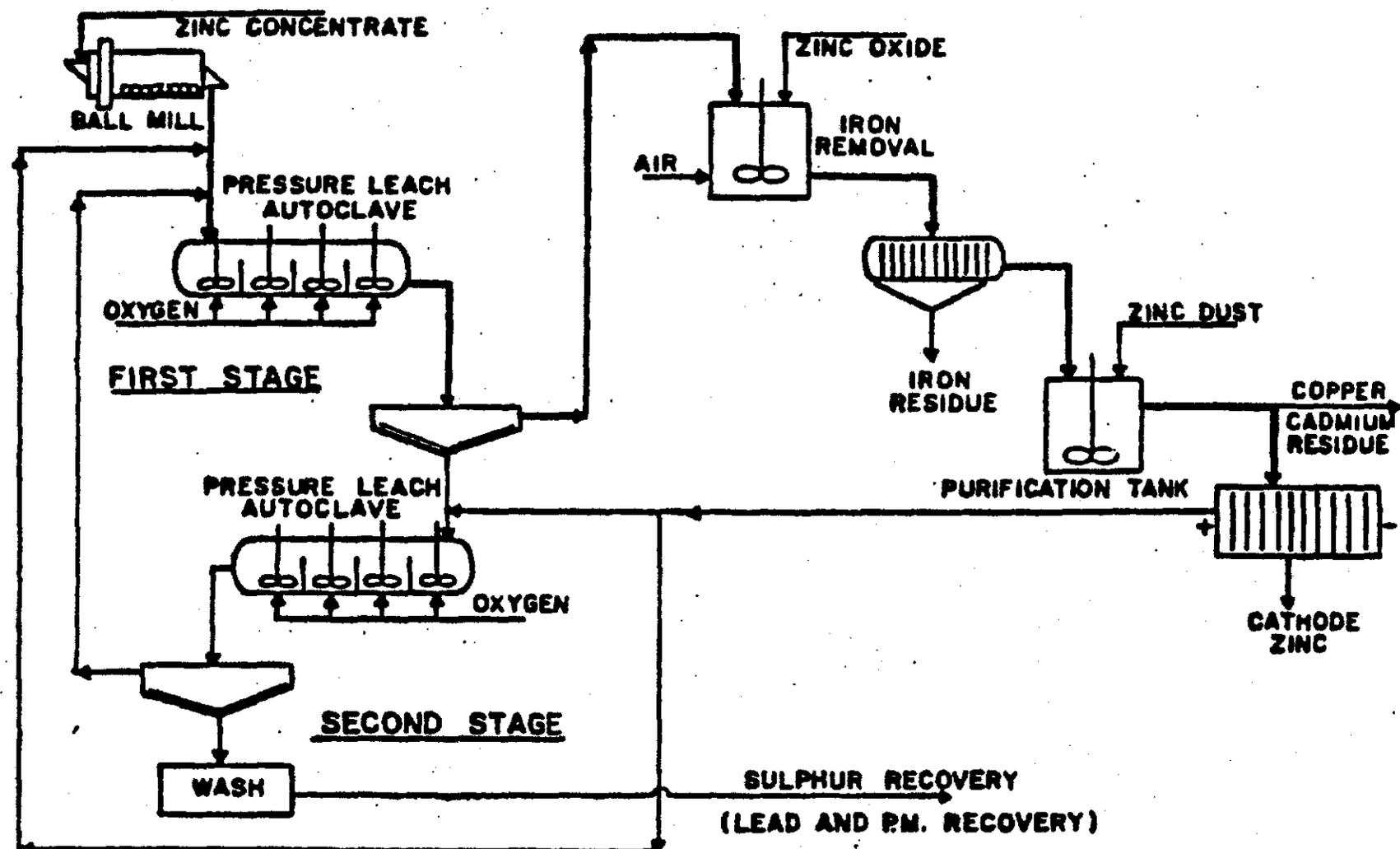
FIGURE 6 : SHERRITT ZINC PROCESS – GRASS ROOTS

## 3.3    Other Routes

### 3.3.1    The Texasgulf Chlorination Process

In the early 1950's Texasgulf developed and patented a process involving the chlorination of pyrite to evolve ferrous chloride and elemental sulphur. Although the reactions of metal sulphides with chlorine have long been known to permit recovery of sulphur, the decomposition temperature was always considered too high, causing difficulties in the sulphur removal due to the volatization of the sulphur and extreme corrosivity on separation equipment of chlorine compounds at such high temperatures. The two main reactions involved in the decomposition of iron sulphides with chlorine are:

$$FeS_2 + Cl_2 = FeCl_2 + 2S$$
and $FeS + Cl_2 = FeCl_2 + S.$
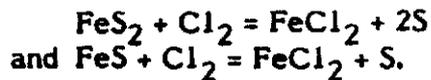
The process developed by Texasgulf has operating temperatures between 100 and 440°C permitting the reaction products to appear in liquid form, in the case of sulphur, and solid form, in the case of ferrous chloride.

The reactions must be carried out within a liquid medium capable of dissolving the chlorination products to prevent the surface of the decomposing pyrite being coated with reaction products and the reaction sequence ceasing. Suitable liquids for this purpose include sulphur and the various sulphur chlorides. When using sulphur as the liquid medium, sulphur chloride will tend to be formed but this in turn reacts with the pyrite to liberate the sulphur, the reaction temperatures also favour ultimate elemental formation rather than compound formation. The reactions between iron sulphides and sulphur chlorides are as follows:

$$FeS_2 + S_2Cl_2 = FeCl_2 + 4S$$
$$FeS + S_2Cl_2 = FeCl_2 + 3S.$$
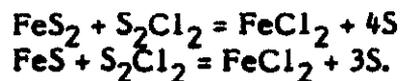
The process follows the following operational steps.

Finely ground iron sulphide is dried before introduction into a bulk or stream of molten sulphur (see Figure 7). Chlorine is also added and the reaction vessel is equipped with agitators. The products leaving the reactor include a suspension of metal chloride together with unreacted sulphide in sulphur. These products pass into a settler or thickener in which a major part of the liquid sulphur is separated from the solid metal chloride. The bottoms from the settler including metal chlorides, unreacted sulphides and sulphur are passed to a second reaction vessel in which the remaining

unreacted sulphides are reacted with further chlorine in the presence of liquid sulphur. Any sulphur chloride formed is recycled to the first reactor operated under such conditions as to permit reduction to it's component elements.

Ferrous chloride is removed in a second settler along with non-ferrous metal chlorides. The ferrous chloride may be heated to liberate the chlorine, for recycling to the process, the iron forming ferric oxide. The sulphur recovery claimed by this process is between 95 and 98%.

