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

**LEACHING SULFIDE CONCENTRATES**

**CLASS**

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LEACHING SULFIDE CONCENTRATES

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**APPLICANT**

THE INTERNATIONAL NICKEL COMPANY OF CANADA, LIMITED

**ACTUAL INVENTOR**

PETER JOHN MICHAEL RYAN

**RELATED ART**

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X689-69-ND-13P.C.
The present invention pertains to a hydrometallurgical process and, more particularly, to an improved process for recovering non-ferrous metal values from sulfide minerals by oxidation of an aqueous slurry of the sulfide mineral.

As a general rule, the use of high temperatures increase the kinetics of the leaching reaction and commercially more attractive leaching rates are realized. However, when sulfide minerals are oxidized in an aqueous suspension at temperatures above about 112°C., the melting point of sulfur, under conditions which produce molten elemental sulfur, the liberated molten elemental sulfur "shuts off" further reaction by wetting and coating unreacted sulfides. The sulfur-coated unreacted sulfides will not react further unless the sulfur coating is removed in one way or another. For example, it has been suggested to employ vigorous agitation during leaching with the view of physically destroying the sulfur coating on the unreacted sulfide surfaces. In order to completely avoid the disadvantages associated with the molten sulfur coating, it has also been suggested that sulfide minerals be leached at temperatures below the melting point of sulfur but this is not a totally satisfactory solution since at temperatures below about 112°C. some non-ferrous mineral sulfides react only
slowly and others do not react at all. Chalcopyrite is a good example of a sulfide mineral that is so un-reactive that it cannot without prior thermal treatment be leached at commercially attractive rates with conventional lixiviants at temperatures below about 112°C. For example, if it is attempted to treat concentrates containing chalcopyrite and more than about 10% pyrrhotite at temperatures above 112°C, oxidation dissolution of the copper values associated with the chalcopyrite initially proceeds at attractive rates but as elemental sulfur is produced the molten elemental sulfur coats and "shuts off" the oxidation reactions.

It has now been discovered that sulfide minerals of non-ferrous metal values can be oxidized in acidic aqueous solutions at temperatures above the melting point of sulfur while minimizing the coating action of the liberated elemental sulfur.

Generally speaking, the present invention contemplates an improved process for treating at least one mineral sulfide in aqueous suspension at temperatures above the melting point of sulfur to oxidize at least a part of the sulfide sulfur to elemental sulfur. The improvement comprises adding a surfactant to the aqueous suspension in small but effective amounts to minimize wetting and coating of the sulfide mineral by molten elemental sulfur so that oxidation of the sulfide sulfur can continue.

An advantageous embodiment of the present invention is the treatment of a sulfide mineral of at least one non-ferrous metal value selected from the group con-
Consisting of cobalt, copper, lead, nickel, and zinc from sulfide minerals with acidic aqueous solutions under oxidizing conditions at temperatures above the melting point of sulfur to liberate elemental sulfur and to dissolve the non-ferrous metal values. A slurry of a finely-divided sulfide mineral of the non-ferrous metal value and an acidic aqueous solution containing a surfactant in a small but effective amount to minimize wetting and coating of the sulfide mineral by molten elemental sulfur is heated to a temperature above the melting point of sulfur to oxidize at least a part of the sulfide sulfur to elemental sulfur and to dissolve the non-ferrous metal value.

Ores, ore concentrates, leach residues, or other metallurgical intermediates containing at least one metal selected from the group consisting of cobalt, copper, iron, lead, nickel, and zinc can be treated by the process in accordance with the present invention. Advantageously, the ore or ore concentrate contains, for economic reasons, at least one non-ferrous metal value selected from the group consisting of cobalt, copper, lead, nickel or zinc. Examples or sulfide minerals include, although the invention is not limited thereto, chalcopyrite, pentlandite, chalcocite, sphalerite, cubanite, galena, pyrrhotite, violarite, covellite, digenite, millerite, bornite, cobaltite, polydymite, and iron monosulfide produced by heating iron pyrites in non-oxidizing atmospheres to drive off the labile.

The ore, ore concentrate or metallurgical intermediate does not have to be treated in any manner other than preliminary crushing or grinding to increase the surface area of the material for facilitating the leaching
reactions. In most instances, grinding to 100% minus 100 mesh Tyler Screen Size (TSS) is advantageous in providing commercially attractive leaching rates. More advantageously, the ore, ore concentrate or other metallurgical intermediate is ground to at least about 90% minus 325 mesh TSS to provide commercially attractive reaction rates and to minimize materials handling problems. For the best results in terms of non-ferrous metal value dissolution, sulfide sulfur conversion, reaction rates and apparatus utilization, the ore or ore concentrate is ground to a particle size of about 100% minus 325 mesh TSS.

