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 (57) Abstract

A process for recovering metals from particulate refractory precious or base metal containing sulphide materials in which a thermotolerant bacteria culture is used to oxidise the sulphide at a temperature from 25 to 55°C.

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(56) Documents cited: US 4822413 US 4729788 US 4740243

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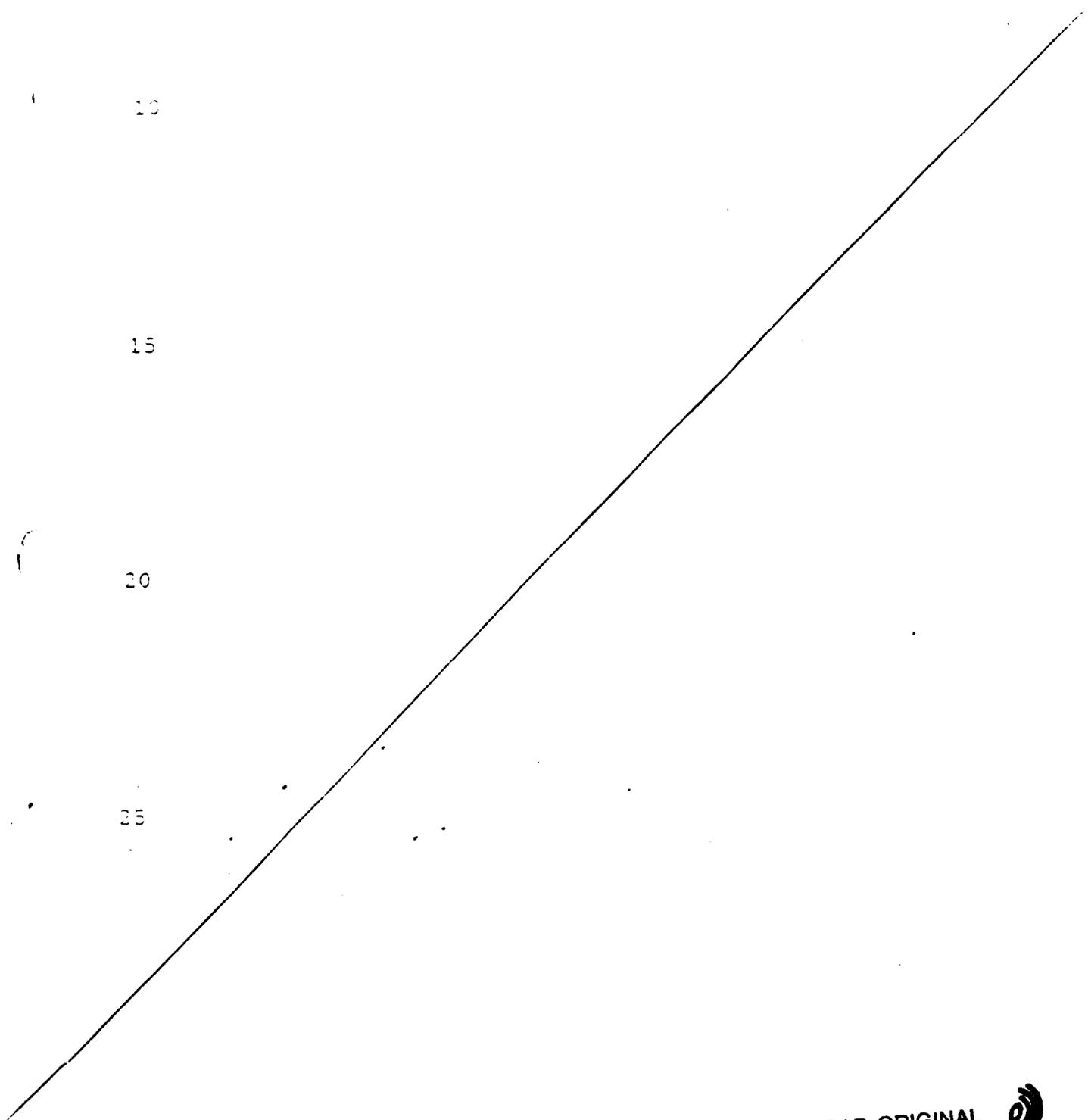
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ABSTRACT

A process for recovering metals from particulate refractory precious or base metal containing sulphide materials in which a thermotolerant bacteria culture is used to oxidise the sulphide at a temperature from 25 to 55°C.

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TITLE

"BACTERIAL OXIDATION OF METAL CONTAINING MATERIALS"

DESCRIPTION

The present invention relates to a process for the treatment  
5 of metal containing materials by bacterial oxidation.

FIELD OF THE INVENTION

It is known that recovery of metals especially precious  
metals and base metals from refractory sulphide materials  
can be enhanced by bacterial oxidation or leaching. The  
10 bacterial treatment subjects the sulphide material to a  
pre-oxidation. The refractory sulphide materials can take a  
wide variety of forms including mineral sulphides,  
carbonaceous sulphide ores, sulphide flotation concentrates,  
sulphide gravity concentrates, sulphide tailings, sulphide  
15 mattes and sulphidic fume.

The precious metals and some base metals remain in the  
oxidised solid residue and can be recovered by conventional  
carbon in pulp or other chemical leaching processes. Some  
base metals such as copper, zinc and nickel go into solution  
20 and may be recovered directly by conventional solvent  
extraction and electrowinning.