There has been no substantial development of this process regarding pyrite treatment but there have been developments in the field of chlorination of complex sulphide minerals (copper, nickel) and adaptations of the process to hydrometallurgical sulphide leaching is known to have been practiced.
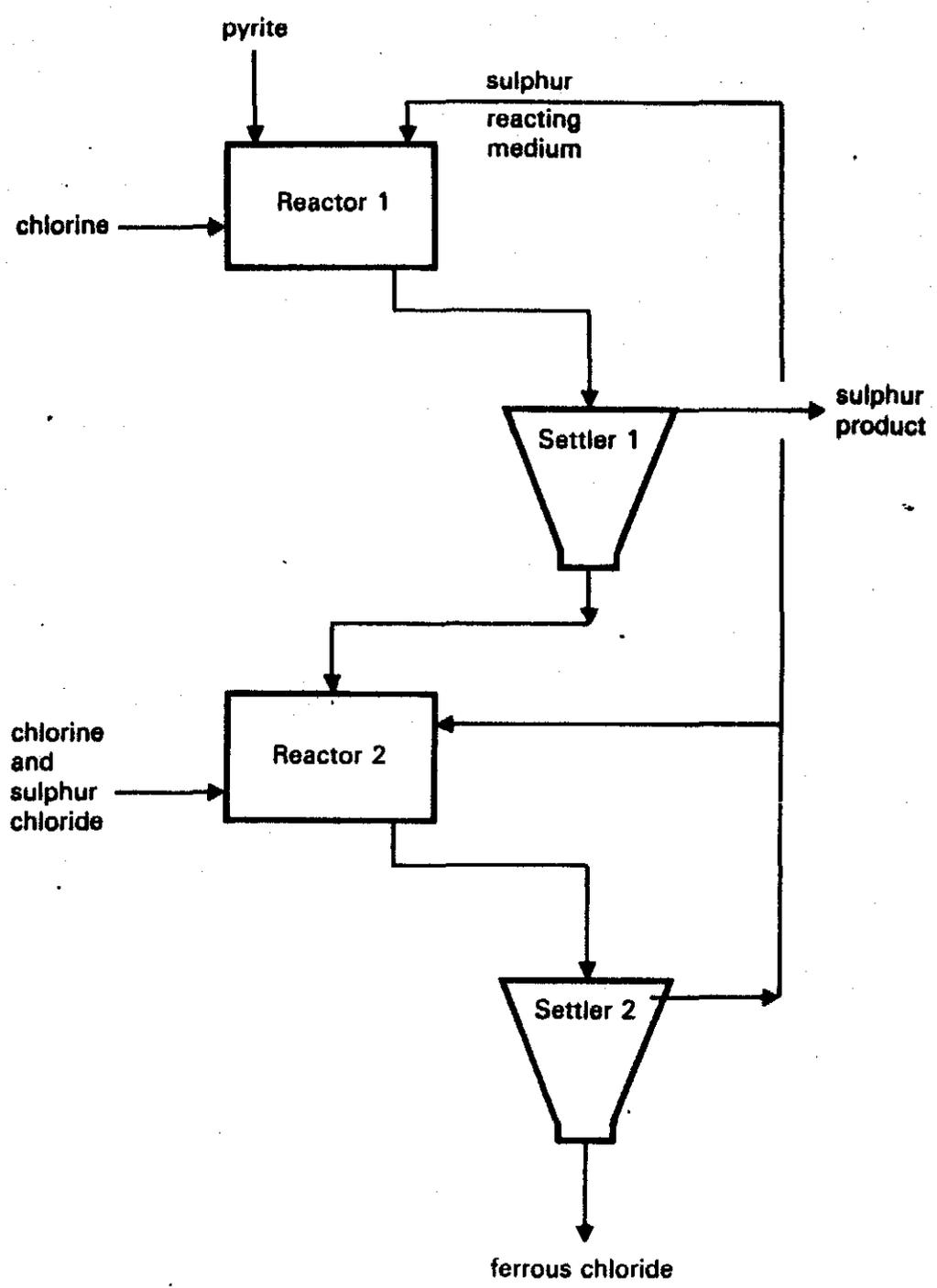
**Fig. 7: The Texasgulf Chlorination Process**

4.      **PROCESS ECONOMICS**

With the exception of the Outokumpu process none of the processes here described have seen full scale commercial operation. Detailed investment and operating cost breakdowns are therefore very difficult to estimate, and this includes the now redundant Outkumpu process. However, during development years, some companies did perform detailed cost estimates and these are updated here to indicate estimated present day costs.

4.1     **The Outokumpu Process**

Without any detailed data regarding the pyrite under consideration, and a knowledge of all the parameters which would make up a process production cost including local prices of utilities and labour, together with the fact that the process was never operated in order to maximise elemental sulphur production, any production cost estimate could be widely inaccurate. However, an overall production cost of around $100 per ton sulphur would be expected.

An indicative capital cost can be estimated, however, on a present day basis, for a plant processing 300,000 tonnes pyrite per annum.

The estimate assumes maximum possible recovery of elemental sulphur i.e. reduction of the pyrite to basic slag for dumping, monosulphide roasting or sulphuric acid production is not included.

Any detailed cost study would require further detailed study in order to perform an accurate calculation.

## Capital Cost Estimate

Plant:      Flash Smelting of Pyrite

Capacity:   300,000 s.t.p.a. Pyrite

Basis:      1984 Instantly Erected

| Item | Cost, US $ |
|---|---|
| Purchased Equipment Cost | |
| Smelter & Oxygen Enrichment plant | 13,000,000 |
| Sulphur Plant | 10,000,000 |
| SUB-TOTAL | 23,000,000 |
| Installation, site preparation, building and ancilliary equipment | 24,150,000 |
| Physical Plant Cost | 47,150,000 · |
| Engineering and Construction | 11,788,000 |
| Contingency | 8,840,000 |
| Offsite and Auxiliaries | 10,167,000 |
| TOTAL FIXED CAPITAL COST | 77,945,000 |
| Working Capital | 7,795,000 |
| TOTAL CAPITAL COST | 85,740,000 |

## 4.2    The Sherrit Gordon Process

The following capital and production cost estimates were calculated in 1967 for a conceptual 500,000 s.t.p.a pyrite processing plant based in Canada.

The total capital cost has been estimated on a present day (1984) basis by assuming a reasonable level of inflation based on British Sulphur's knowledge of plant cost indexes over the period in question.

Production cost estimates have been presented on an estimated present day basis by consideration of the approximate present day prices of production cost items.

All costs, are in U.S. dollars.

### 4.2.1    Capital Cost

#### Basis for capital cost estimate

1.  Battery limit plant costs are calculated as a function of purchased equipment cost..

2.  Off-site facilities for the grass-root plants include:

> Utility Distribution
> Yard Piping
> Land
> Maintenance Shop
> Laboratory and office buildings
> Railway siding and roads
> Fire Protection
> Etc.

3.  Process Development Costs are not included.
4.  Royalties are not included and would be extra.
5.  Capital cost is on an instantly erected basis.

## Capital Cost Estimate

Plant:      Thermal Decomposition of Pyrite
Capacity:   500,000 s.t.p.a. Pyrite
Basis:      1984, Instantly Erected.

| ITEM | COST, U.S. $ |
|---|---|
| **Purchased Equipment Cost** | |
| Concentrate Handling and Storage | 211,000 |
| Drying Station | 421,000 |
| Thermal Decomposition System | 1,143,000 |
| Dust Removal and Gas Cooling | 722,000 |
| Sulphur Conversion and As Removal | 1,113,000 |
| Sulphur Handling and Storage | 301,000 |
| SUB TOTAL | 3,911,000 |
| Installation Cost at 25% of P.E. Cost | 978,000 |
| Piping Cost at 20% of P.E.Cost | 782,000 |
| Instrumentation Cost at 12% of P.E. Cost | 469,000 |
| Electricals Cost at 10% of P.E. Cost | 391,000 |
| Insulation and Painting Cost at 8% of P.E. Cost | 313,000 |
| Site Preparation and Building Cost at 30% of P.E. Cost | 1,173,000 |
| Physical Plant Cost | 8,017,000 |
| Engineering and Construction Cost at 25% of Physical Plant Cost | 2,004,000 |
| Direct Plant Cost | 10,021,000 |
| Contingency at 15% of Direct Plant Cost | 1,503,000 |
| Battery Limit Plant Cost | 11,524,000 |
| Off-site and Auxiliaries at 15% of Battery Limit Cost | 1,729,000 |
| TOTAL FIXED CAPITAL COST | 13,253,000 |
| Working Capital at 10% of Fixed Capital Cost | 1,325,000 |
| **TOTAL CAPITAL COST** | **14,578,000** |

## Capital Cost Estimate

**Plant:** Aqueous Oxidation of 'Dirty' Iron Monosulphide
**Capacity:** 500,000 S.T.P.A. Pyrite
**Basis:** 1984, Instantly Erected

| ITEM | COST, U.S.$ |
|---|---|
| Purchased Equipment Cost | |
| Slurry Handling and Pumping | 650,000 |
| Aqueous Oxidation Autoclave | 1,525,000 |
| Iron Dissolution and L/S Separation | 1,398,000 |
| Sulphur Granulation and Hot Filtration | 511,000 |
| Metal Stripping and Sulphide Filtration | 541,000 |
| Hydrolysis | 2,917,000 |
| Hydrated Iron Oxide Separation | 1,119,000 |
| Sulphur Handling and Storage | 3,641,000 |
| Recycle Residue and Solution Handling | 559,000 |
| SUB-TOTAL | 9,581,000 |
| Installation at 25% of P.E. Cost | 2,395,000 |
| Piping at 20% of P.E. Cost | 1,946,000 |
| Instrumentation at 12% of P.E. Cost | 1,150,000 |
| Electricals at 10% of P.E. Cost | 958,000 |
| Insulation and Painting at 8% of P.E. Cost | 766,000 |
| Site Preparation and Buildings at 30% of P.E. Cost | 2,874,000 |
| Physical Plant Cost | 19,640,000 |
| Engineering and Construction at 25% | 4,910,000 |
| Direct Plant Cost | 24,550,000 |
| Contingency at 15% of Direct Plant Cost | 3,683,000 |
| Battery Limit Plant Cost | 28,233,000 |
| Air Compressor Unit (95,000 SCFM at 850 psia, 38,000 HP) | 16,000,000 |
| Calcination Plant (1,200 TPD) | 10,526,000 |
| Iron Ore Reduction Plant (750 TPD) | 14,662,000 |
| Total Battery Limit Plant Cost | 69,421,000 |
| Off-Sites at 15% of Battery Limit Cost | 10,413,000 |
| | |
| TOTAL FIXED CAPITAL COST | 79,834,000 |
| Working Capital at 10% Fixed Capital | 7,983,000 |
| | |
| **TOTAL CAPITAL COST** | 87,817,000 |
| | |
| **TOTAL CAPITAL COST OF PROJECT:** | **US$ 102,395,000** |

