The following statement is a full description of this invention, including the best method of performing it known to us:

X991-74-N.D.-13 P.C.
This invention is concerned with a method for treatment of chalcopyrite ore or concentrate to achieve at least partial separation of the copper and iron components to be separated, and thereby to convert the copper component to a reactive, readily leached copper sulphide product.

Hydrometallurgical routes for treatment of copper concentrates are receiving increased consideration as sulphur dioxide emissions from smelting operations become less acceptable in industrialized societies. The recovery of sulphur is often the main object of such routes, although lower capital costs and flexibility of scale are often claimed as additional advantages over the more usual smelting routes.

To date, the conventional hydrometallurgical approach to copper winning has been to get the copper into solution by an oxidation process and thereafter to recover it by a reduction process. The large number of hydrometallurgical procedures so far devised have all been variations of the steps of this basic sequence. One of the chief problems encountered has been that the most important copper bearing
mineral, chalcopyrite, is particularly resistant to leaching reagents and, moreover, the leaching which does occur generally proceeds non-selectively, with approximately equivalent quantities of copper and iron entering solution.

The so-called "activation" of chalcopyrite has been proposed in several prior art efforts to avoid the abovedescribed shortcomings. The term "activation" is somewhat of a misnomer in that, in all but one of the activation procedures suggested, the chalcopyrite is actually converted to another sulphide or a mixture of sulphides. The exception is a process in which increased leachability is achieved by a special type of impact milling. "Activation" has been carried out by heating chalcopyrite with elemental copper, hydrogen, iron and sulphur or in a vacuum. These prior art activation processes generally succeed in both improving the leaching characteristics of the mineral and achieving a limited degree of selectivity between copper and iron dissolution.

It has now been found that cathodic electrolysis will convert the copper-iron sulphide mineral, chalcopyrite (CuFeS₂) to simple insoluble copper sulphides, such as chalcocite (Cu₂S), the closely related sulphide djurleite (Cu₁.₉₇S), digenite (approx. Cu₉S₅), or other copper sulphides in the composition range Cu₁.₇₅S to Cu₂S, together with, in some cases, a small proportion of elemental copper. The iron which has reacted is removed in the soluble ferrous form. The sulphur which has reacted is partly evolved as hydrogen sulphide and partly retained as an insoluble copper sulphide in the solid residue. The procedure therefore constitutes a type of activation of chalcopyrite. The reactions consume acid and the following chemical
equations show the typical courses of the reactions for the particular case where hydrochloric acid is used as electrolyte:

$$2\text{CuFeS}_2 + 6\text{HCl} + 2\text{e}^- \rightarrow \text{Cu}_2\text{S} + 3\text{H}_2\text{S} + 2\text{FeCl}_2 + 2\text{Cl}^-$$

$$9\text{CuFeS}_2 + 26\text{HCl} + 8\text{e}^- \rightarrow \text{Cu}_9\text{S}_5 + 13\text{H}_2\text{S} + 9\text{FeCl}_2 + 8\text{Cl}^-$$

Pyrite in the concentrate is unaffected or dissolved to only a small extent by the electrolysis procedure.

According to one aspect of the present invention there is provided a method for upgrading chalcopyrite ore or concentrate by electrolytic reduction to insoluble copper sulphides, which comprises electrolysing the ore or concentrate in particulate form in an electrolytic cell containing a strong acid electrolyte, with the ore or concentrate in contact with the cathode of the electrolytic cell, the cathode material, electrolyte composition, temperature and current being chosen so as to minimise hydrogen evolution and maximise reduction of the chalcopyrite.

Other aspects and preferred features of the invention will become apparent from the following discussion.
Electrolysis is carried out with a charge of the particulate concentrate resting on, or otherwise contacting, a metal cathode. Copper concentrates can be used directly in the condition in which it is normally produced and require no pre-grinding or pre-treatment of any kind.

The achievement of electrolysis of a bed of particles in this form depends on the fact that there is periodic electrical contact between the electrically conducting sulphide mineral particles and the metal cathode, either directly or via other contacting particles. During the time of electrical contact, current passes across the particle-solution interface at which an electrochemical reaction therefore occurs. Moreover, in the case of cathodic electrolysis of sulphide minerals, the solid products of such a reaction which form on the particle surfaces are themselves either electrically conducting sulphides, as in the above equations, or are metals, for example, as in the case of lead sulphide. This behaviour is critical in allowing the reduction of a bed of sulphide particles to approach completion.