After crushing or grinding, if necessary, the ore, ore concentrate or other metallurgical intermediate is pulped with water or an acidic aqueous leaching solution. A wide range of pulp densities, e.g., from about 2% solids by weight to about 50% solids by weight, can be employed. However, it is preferred to employ pulp densities between about 5% solids, by weight, and 30% solids, by weight, to minimize materials handling problems, to provide efficient utilization of process apparatus, and to produce pregnant solutions more concentrated in the non-ferrous metal values.

Any leaching process that oxidizes the sulfide sulfur associated with non-ferrous metal value sulfide minerals to elemental sulfur and dissolves the non-ferrous metal value can be employed. For example, solutions of at least one ferric salt selected from the group consisting of sulfate, chloride and nitrate can be employed to oxidize sulfide sulfur of non-ferrous metal sulfide minerals to elemental sulfur while dissolving the non-ferrous metal value with spent leaching solutions being regenerated by
known chemical or electrolytic techniques. Of course, other polyvalent metal salts, such as chromic and manganic salts, can also be used. In another embodiment, the sulfide mineral can be oxidized to dissolve the metal value and to oxidize sulfide sulfur to elemental sulfur by passing gaseous chlorine through an aqueous slurry of the sulfide mineral. Most advantageously, leaching is conducted by oxidizing an aqueous slurry of the sulfide mineral with a free-oxygen-containing gas.

In an advantageous embodiment of the process, an aqueous slurry of the finely divided sulfide mineral is established in an autoclave made of a suitable acid-resisting material and equipped with means for agitating the slurry. The slurry is heated to a temperature above about 112°C. under an oxygen partial pressure of at least about 3 atmospheres to oxidize the sulfide sulfur to elemental sulfur and to dissolve the metal value. Advantageously, the slurry is heated to a temperature between about 120°C. and 250°C. under an oxygen partial pressure between about 10 atmospheres and 30 atmospheres. At temperatures between about 120°C. and 170°C. and under oxygen partial pressures between about 10 atmospheres and 30 atmospheres the oxidation reactions take place at commercially attractive rates without requiring unduly heavy equipment. At temperatures much above 190°C., elemental sulfur is not produced with the sulfide sulfur being oxidized to sulfate sulfur which must be neutralized when recovering dissolved metal values from solution.

Liberated elemental sulfur is molten at temperatures above 112°C. and has a tendency to wet and coat the

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sulfide minerals. As more and more elemental sulfur is liberated, the wetting and coating action of the molten sulfur and the oxidizing reaction compete. Once sufficient molten elemental sulfur to wet and coat the sulfide minerals has been liberated the oxidizing reactions come to a halt. In order to avoid the cessation of the oxidizing reactions, a surfactant is added to the aqueous slurry in a small but effective amount to minimize wetting and coating of the sulfide minerals by molten elemental sulfur. Although the invention is not limited thereto, it is believed that the surfactants act to retard wetting of the unreacted sulfide minerals by the molten sulfur. Advantageously, the surfactants are water-miscible organic compounds that are liquid at leaching temperatures. An exemplary list of surfactants that can be employed include, although the invention is not limited thereto, mixtures of water-soluble aliphatic amines, polyalkylene glycol esters, polyoxyethylene lauryl ethers and sulfonated aromatics.

The surfactant is added to the aqueous slurry of the sulfide mineral in small but effective amounts to insure that leaching liquor will replace molten sulfur on the mineral sulfide surface. Although the sulfide mineral itself, the ore or ore concentrate, and the degree of comminution will affect the amount of surfactant employed, the surfactant is generally added to the slurry in amounts between about 0.5 pounds per ton (lb/t) or sulfide mineral slurry and 10 lb/t of sulfide mineral. Advantageously, the surfactant is employed in amounts between about 1 lb/t of solids in the slurry and 5 lbs/t of solids in the slurry to maximize the effects of the surfactant while minimizing its consumption.
In an advantageous embodiment of the present invention, a sulfide ore or ore concentrate containing pyrrhotite and at least one sulfide mineral of a non-ferrous metal value selected from the group consisting of nickel or copper is treated by aqueous oxidation at temperatures above the melting point of sulfur to recover elemental sulfur, readily separable iron oxide and a pregnant solution having dissolved therein a preponderant part of the non-ferrous metal value. The sulfide minerals of nickel include pentlandite, violarite and millerite while the copper minerals include chalcocite, covellite, digenite, chalcopirite, cubanite, and bornite, all of which are associated with pyrrhotite. The ore or ore concentrate is pulped with water, advantageously to provide a pulp containing between about 5% solids, by weight, and 30% solids, by weight, and a surfactant in a small but effective amount to minimize wetting and coating of the pyrrhotite and the non-ferrous metal sulfide value by molten elemental sulfur is added to the pulp. The surfactant is advantageously at least one member selected from the group consisting of mixtures of water-soluble aliphatic amines, polyalkylene glycol esters, polyoxyethylene lauryl ethers and sulfonated aromatics and is advantageously added to the pulp in amounts between about 1 lb/t of sulfide mineral and 5 lb/t of sulfide mineral. The pulp is fed to an autoclave and is heated to a temperature between about 120°C. and 160°C. under an oxygen partial pressure of at least about 3 atmospheres, advantageously between about 10 atmospheres and 30 atmospheres, to oxidize at least a part of the sulfide sulfur to elemental sulfur and to
dissolve the non-ferrous metal value. During the oxidation treatment, the pulp is vigorously agitated to promote the oxidation reactions and to insure that freshly exposed sulfide surfaces are contacted with the surfactant. When the oxidation reactions are substantially complete, the pulp is cooled with controlled agitation to produce solidified sulfur pellets. The sulfur pellets and iron oxide can be separated from the pregnant solution and from each other while dissolved nickel and copper values can be recovered from the pregnant solution.