### 4.2.2 Production Cost

**Basis for Direct Production Cost Estimate**

1. Labour (Including overheads)

   Average:          US$40,000/man year

2. Utilities

   | | | |
   |---|---|---|
   | Power: | 0.04 | $/kWh |
   | Natural Gas: | 3.3 | $/million Btu |
   | Fuel Oil: | 5.0 | $/million Btu |
   | Cooling Water: | 0.01 | $/m$^3$ |
   | Process Water: | 0.1 | $/m$^3$ |
   | Boiler Feed Water: | 0.1 | $/m$^3$ |
   | Surfactant: | 1.0 | $/lb |
   | Filter Aid: | 4.0 | $/lb |

3. Maintenance Materials

   Thermal Decomposition:   3% of Fixed Capital Cost per annum
   Aqueous Oxidation:       4% of Fixed Capital Cost per annum

4. Property Taxes and Insurance: 1.25% of Fixed Capital Cost per annum

## Direct Production Cost Estimate

Plant:        Thermal Decomposition of Pyrite

Capacity:     500,000 S.T.P.A. Pyrite

Operation:    330 days per annum

Basis:        1984

| ITEM | UNIT QUANTITY | ANNUAL COST US$ |
|---|---|---|
| Labour | 5 men/shift | 200,000 |
| Power | 315 kW | 100,000 |
| Natural Gas | 17.3 million Btu/h | 450,000 |
| Fuel Oil | 137.5 million Btu/h | 5,445,000 |
| Boiler Feed Water | 13.6 m$^3$/h | 11,000 |
| Maintenance Materials | @ 3% of fixed capital | 398,000 |
| Taxes and Insurance | @ 1.25% of fixed capital | 166,000 |
| | sub-total | 6,770,000 |
| Contingency | @ 10% of sub-total | 677,000 |
| | Total Direct Annual Production Cost | 7,447,000 |
| | Cost per ton pyrite | $15.00 |

## Direct Production Cost Estimate

**Plant:** Aqueous Oxidation of 'Dirty' Iron Monosulphide

**Capacity:** 500,000 s.t.p.a. by pyrite

**Operation:** 330 days per annum

**Basis:** 1984

| ITEM | UNIT QUANTITY | ANNUAL COST US$ |
|---|---|---|
| Labour | 7 Men shift | 280,000 |
| Power | 1,260 kW | 399,000 |
| Natural Gas (for Air Compressor) | 316 million Btu/h | 8,259,000 |
| Boiler Feedwater | 19 m$^3$/h | 15,000 |
| Cooling Water | 4,910 m$^3$/h | 389,000 |
| Process Water | 191 m$^3$/h | 137,000 |
| Surfactant | 120 lb/day | 40,000 |
| Filter Aid | 160 lb/day | 211,000 |
| Recycling Iron & Sulphur | (Fe and S$^o$ charged at selling price) | 4,224,000 |
| Maintenance Materials | @ 4% of fixed capital | 3,193,000 |
| Insurance and Taxes | @ 1.25% of fixed capital | 998,000 |
| | Sub Total | 18,145,000 |
| Contingency | @ 10% of sub total | 1,815,000 |
| Calcination Plant | ($14.0/ton, 1,200 TPD) | 5,544,000 |
| Iron Ore Reduction Plant | ($61/ton, 700 TPD) | 14,091,000 |
| | Total Direct Annual Production Cost | 39,595,000 |
| | Cost per ton pyrite | **$79.00** |

**Total Production Cost Per Ton Pyrite**          **US $94.00**

On a present day basis, the economics would be much more streamlined with higher energy efficiencies and less emphasis on the use of expensive fuel oil (when the original calculations were performed in 1967 the cost of fuel oil was 0.4 C$/million BTU), but the process would still be very expensive to operate. In addition, the process includes the production of high purity iron powder which, if not required, would obviously reduce capital and operating costs. Based on the rejection of the iron compounds, instead of treatment and recovery, this would reduce the direct production costs by around US $20 million per annum, thus yielding a total production cost of around $50/ton pyrite.

In terms of sulphur, assuming a pyrite containing 50% S and a claimed recovery of 91%, the direct production cost per ton of sulphur would be around US $110/ton S.

Total capital investment would be of the order of US $70 million.

For a plant processing 300,00 s.t.p.a. pyrite the total capital investment would be approximately US $ 52 million.

### 4.3    The Dorr-Oliver Process

A production cost estimate for the production of elemental sulphur from pyrites using this process was calculated and presented in 1967. The following production cost estimate is an estimated update of this production cost using the same cost bases as for the Sherrit Gordon process case in Section 4.2.

The total capital cost of the process is estimated to be around US $50 million for a plant producing 135,000 STPA sulphur from pyrite with a sulphur content of about 50%. This is based on the estimated capital cost of the same plant in 1966-67 and includes a reasonable level of inflation to bring the cost up to a present day basis.

On a similar basis, the approximate cost of a plant producing 300,000 s.t.p.a. pyrite would be approximately US $ 53 million.

Production Cost Estimate

Plant:   Elemental Sulphur from Pyrite (100% Recovery Process)

Capacity:  135,000 S.T.P.A. Sulphur

Operation:  330 days per annum

Basis:  1984

| Item | Unit Consumption Per Ton Sulphur | Unit Cost Per Ton Sulphur, US$ |
|------|----------------------------------|--------------------------------|
| **Direct Costs** | | |
| Labour (inc. overheads) | 24 personnel @ $40,000 p.a. | 7.11 |
| Utilities | | |
| Electric Power | 73 kWh | 2.92 |
| Fuel Oil | 9.34 mm BTU | 46.70 |
| Boiler Feedwater | 3.80 m$^3$ | 0.38 |
| Cooling Water | 24.2 m$^3$ | 0.24 |
| Maintenance Materials | @ 3% of total capital cost p.a. | 11.11 |
| Total Direct Costs | | 68.46 |
| **Indirect Costs** | @ 16.6% of total capital cost p.a. | 61.48 |
| **By Product Steam (Credit)** | (3,480 lb L.P. steam) | (22.0) |
| **Raw Material** | 2.35 ton pyrite (50% S), 85% overall recovery | Assume Free to plant. |
| Total Production Cost: | | $107.94/ton S |

## 4.4 The Sherritt Gordon Hydrometallurgical Process

It is virtually impossible to estimate a cost for this process as applied to the treatment of pyrite in this way.

The published capital cost figure for the Cominco zinc sulphide pressure leach process in Canada in 1980 was C$23 million for a plant processing 400 S.T.P.D. zinc sulphide concentrate containing approximately 50% zinc.

Pressure leaching of a concentrate containing cobalt sulphides where the cobalt concentration is only up to 0.22% would require large throughputs of material. As has been stated previously, the direct leaching of pyrite to produce elemental sulphur and iron is not possible without the addition of a thermal treatment step.

If, hypothetically, we assumed the addition of a thermal decomposition plant similar to the Sherritt process discussed earlier, and assumed the cost of the iron monosulphide leaching plant would be equivalent to a similar size zinc sulphide leaching plant, the total capital cost would be approximately as follows for a 300,000 STPA pyrite treatment plant.

| | | |
|---|---|---|
| Thermal Decomposition plant | : | US $10,000,000 |
| Oxygen enrichment plant | : | US $15,000,000 |
| Pressure leaching plant | : | US $30,000,000 |
| **TOTAL** | : | **US $55,000,000** |

## References and Further Reading

1.  'Outokumpu Process for the Production of Elemental Sulphur from Pyrites'.
    Sulphur 50 (February 1964) 33-38.