Because the electrochemical potential required to drive the reduction of many sulphide minerals is also sufficient, in theory, to cause the reduction of protons to hydrogen, it is important that electrolysis be carried out under conditions in which such evolution of hydrogen is minimised and the rate of reduction of the sulphide is maximised. Otherwise, the current efficiency for the desired reduction of the sulphide mineral would become uneconomically small. Such conditions have been determined.
for the reduction of chalcopyrite and are as follows:

The proportion of the current which is used in the direct evolution of hydrogen from the cathode depends on the hydrogen overvoltage properties of the cathode material. Such direct evolution will be lower the higher is the hydrogen overvoltage. Modern practice is to characterize the hydrogen overvoltage properties of a material by means of a single parameter, the exchange current density for hydrogen evolution, which decreases as the hydrogen overvoltage increases. Materials such as mercury and lead have amongst the lowest known exchange current densities, (which have been stated to be from $10^{-7}$ to $10^{-8}$ A m$^{-2}$) and are therefore the most suitable for the present purpose. Copper and graphite, with exchange currents about $10^{-3}$ A m$^{-2}$, are also found to be adequate in practice, while metals such as platinum and palladium, with exchange currents of $10$ A m$^{-2}$, are not suitable. In practice, the contribution of hydrogen evolved directly from the cathode can be made negligibly small, the major contribution coming from hydrogen evolved from sulphide surfaces.

The electrolyte should be a strong acid such as hydrochloric acid or sulphuric acid or a mixture thereof. The optimum acid concentration depends on the nature of the acid as well as the current density but is usually in the range of 2N to 6N. Hydrochloric acid is the preferred acid for which, at the high current densities favoured for application of the method, the optimum concentration range is 4N to 6N. In batch runs, excess acid may be used at the start, or acid additions
can be made during the run.

The optimum cell temperature is in the region of 60 - 90°C.

The dependence of current efficiency on current density is unexpected. When the optimum electrolyte, as described above, is used, the current efficiency increases as the current density is increased up to about 5000 A m⁻². The current efficiency shows no significant decrease with further increase in current density levels at least up to the maximum current density (15,000 A m⁻²) available to us in the test cell used.
Under the test conditions so far studied, there is no significant effect of external agitation on the current efficiency. In such a system, the main function of agitation is to bring fresh material near the cathode and the necessary turnover is adequately maintained by the action of electrolytically produced bubbles of hydrogen sulphide and hydrogen. Such action may not be sufficient, however, in all systems and additional stirring or agitation may be required. Here again simple routine experiments will determine the best conditions.

The present discovery is concerned only with a method of pretreating or upgrading sulphide concentrates and does not constitute a complete process for recovery of metal values. Usually, therefore, the method will be used in conjunction with other known procedures to provide a complete metal extraction process. Example 1 (below) therefore gives the result of leaching a typical product of the electrolytic reduction of a copper concentrate with an acidified cupric chloride solution in order to show the amenability of this material to leaching by one possible known procedure. The copper sulphide product is finely divided and porous, properties which enhance its leaching characteristics. Pyrite in the reduction product is not attacked significantly by the leachant, and the resulting high copper:iron extraction ratio makes the leach liquor very suited to the economic recovery of copper metal by electrowinning. The leach residue contains elemental sulphur, pyrite and gangue minerals and is suitable for sulphur recovery by solvent extraction or other known methods.

As well as the solid product containing copper...
sulphides, electrolytic reduction of copper concentrate gives as products gaseous hydrogen and hydrogen sulphide and an acid solution containing ferrous iron. The gases can be separated by cooling and sulphur recovered from the hydrogen sulphide by, for example, the Claus process. The electrolyte can be treated, for example, by the Aman process to recover acid and discharge iron in a solid form (ferric oxide).

In particular, when hydrochloric acid is used as electrolyte, the electrolytic reduction process can produce a solution which has a favourable composition for economic application of the Aman process, with ferrous chloride content in the range of 10-20% and hydrochloric acid in the range 5 - 10%.

The invention is illustrated by the following non-limiting examples.