An advantageous embodiment of the present invention when treating an ore or ore concentrate containing pyrrhotite, pentlandite and chalcopyrite is to conduct the aqueous oxidation to oxidize substantially all of the sulfide sulfur associated with the pyrrhotite and the pentlandite and only minor amounts of the sulfide sulfur associated with the chalcopyrite to produce a slurry of elemental sulfur, iron oxide and unreacted chalcopyrite in a pregnant nickel-containing solution. After liquid-solid separation, the elemental sulfur and chalcopyrite can be separated from the iron oxide and then in turn separated from each other so the chalcopyrite can be treated for copper recovery. The pregnant nickel-containing solution can be treated to selectively precipitate any dissolved copper and then to recover nickel. In carrying this embodiment into practice, an ore or ore concentrate containing pyrrhotite, pentlandite and chalcopyrite and advantageously ground to a particle size of at least about 100% minus 325 mesh TS3 is pulped with water, e.g., to produce a slurry containing between about 5% solids, by
weight, and 30% solids, by weight. A surfactant is added
to the slurry in small but effective amounts to minimize
wetting and coating of the pyrrhotite and pentlandite by
molten elemental sulfur to insure that substantially all
the sulfide sulfur of the pyrrhotite and pentlandite are
oxidized. For example, at least one surfactant selected
from the group consisting of mixtures of water-soluble
aliphatic amines, polyalkylene glycol esters, polyoxyethylene
lauryl ethers and sulfonated aromatics is added to the
slurry in amounts between about 1 lb/t of ore and 5 lbs/t
of ore. The slurry is fed to an autoclave, is heated to
a temperature between about 120°C. and 160°C. under an
oxygen partial pressure of at least about 3 atmospheres,
advantageously between about 10 atmospheres and 30 atmo-
spheres, and is vigorously agitated to oxidize substan-
tially all the sulfide sulfur of the pyrrhotite and
pentlandite to elemental sulfur and sulfate sulfur.
When substantially all the pyrrhotite and pentlandite
have been oxidized, the oxidation reactions are termi-
nated before substantial amounts of chalcopyrite are
oxidized. This oxidation treatment produces a slurry
of elemental sulfur, iron oxide, gangue and unreacted chal-
copyrite in a pregnant nickel-containing sulfate solution.
The chalcopyrite, after separation from the elemental sulfur,
iron oxide and pregnant solution, can be treated for copper
recovery, and nickel can be recovered from the pregnant
solution.

In order to give those skilled in the art a better
appreciation of the invention, the following illustrative
examples are given:

Example I

Samples of a pyrrhotite flotation concentrate
containing 0.5% copper, 1.3% nickel, 53% iron, 33% total sulfur and the remainder substantially gangue were pulped at 30% solids, by weight, with a recycle liguror and a surfactant, a mixture of water-soluble aliphatic primary, secondary, and tertiary amines containing approximately 85% primary amines having a mean molecular weight of 265 were added in varying amounts to all the pulps except in Tests 1 to 3 and 9 which were conducted for comparative purposes. The pulps were fed to a titanium autoclave, equipped with a driven impeller to vigorously agitate the pulp and cooling coils to control the pulp temperature. The pulps were heated to 110°C. and oxygen was then introduced into the autoclave to bring the pressure up to 300 pounds per square inch gauge (psig), i.e., oxygen partial pressures of about 20 atmospheres. Once the oxidation reactions were initiated releasing heat, the pulps were allowed to rise to a predetermined temperature and then maintained at that temperature by extracting heat through the cooling coils. The amount of surfactant added to the pulps, the reaction temperatures and times, and the results of tests are given in Table I. Comparing Test 4 with Test 3 and Tests 10 to 13 with Test 9 confirms that the use of the surfactant increases the dissolution of nickel at all temperatures and that at 160°C. conversion of sulfide sulfur to elemental sulfur and sulfate sulfur is more complete, even in Test 13 which was conducted for only 0.5 hour, when a surfactant is employed. And comparing Test 12 with Test 2 indicates that use of higher temperatures, which are generated autogenously, improved nickel dissolution in half the time.
TABLE I