2.  'Outokumpu adds second catalyzer to raise pyrite-to-sulphur converstion to 91 percent'.
    World Mining (March 1967) 42-46.

3.  Mehta, B.R. and O'Kane, P.T.:
    'Economics of Iron and Elemental Sulphur Recovery from Pyrite using Low Temperature Decomposition and Aqueous Oxidation'.
    C.I.M. Conference of Metallugists, Kingston, Ont.
    (August 28-30 1967).

4.  Graves, T. and Heath T.D.:
    'Sulphur Dioxide and Sulphur from FluoSolids Systems'
    National Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers, Los Angeles, Calif. (Feb 21, 1967).

5.  Bolton, G.L.: 'Sulphur Production By Pressure Leaching of Metal Sulphides'
    Sulphur Development Institute of Canada, Government of Alberta and The British Sulphur Corporation Conference - Sulphur '81.
    Calgary, Alberta (May 25-28, 1981).

6.  Kunda, W et al.:  'Recovery of Elemental Sulphur from Sulphur Bearing Minerals' Canadian Sulphur Symposium, Calgary (May 30-31, 1974).

7.  United Kingdom Patent Specification
    Number 805,922
    Inventor: Cyril Thomas Hill of Texas Gulf Sulphur Company
    'Improvements in or relating to Decomposition of Sulfide Minerals'.

APPENDIX C

M 1588

### DEPARTMENT OF MINES—TASMANIA

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23rd May 1984

Mr. S. R. M. Harvey,
C/- Elisna/Aberdare,
Box 2211
Princeton N.J. 08540    U.S.A.

R797

Dear Sir,

     Please find enclosed a copy of a preliminary report on the coarser fractions of the King River delta sized fractions.

Yours faithfully,

(H. K. Wellington)
Chief Chemist & Metallurgist

DEPARTMENT OF MINES

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ROSNY PARK
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Chief Chemist and Metallurgist,
Department of Mines,
LAUNCESTON

R797 - MACQUARIE HARBOUR - KING RIVER DELTA SEDIMENTS

Mineralogy of sized samples (>38µ) - Preliminary report

All of the sized fractions submitted were examined briefly by optical
means and the following assemblage recorded:

pyrite, chalcopyrite, quartz, sericite, magnetite, haematite, limonite,
siderite, barite, monazite, zircon, rutile.

No gold and only 1 grain of cassiterite were recorded at this point.

Two fractions were subject to further treatment by TBrE gravity separation
and magnetic separation (Cooke).

(a)   +38µ

Total weight 82.29 g

wt. taken      43.53 g

wt. heavy fraction 33.65 g                          XRD results (<5%)

| | | |
|---|---|---|
| Magnetics (hand magnet) | 0.45 g | - magnetite |
| Magnetic at 0.2A | 2.46 g | - chlorite, haematite |
| Magnetic at 0.5A | 2.67 g | - chlorite, haematite to pyrite, sericite composites |
| Magnetic at 1.2A | 2.51 g | - chlorite, sericite, zircon rutile |
| Nonmag. at 1.2A | 25.53 g | pyrite concentrate |

The pyrite concentrate was further examined by electron microprobe
after mounting (with an inert filler of graphite) in epoxy resin
(see Jackson et al., Proc. Australas. Inst. Min. Metall. No. 289,
1984, p. 93).

The microprobe mounts showed pyrite and chalcopyrite as the only sulphide phases under reflected light and this was confirmed by microprobe analysis. The pyrite fragments are subangular, free of inclusions - photo*1 shows a fragment 65 x 25μ. Photo 2 shows a fragment of chalcopyrite, also free of inclusions, and measuring 50 x 25μ. This mount also shows a fragment of bismuthinite 15 x 10μ and a rare earth-bearing phase with an etched structure (Photo 3 - 16 mm diameter fragment). Other heavy minerals are zircon, rutile and monazite. The cobalt content of these representative pyrite grains was just at, or below, the detection limit (0.2% = 2000 g/ton). The typical X-ray energy spectrum (photo 4) for chalcopyrite (photo 2) was recorded for later comparison with possible included phases.

The non magnetic fraction was examined as a grain mount on double sided tape (photo 5, X120 - av. grain diameter 60μ). No inclusions or intergrowths were seen on magnifications up to 1000X - i.e. on the scale of a few microns, and eight typical fragments were checked for absence of copper on the EDAX spectrum. Barite and sericite are readily identified in this fraction. The sericite is often a composite, even at this size, and contains sufficient pyrite to appear in the MeI "sinks".

(b) The 'magnetic at 0.2A' fraction also was examined as a grain mount. Phases identified included chlorite, haematite, magnetite with low $TiO_2$, pyrite and chalcopyrite in a haematite-silicate-sulphide intergrowth. The areas of chalcopyrite in this intergrowth are only 6 x 4μ in size (photo 6) and copper is only recognised as a minor peak on the broad area scan EDAX spectrum (photo 7).

(c) +150μ fraction

| | | | |
|---|---|---|---|
| Total weight | 104.41 g | | |
| Wt. taken | 53.26 g | | |
| Wt. heavies | 2.97 g (TBrE) | | XRD results (>5%) |
| Magnetics | 0.71 g | | magnetite |
| Magnetic at 0.3A | 1.28 g | | chlorite, sericite |
| Magnetic at 0.7A | 0.73 g | | "          " |
| Magnetic at 1.2A | 0.18 g | | "          " |
| Non magnetite at 1.2A | 0.74 g | | pyrite concentrate |

The nonmagnetic fraction was further purified by MeI flotation and the heavy fraction mounted in epoxy as previously described.

The major component is pyrite, some as composite grains with quartz and haematite, and one pyrite grain with inclusions of rutile. In general, the pyrite at this size range is clearly separated and uniform in appearance. A typical haematite fragment (X600) is shown in photo 8 and a composite grain of sericite, monazite and apatite is shown in photo 9 (X500) with the EDAX spectrum of the monazite as photo 10.

*Photographs are secondary electron images; in general an increase in brightness means an increase in average atomic no. - i.e. heavier elements appear brighter.

Other composite fragments include an unidentified rare earth-bearing phase with K and Si. This is shown in photo 11 (X1000, a light coloured grain of 45µ diameter with irregular outline) with EDAX spectrum as photo 12 (Note lack of Ce compared to monazite, photo 10).

Other non-silicate minerals identified include barite, rutile (in quartz) and apatite. A fragment of presumed glassy slag (photo 13) containing silica ∿63%, iron ∿22% and sodium ∿14% was examined for copper content but none was recorded at a detection limit of 0.2%.

Chalcopyrite is present as separate grains (Photo14 X150, size 180µ x 70µ) but more commonly as small grains in chlorite, phosphate or rutile matrices. Photo 15 shows a chalcopyrite grain (40µ x 24µ) in a rutile/sericite matrix, photo 16, a small rectangular crystal of about 16µ edge in a sericite, rutile, barite, pyrite matrix and photo 17 a small fragment of chalcopyrite (16µ x 7µ) in a sericite/ chlorite matrix. An unusual occurrence of chalcopyrite in association with $Al_2SiO_5$ (?andalusite) and an aluminium phosphate with rare earth content of ∿8% is shown in photo 18.

Four analyses of pyrite, two of chalcopyrite and analyses other non sulphide phases are listed in accompaning tables. The pyrite analyses show no evidence of copper as an inclusion or exsolved phase, similarly the chalcopyrite is essentially stochiometric and shows no evidence of copper sulphide phases. The small but measurable amount of Co recorded in two of the pyrite analyses supports the conclusion that cobalt is associated with the pyrite and does not occur as a separate phase.

The question of low copper recovery in flotation is only able to be explained as due to a considerable amount of chalcopyrite as "locked" small particles in a phyllosilicate-rutile-barite matrix. Although a small amount of copper-bearing silicate was seen in a preliminary scan, the only confirmed slag particle contained no detectable copper (less than 2000 g/ton).