EXAMPLE 1

Copper concentrate (100 gm, 25.9% copper, 30.7%
approximate sulphide mineral content by weight = 74% chalcopyrite, 18% pyrite) iron, 35.6% sulphur; was placed in a lead-bottomed glass vessel containing 1 litre of 2 molar hydrochloric acid at 70°C. The cell contained a platinum anode separated from the lead cathode by a glass sinter. A current of 4 amp. (1000 A m⁻²) was passed for 5-3/4 hr. (total 80,000 coulombs) without external agitation of the cell contents. The solid residue weighed 53 gm. and contained 44.3% copper, 13.9% iron and 28.5% sulphur. The copper sulphide in this residue was identified as digenite (Cu₉S₅) by x-ray diffraction analysis. The solution contained 21.4 gm ferrous iron, equivalent to 10% FeCl₂. Results indicated at least 97% conversion of chalcopyrite to digenite. Current efficiency for this process was 43%. Power expended was 0.10 kw-hr.

The solid product was subjected to leaching with a
solution containing 0.5 molar cupric chloride, 1 molar hydrochloric acid and 2 molar sodium chloride. A 15 minute leach at 105°C gave a copper recovery of 99.4%. Under these conditions, iron extraction was such as to give a copper to iron extraction ratio of approximately 220 to 1.

**EXAMPLE 2**

The same quantity of the same copper concentrate as in Example 1 was placed in a similar lead-bottomed glass cell of cathode area 30 cm². The electrolyte was 1 litre of 5 molar hydrochloric acid at 70°C. The anode arrangement was the same as in Example 1. A current of 30 amp. (7,900 A m⁻²) was passed for 33 minutes, giving a total charge of 60,000 coulombs. The solid residue weighed 57.6 gm and contained digenite and a form of djurleite. No chalcopyrite was detectable in the residue and the iron content of the solution indicated at least 90% conversion of chalcopyrite, with a current efficiency of at least 58%. Power expended in the process was 0.22 kW-hr.

**EXAMPLE 3**

100g of the same concentrate as in Example 1 was placed in a glass cell whose base was a copper cathode of area 40 cm². The anode compartment was a PVC tube closed by means of a polyester cloth diaphragm. The anode was a piece of platinized titanium expanded mesh. The electrolyte was 1 litre of 5 molar hydrochloric acid at 75°C. A current of 60 amp. (15,000 A m⁻²) was passed for 17 minutes. The solid residue weighed 59.9 g and contained djurleite, digenite and elemental copper. The solution contained 20.2 g ferrous iron, indicating 90% conversion of chalcopyrite with a current efficiency of 58%. Power expended was 0.12 kW-hr.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for upgrading chalcopyrite ore or concentrate by electrolytic reduction to insoluble copper sulphides, which comprises electrolysing the ore or concentrate in particulate form in an electrolytic cell containing a strong acid electrolyte, with the ore or concentrate in contact with the cathode of the electrolytic cell, the cathode material, electrolyte composition, temperature and current being chosen so as to minimise hydrogen evolution and maximise reduction of the chalcopyrite.

2. A method as claimed in Claim 1, in which the cathode material is lead, copper, mercury or graphite.

3. A method as claimed in Claim 1 or Claim 2, in which the current density at the cathode is at least 5000 A m\(^{-2}\).

4. A method as claimed in any one of Claims 1 to 3, in which the acid is hydrochloric acid or sulphuric acid or a mixture thereof.

5. A method as claimed in Claim 4, in which the acid concentration in the electrolyte is from 2N to 6N.

6. A method as claimed in Claim 4 and Claim 5, in which the acid is hydrochloric acid and the concentration is from 4N to 6N.
7. A method as claimed in any one of Claims 1 to 6, in which the cell temperature during electrolysis is in the range $60^\circ$ to $90^\circ$C.

8. A method as claimed in any one of the preceding claims in which the ore or concentrate in the vicinity of the cathode is agitated during the electrolysis.

9. A method for upgrading a metal sulphide ore or concentrate, substantially as hereinbefore described with reference to any one of the Examples.

10. An upgraded copper ore or concentrate comprising copper and/or one or more copper sulphides in the composition range $\text{Cu}_{1.75}S$ to $\text{Cu}_2S$, whenever produced by the method claimed in any one of the preceding claims.

Dated the 20th day of September, 1977.

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION

By its Patent Attorneys
DAVIES & COLLISON