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Temp., °C.</th>
<th>Time, hrs.</th>
<th>Addition, lbs/ton Conc.</th>
<th>% Dissolved</th>
<th>% Sulfur Conversion</th>
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<td></td>
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</table>

Example II

This example confirms that nickel sulfide flotation concentrates can be treated by the process in accordance with the present invention. The tests in this Example were conducted in a manner similar to Example I except that water was used to form the slurry and varying feed grinds were employed. Tests 14, 15, and 23 were conducted in accordance with prior art practices for comparative purposes. The feed assays, and grinds, oxidation temperatures and times, surfactant addition (the same as used in Example I) and the results are given in Table II. Comparing Test 16 with Test 14, 17 with Test 15 confirms that the use of a surfactant permits...
the use of higher oxidation temperatures which provide greater nickel dissolutions for equal times. Likewise, Test 24 through 28 when compared to Tests 23 and 24 confirm that the use of a surfactant gives materially higher nickel recoveries than when no surfactant is used at the same temperatures. Tests 21, 22 and 29 through 31 confirm that nickel dissolution is highly dependent on the feed grind size.
<table>
<thead>
<tr>
<th>Test No.</th>
<th>Feed Assay</th>
<th>% Cu</th>
<th>% Ni</th>
<th>% Fe</th>
<th>% TS</th>
<th>Mesh XSS</th>
<th>Surfactant</th>
<th>Time</th>
<th>Addition</th>
<th>Dissolved</th>
<th>S</th>
<th>Sulfur Converted, %</th>
<th>Total</th>
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</table>
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A leaching process for treating at least one finely divided sulfide mineral in aqueous suspension to dissolve non-ferrous metal values and oxidize at least part of the sulfide sulfur to elemental sulfur at temperatures above the melting point of sulfur, in which a surfactant is added to the aqueous suspension in a small but effective amount to minimize wetting and coating of the sulfide mineral by molten elemental sulfur so that oxidation of the sulfide mineral can continue.

2. A process according to claim 1, wherein at least some of the molten elemental sulfur is formed by heating a slurry of the sulfide mineral and an acidic aqueous solution is heated to a temperature above the melting point of sulfur and a non-ferrous metal value which is at least one of cobalt, copper, lead, nickel and zinc is leached from the mineral.

3. A process according to either of claims 1 and 2, wherein the sulfide mineral includes at least one non-ferrous metal value sulfide and substantial amounts of pyrrhotite and the sulfide mineral is slurred with water and the slurry is heated to a temperature above 112°C. under an oxygen partial pressure of at least 3 atmospheres to oxidize at least part of the sulfide sulfur of the pyrrhotite to elemental sulfur and to dissolve the non-ferrous metal values.

4. A process according to claim 3, wherein the metal sulfides include pyrrhotite, pentlandite and pyrite and the aqueous suspension is heated to from 120°C. to 250°C. to
oxidize the sulfide sulfur of the pyrrhotite and pentlandite to elemental sulfur and sulfate sulfur, to oxidize and precipitate iron oxide compounds, to dissolve the nickel and to provide a residue containing unreacted chalcopyrites and the precipitated iron oxide compounds.

5. A process according to either of claims 3 and 4, wherein the slurry is heated to a temperature of from 130°C to 170°C, under an oxygen partial pressure of from 10 atmospheres to 30 atmospheres.

6. A process according to any one of claims 1 to 5, wherein the sulfide mineral has a particle size range of about 100% minus 100 mesh TSS.

7. A process according to any one of claims 1 to 6, wherein the slurry contains from 2% solids, by weight, to 50% solids, by weight.

8. A process according to claim 7, wherein the slurry contains from 5% solids, by weight, to 30% solids, by weight.

9. A process according to any one of claims 1 to 8, wherein the surfactant is at least one of mixtures of water-soluble aliphatic amines, polyalkaline glycol esters, polyoxyethylene lauryl ethers and sulfonated aromatics.

10. A process according to any one of the preceding claims, wherein the surfactant is added to the aqueous suspension in amounts of from 0.5 pound per ton of solids in the suspension to 10 pounds per ton of solids in the suspension.

11. A process according to claim 10, wherein the surfactant is added in from 1 pound to 5 pounds per ton of solids in the suspension.

13. A metal value or sulfur recovered from a sulfide mineral by a process including an oxidation step as defined in any one of claims 1 to 12.

DATED this THIRTIETH day of APRIL, 1973

THE INTERNATIONAL NICKEL COMPANY OF CANADA, LIMITED

Patent Attorneys for the Applicant
SPRUSON & FERGUSON