Comments

There is no evidence in this sample of the framboidal, secondary sulphide phases required to substantiate this deposit as a authentic authigenic "black shale" deposit. The mineral assemblage is that of the hydrothermal mineralised hinterland drained by the King River. The cobalt content of the pyrite is essentially that of Mt Lyell pyrite and does not require a secondary origin. There is no evidence of gold or cassiterite in the +38µ fractions, however, the sizing analysis and Annual report 83-2061-EL2/74 suggest that examination of the C/S fractions may be required. As the economics of recovery in this size range pose substantial problems, the mineralogical work has stopped at this point and would require additional funds for microprobe operation.

The copper content is partly derived from liberated grains of chalcopyrite with the remainder as smaller grains in the phyllosilicate (sericite + chlorite) - phosphate-barite matrix. This would provide problems in flotation. No evidence for the pyrite-chalcopyrite intergrowths so typical of the West Lyell and Crown Lyell area were seen. The conclusion of Mineral Deposits Ltd. that some "copper is not with the sulfur minerals to a large extent" is substantiated, along with the comment of Robertson Research that "gravity concentration effectively recovers the pyrite, but not the copper" (quotes from 82-1717 - Macquarie Harbour Tailings Study EL 2/74, Molycorp Inc.). Secondary copper minerals such as chalcocite, covellite and bornite were not identified by microprobe although over 200 sulphide grains were closely examined during the course of this study.

4.

It is likely that further work on the C/S fractions will be required
to adequately investigate the reported occurrence of secondary
copper sulphides and cassiterite/gold.  With the implementation of the
Jackson *et al*, 1984, mounting technique, it is possible that these
questions can be resolved if the chalcocite etc. identified optically
in ultrafine particles by Robertson Research can be accurately marked
for probe analysis.  Chlorite and sericite (phengite) analyses are
essentially identical to those from the Mt. Lyell area and are
consistent with hydrothermal alteration assemblages.

(D.C. Green)

Chalcopyrite analyses    (microprobe 20kv, Edax  C.S.I.R.O.  Min-36)

| | | |
|---|---|---|
| Cu % | 34.67 | 34.29 |
| Fe % | 31.46 | 31.50 |
| S % | 34.72 | 34.54 |
| TOTAL % | 100.85 | 100.33 |

No of atoms on basis of total atoms  =  1.00

| | | |
|---|---|---|
| Cu | 0.249 | 0.247 |
| Fe | 0.257 | 0.259 |
| S | 0.494 | 0.494 |

Chlorite analysis  (microprobe 15kv, Edax – silicate)

No of atoms on basis of total O = 28

| | | | |
|---|---|---|---|
| $SiO_2$ % | 23.37 | Si = | 5.214 |
| $Al_2O_3$ % | 21.27 | Al = | 5.592 |
| FeO % | 27.50 | Fe = | 5.131 |
| MgO | 12.18 | Mg = | 4.051 |
| | 84.33 | | 19.988 |

Sericite(phengite) analysis        (microprobe 15kv, Edax – silicates)

No of atoms on basis of total O = 22

| | | | |
|---|---|---|---|
| $SiO_2$ % | 42.57 | Si = | 6.246 |
| $TiO_2$ % | 0.35 | Ti = | 0.039 |
| $Al_2O_3$ % | 28.28 | Al = | 4.891 |
| FeO % | 6.36 | Fe = | 0.780 |
| MgO % | 2.27 | Mg = | 0.496 |
| $K_2O$ % | 8.72 | K = | 1.633 |
| TOTAL % | 88.55 | | 14.085 |

Pyrite analyses   (microprobe 20kv,   Edax   CSIRO Min – 36)

| | | | | |
|---|---|---|---|---|
| Fe % | 46.88 | 47.24 | 47.22 | 46.80 |
| Ni % | 0.21 | n.d. | n.d. | n.d. |
| Co % | ∠0.51 | n.d. | < 0.42 | n.d. |
| S % | 53.60 | 53.69 | 54.61 | 54.42 |
| TOTAL % | 101.20 | 100.93 | 102.25 | 101.22 |

*n.d.*
*not determined*
*but below det lt.*
*u < 2*

No. of atoms on basis of total atoms   =   1.0

| | | | | |
|---|---|---|---|---|
| Fe | 0.333 | 0.335 | 0.332 | 0.331 |
| Ni | 0,001 | – | – | – |
| Co | 0.003 | – | 0.003 | – |
| S | 0.663 | 0.665 | 0.665 | 0.669 |

Aluminosilicate phase   (microprobe 15kv, Edax – silicate)

| | | | |
|---|---|---|---|
| $S_1O_2$ | 38.53 | Si = | 1.04 |
| $al_2O_3$ | 61.47 | Al = | 1.95 |
| | 100.00 | | 2.99 |

266072

1

pyrite

(1000 x)

2

chalcopyrite
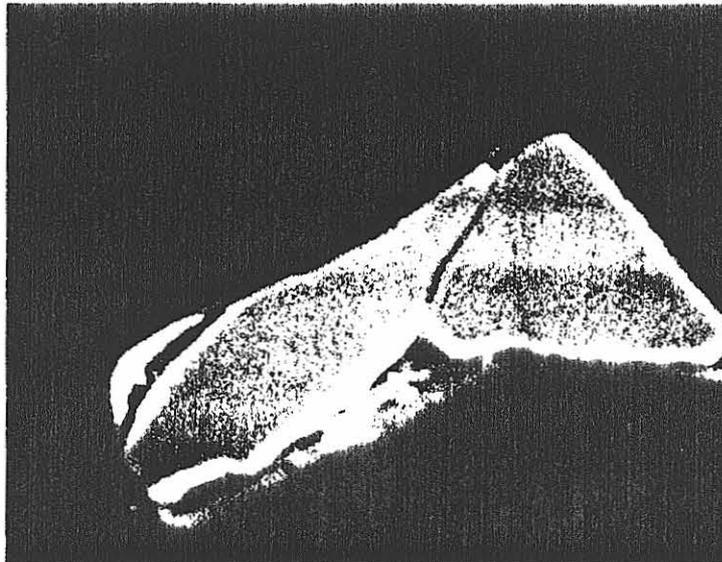
(x1500)

3

R E E phase

(x1500)

266073



EDAr
spectrum

Cu   S          Fe   Cu



5
grain
mount
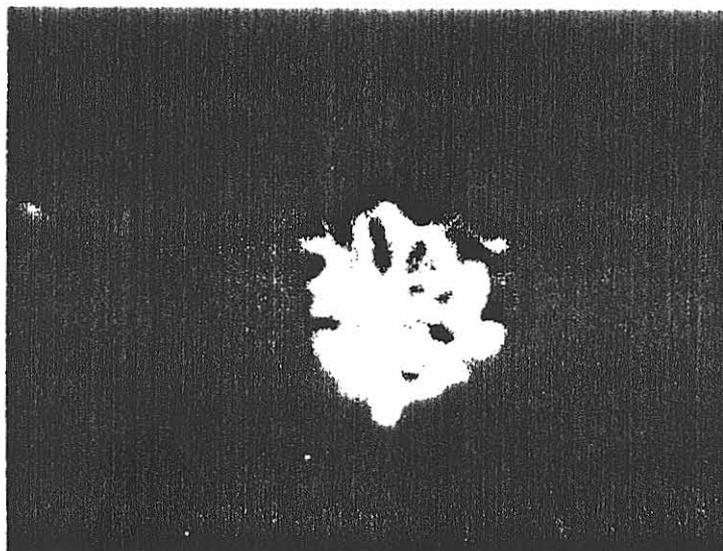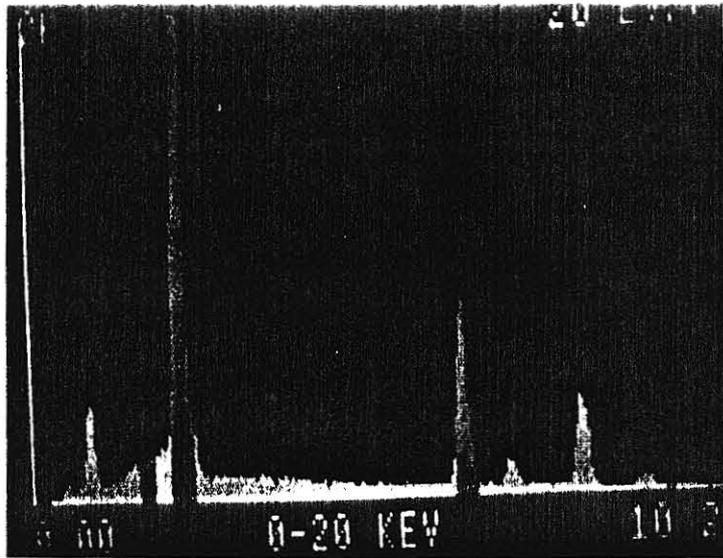
(×120)
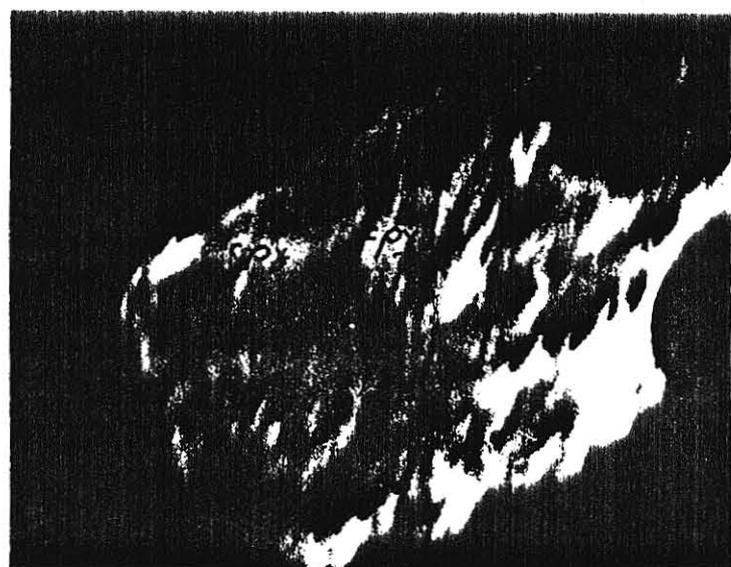


6
Composite
grain with
chalcopyrite

(×2000)

073

266074



0-20 KEV

AlSiS ? Ti FeFe Cu
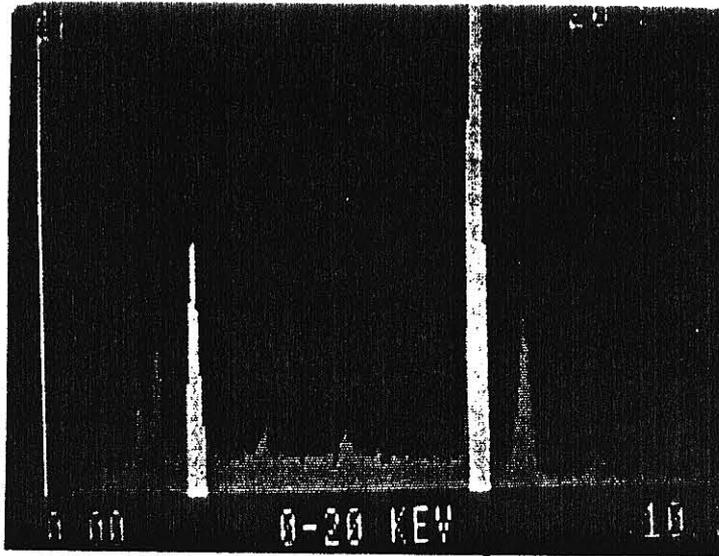
7

EDAX
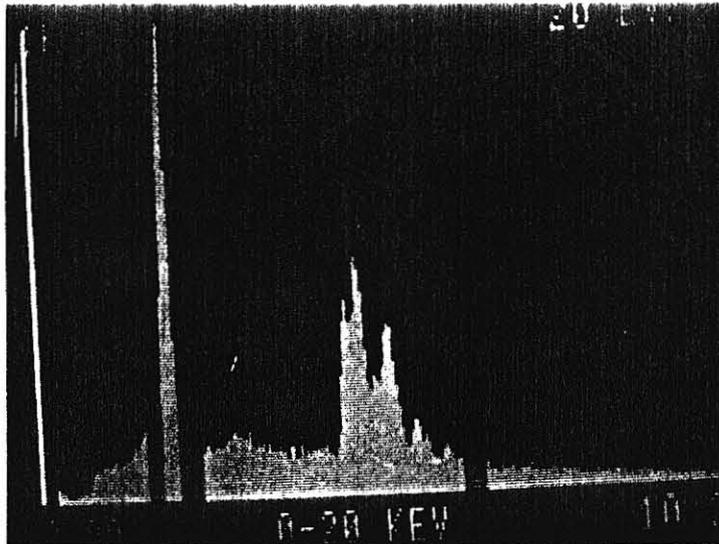Spectrum
(broad area
scan No6)



8

Haematite

(×600)



C11
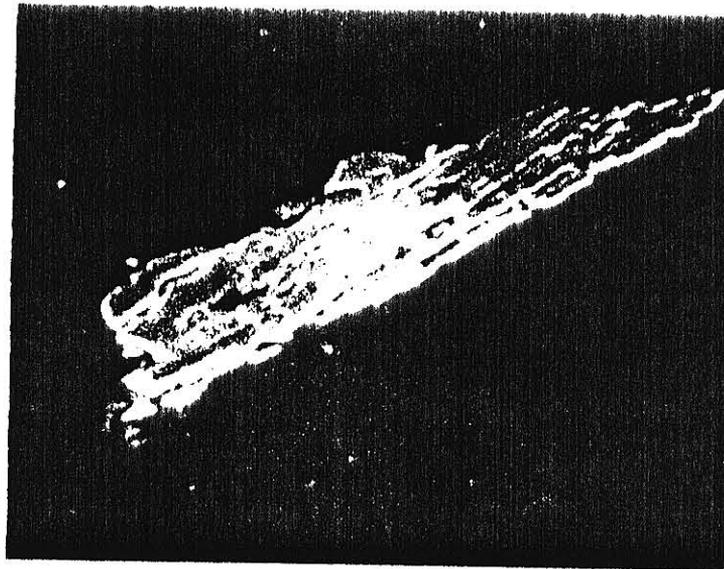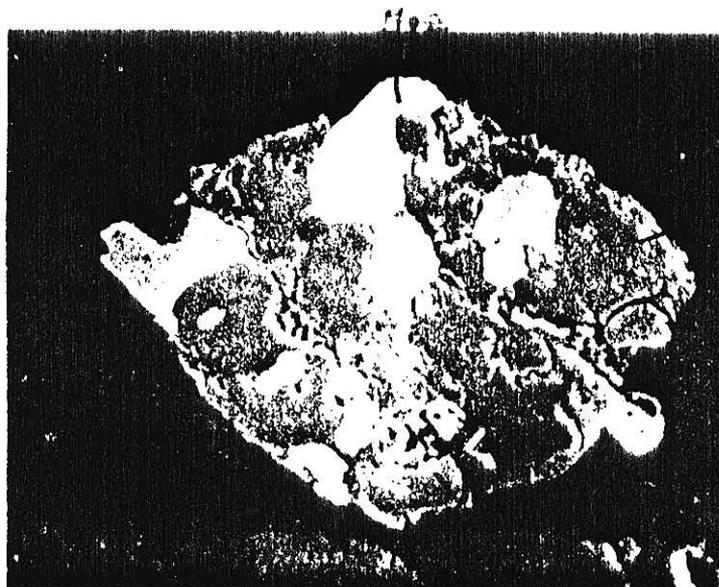
seric

9

Composite
grain -
monazite,
apatite,
sericite

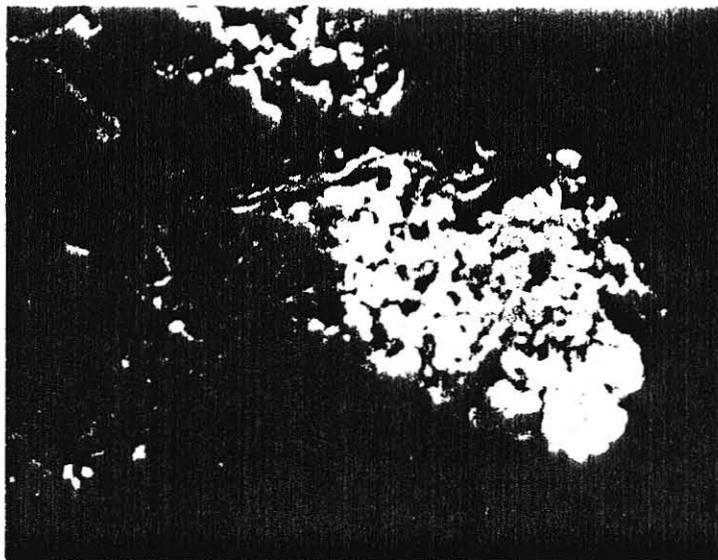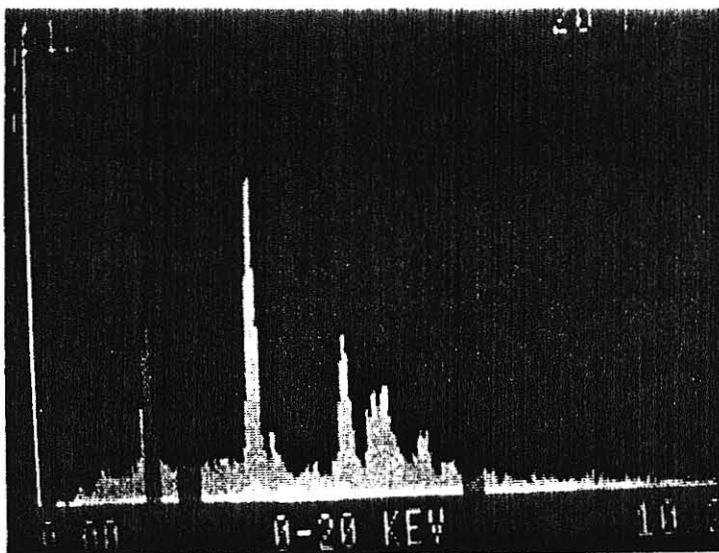(×500)

266075



0-20 KEV

P          LaCe Nd ?Sm

Edax
spectrum
monazite
(from 9)



11

REE + K + Si
phase
(light coloured)
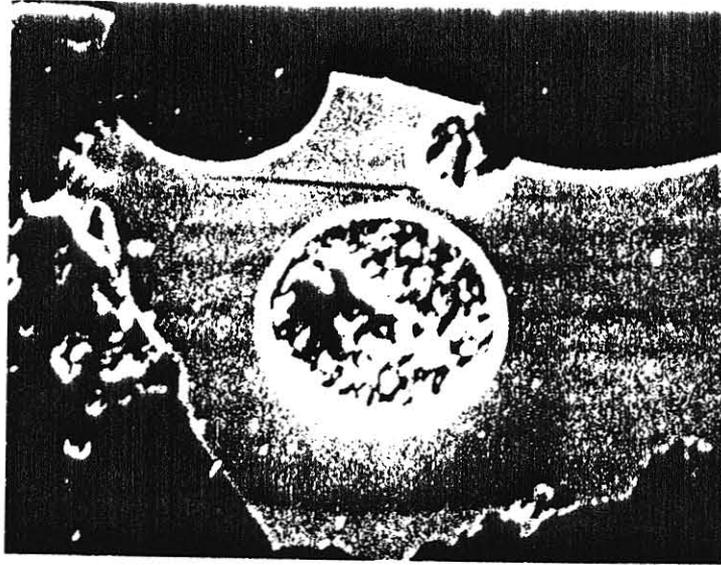
(×1000)



0-20 KEV

Si     K     La P Nd ?Gd

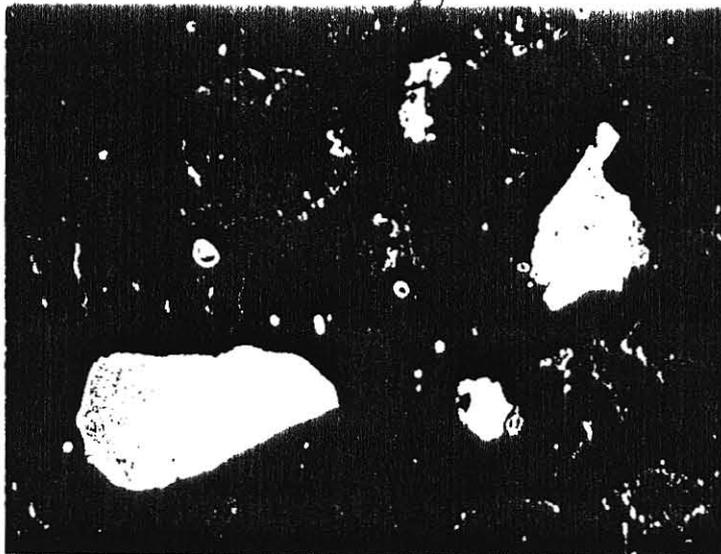12

Edax
spectrum
of 11
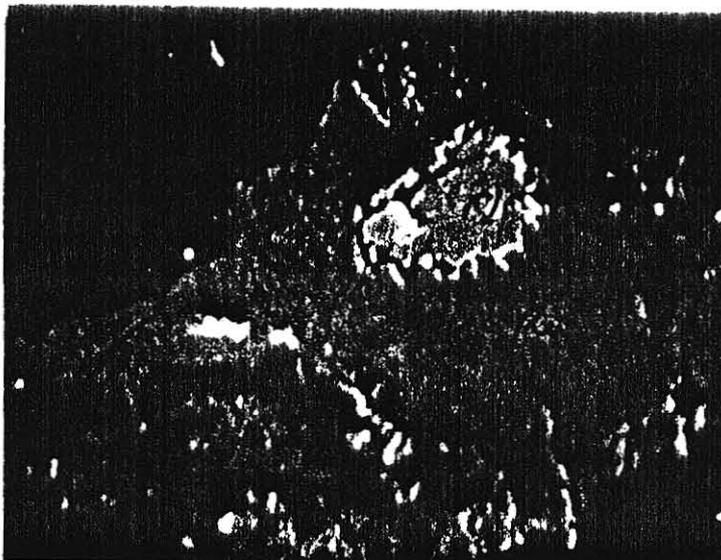
C12

266076

13

Glassy
slag

(×600)



14

(×150)



Chalco                    Py

15

Chalcopyrite

(×600)
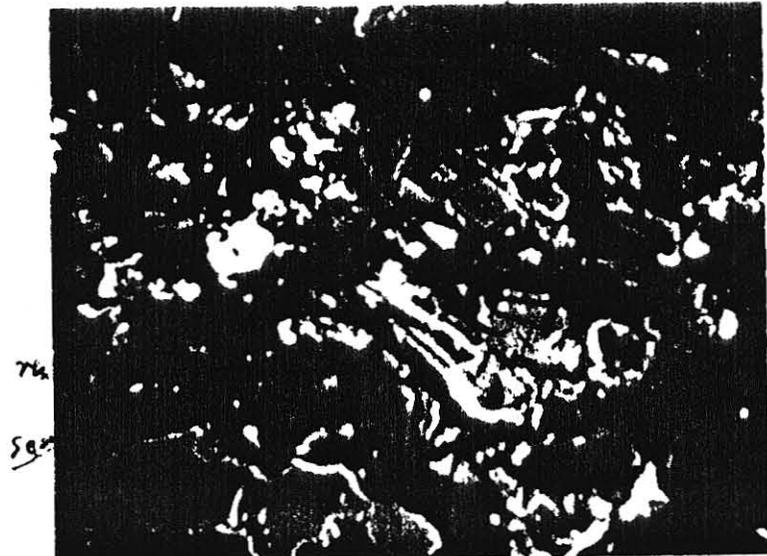
266077



16

chalcopyrite
in sericite,
barite, rutile
pyrite
matrix

(×500)



17

Chalcopyrite
in chlorite-
sericite
matrix

(×500)



18

Chalcopyrite
in ?andalusite
Al-phosphate
matrix

(×600)

C14

APPENDIX D

amdel

27 June 1984

GS 6/625/0

Aberdare Incorporated
Box 2211
PRINCETON      NEW JERSEY     08540
USA

Attention:  Mr R. Harvey

REPORT GS 6110/84

| | |
|---|---|
| YOUR REFERENCE: | Letter dated 15 October 1983 |
| ODENTIFICATION: | Drum A |
| MATERIAL: | Deltaic sand |
| LOCALITY: | King River Delta, Tasmania |
| DATE RECEIVED: | 21 October 1983 |
| WORK REQUIRED: | Heavy liquid separation and gold analyses |

Investigation and report by:  Dr Keith Henley

Chief - Geological Services Section:  Dr Keith J. Henley

for Dr William G. Spencer
     Manager, Mineral and Materials Sciences Division

cap

Di

## GOLD IN KING RIVER DELTA SEDIMENTS

### 1. INTRODUCTION

Following correspondence between R. Harvey and K. Henley (AMDEL), on further work on King River Delta material stored at AMDEL, a programme of testwork was agreed. The objective of the testwork was to quantify the proportion of mercury-soluble gold in the delta material. The programme was unfortunately delayed for some months because the relevant samples could not be located at AMDEL. However, they were eventually found and this report gives the results of the investigation.

### 2. PROCEDURE

Two aliquots of ~300 g were riffled out of material from Drum A and separated statically in tetrabromoethane (sp.gr. 2.96); the >2.96 sp.gr. product was then separated centrifugally in Clerici's Solution (sp.gr. 4.3). The >2.96 and 2.96-4.3 sp.gr. products were pulverised and ~10 g and ~25 g aliquots riffled out for Au determination by AAS (Code C3/2) and fire-assay (Code K4/2) respectively. The whole of each of the >4.3 sp.gr. products was analysed for mercury-soluble and mercury-insoluble gold.

### 3. RESULTS

The distribution of weight and gold is as follows:

| Sp.Gr. | Wt % | | Au Assay, ppm | | Au Distribution, % | |
|---|---|---|---|---|---|---|
| | A | B | A | B | A | B |
| <2.96 | 84.48 | 83.79 | 0.15 | 0.03 | 67.8 | 23.9 |
| 2.96-4.3 | 9.76 | 10.28 | 0.15 | 0.19 | 7.8 | 15.7 |
| >4.3 | 5.76 | 5.93 | 0.79 | 1.02 | 24.4 | 57.6 |
| Hg-soluble | | | (0.05) | (0.35) | (1.5) | (19.8) |
| Hg-insoluble | | | (0.74) | (0.67) | (22.9) | (37.8) |
| Total | 100.0 | 100.0 | (0.19) | (0.11) | 100.0 | 100.0 |

The two aliquots contain 0.1-0.2 ppm gold of which <20% is mercury-soluble. The similarity in values for the mercury-insoluble content of the two >4.3 sp.gr. products (0.74 and 0.67 ppm) suggests that about 0.7 ppm Au is locked up in pyrite - probably in solid solution.

The AAS gold values of the <2.96 and 2.96-4.3 sp.gr. products are as follows:

| Sp.Gr. | A | B |
|---|---|---|
| <2.96 | 0.38 | 0.08 |
| 2.96-4.3 | 0.06 | 0.08 |

These values differ slightly for the fire-assay values but the differences are not considered significant.

APPENDIX E

Table 2 King River Delta sediment: Calculated head values
Elisna's values recalculated from elemental contents shown in Mines' Report 797

| | Ba % | Sn ppm | Cu ppm | Co ppm | Pb ppm | Zn ppm | As ppm | Bi ppm | Au ppm | S % |
|---|---|---|---|---|---|---|---|---|---|---|
| Report 797 values | 0.42 | 50 | 1040 | 64 | 100 | 216 | 21 | 4 | 0.1 | 3.65 |
| Elisna's values | 0.42 | 50 | 1232 | 64 | 101 | 216 | ~16? | ~5? | ~0.12 | 3.64 |

Table 3 King River Delta sediment: Elemental distribution in weight percent
Derived from elemental contents shown in Mines' Report 797

| Fraction, microns | Mass, % | Ba | Sn | Cu | Co | Pb | Zn | As | Bi | Au | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| + 2,360 | Trace | | | | | | | | | | |
| + 1,180 | 0.1 | 0.21 | 14.87 | 0.39 | 0.15 | 1.46 | 0.96 | 1.66 | 0.57 | | 0.28 |
| + 600 | 0.2 | | | | | | | | | | |
| + 300 | 3.7 | 1.85 | 2.27 | 4.20 | 1.03 | 2.61 | 4.10 | ~ 2.29 | ~ 3.54 | | 0.93 |
| + 150 | 52.1 | 32.33 | 17.56 | 50.64 | 13.73 | 26.93 | 38.51 | ~ 16.13 | ~ 19.92 | | 11.28 |
| + 75 | 27.3 | 37.80 | 8.12 | 19.90 | 44.43 | 18.18 | 23.96 | 37.20 | ~ 15.65 | | 40.69 |
| + 38 | 5.4 | 14.18 | 2.46 | 5.25 | 29.30 | 3.76 | 5.24 | 17.06 | ~ 7.22 | | 25.89 |
| C/S 1 | 0.3 | 1.22 | 3.03 | 1.14 | 3.72 | 0.63 | 0.28 | 2.79 | 2.12 | ~100 | 3.02 |
| 2 | 0.3 | 0.77 | 2.74 | 1.12 | 1.58 | 0.39 | 0.60 | 1.06 | 1.20 | | 1.35 |
| 3 | 0.8 | 1.09 | 4.12 | 2.14 | 1.86 | 0.83 | 1.44 | 2.43 | 3.21 | | 1.90 |
| 4 | 0.5 | 0.67 | 3.60 | 1.30 | 0.85 | 0.70 | 1.32 | 1.24 | 1.15 | | 0.75 |
| 5 | 0.3 | 0.40 | 3.75 | 0.61 | 0.37 | 0.63 | 1.03 | 0.87 | 0.69 | | 0.30 |
| O/F | 9.0 | 9.45 | 37.48 | 13.12 | 2.93 | 43.84 | 22.45 | 17.28 | 44.72 | | 13.46 |
| 13 | 100.0 | 99.97 | 100.00 | 99.81 | 99.95 | 99.96 | 99.89 | 100.01 | 99.99 | 100 | 99.85 |

21 May 1984

## R797
### KING RIVER DELTA SEDIMENT  —  MACQUARIE HARBOUR.

Sizing Analysis - For information of Dr. D. Green   Re possible mineralogy of sized fractions.

| Fraction | % Mass | % Ba | Assays Grams Per Tonne Sn | Cu | Co | Pb | Zn | As | Bi | Au | % S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| +2.36mm | Trace | | * | | | | | | | | |
| +1.18mm | 0.1 | 0.29 | 0.25% | 1600 | 33 | 490 | 690 | 39 | 10 | | 3.42 |
| +600µm | 0.2 | | | | | | | | | | |
| +300 " | 3.7 | 0.21 | 31 | 1400 | 13 | 71 | 240 | <15 | <10 | | 0.92 |
| +150 " | 52.1 | 0.26 | 17 | 1200 | 17 | 52 | 160 | <15 | <10 | | 0.79 |
| + 75"" | 27.3 | 0.58 | 15 | 900 | 105 | 67 | 190 | 22 | <10 | | 5.44 |
| - 38 " | 5.4 | 1.10 | 23 | 1200 | 350 | 70 | 210 | 51 | <10 | | 17.5 |
| C/S 1 | 0.3 | 1.70 | 510 | 4700 | 800 | 210 | 900 | 150 | 37 | ≃40 | 36.8 |
| 2 | 0.3 | 1.07 | 460 | 4600 | 340 | 130 | 430 | 57 | 21 | | 16.4 |
| 3 | 0.8 | 0.57 | 260 | 3300 | 150 | 105 | 390 | 49 | 21 | | 8.67 |
| 4 | 0.5 | 0.56 | 360 | 3200 | 110 | 140 | 570 | 40 | 12 | | 5.47 |
| 5 | 0.3 | 0.56 | 630 | 2500 | 80 | 210 | 740 | 47 | 12 | | 3.71 |
| O/F | 9.0 | 0.44 | 210 | 1800 | 21 | 490 | 540 | 31 | 26 | | 5.46 |
| C. Head | 100.0 | 0.42 | 50 | 1040 | 64 | 100 | 216 | 21 | 4 | 0.1 | 3.65 |

* Note:  Sn as percentage this fraction

Research Officer...................

(H. K. Wellington)
Chief Chemist & Metallurgist