In the past, bacterial oxidation of precious or base metal  
containing sulphide materials has typically been conducted  
using bacteria of the Thiobacillus species. However, the  
25 Thiobacillus species can only operate at temperatures up to  
about 40°C. Further, the oxidation effected by Thiobacillus  
bacteria is an exothermic reaction and it is sometimes  
necessary to cool the process reactors to prevent the  
temperature exceeding that at which the Thiobacillus



bacteria can operate.

#### SUMMARY OF THE INVENTION

The present invention provides a process for the bacterial oxidation of metal containing sulphide materials using thermotolerant bacteria which can operate at higher temperatures than conventional Thiobacillus bacteria. In accordance with one aspect of the present invention there is provided a process for recovering metals from particulate refractory precious or base metal containing sulphide materials which comprises contacting the sulphide material with an aqueous solution containing a thermotolerant bacteria culture (as herein defined) capable of promoting oxidation of the sulphide material at a temperature in the range from 25 to 55°C, separating the oxidised residue from the aqueous liquid and treating the oxidised residue and/or the aqueous liquid to recover metal therefrom.

#### DESCRIPTION OF THE INVENTION

The thermotolerant bacteria used in the present invention are as described in "Thermophiles General, Molecular, and Applied Microbiology" edited by Thomas D. Brock and published by John Wiley & Sons (1986). In Chapter 1 of this publication, there is illustrated in Figure 1(b) a graph showing that thermotolerant bacteria grow at temperatures lower than those preferred by moderate and obligate or extreme thermophiles.

In the context of the present invention, a thermotolerant bacteria is one which has an optimum growth temperature of 40 to 45°C and an operating temperature of 25 to 55°C.



Thermotolerant bacteria are found in soil and water in certain locale. Any suitable method for isolation of the thermotolerant bacteria may be used, such as agar plating, critical end point dilution or solution growth, all of which are standard microbiology procedures.

The thermotolerant culture is preferentially acidophilic and operates most effectively in the temperature range of 40-45°C. An example of a thermotolerant acidophile is *Sulfobacillus* species. These bacteria are generally found in sulphide deposits and hot springs. Examples of the locale where such bacteria are found include hot springs located in Iceland and New Zealand.

Preferably, the aqueous solution used in the process of the

present invention is acidic. It has been found that the optimum acidity of the aqueous liquid for growth of the thermotolerant bacteria culture used in the present invention is in the range from pH 1.8 to 2.0, whilst the optimum acidity of the aqueous liquid for operation of the process of the present invention is in the range from pH 0.5 to 2.5.

The bacterial oxidation step of the process of the present invention is conducted in the presence of nutrients which are typically dissolved salts of nitrogen, potassium and phosphorus. The nutrients may already be present in the aqueous liquid or they may be added thereto. The nutrient materials promote the growth of the thermotolerant bacteria.

It is preferred that the thermotolerant bacteria be acidophilic in view of the pH conditions under which the process of the present invention is preferably conducted. Further, the thermotolerant bacteria used in the process of the present invention are typically aerobic and thus the aqueous liquid is preferably aerated during the operation of the process to ensure that there is an adequate supply of oxygen for the bacteria. Still further, it is found that the thermotolerant bacteria culture used in the process of the present invention is typically capable of autotrophic growth. Yet further, the thermotolerant bacteria culture typically does not require additional CO<sub>2</sub> over and above that normally available from ambient air.

The thermotolerant bacteria culture used in the process of



the present invention may be capable of oxidising arsenic (III) to arsenic (V) in acidic aqueous solutions containing soluble iron salts. Further, the thermotolerant bacteria culture used in the process of the present invention may be  
5 capable of oxidising iron (II) to iron (III) in acidic aqueous solutions and may be capable of oxidising reduced sulphur species to sulphate ion in acidic aqueous solutions.

Also, the thermotolerant bacteria culture used in the  
10 process of the present invention is preferably capable of oxidising iron and sulphides in an aqueous liquid containing up to 20 grams/litre of sodium chloride without the addition of special nutrients or employment of the special conditions. Thus, in this case extracting the pH,  
15 temperature, oxygen, nitrogen phosphate and potassium levels are maintained as discussed above, oxidation will proceed.

Typically, a particular culture of thermotolerant bacteria contains one or more bacteria species.

20 The process of the present invention can be operated in heaps, dumps, agitated systems or dams.

After completion of the oxidation step the oxidised solid residue and the aqueous liquid are typically separated. In the case of precious metal recovery, the oxidised solid  
25 residue would preferably be washed and then the pH of the oxidised solid residue adjusted to a level compatible with the use of a cyanide leaching agent. Alternatively, another reagent such as thiourea could be used under acidic conditions and so the need to adjust the pH is obviated.



EXAMPLES

The present invention will now be illustrated by the following examples.

EXAMPLE 1

5 A pyrite - gold concentrate designated P 1 was treated in accordance with the present invention. The concentrate contained pyrite as the major sulphide mineral with minor amounts of chalcopyrite, sphalerite, galena and arsenopyrite. Other minerals present were quartz, sericite  
10 and siderite.

The concentrate had the following assay.

Table 1Assay of Pyrite Concentrate P 1

<u>Element</u>	<u>Symbol</u>	<u>Assay (by weight)</u>
15 Gold	Au	52.0 ppm
Iron	Fe	26.0%
Sulphur	S	27.5%
Nickel	Ni	113 ppm
20 Copper	Cu	880 ppm
Zinc	Zn	320 ppm
Lead	Pb	160 ppm
Arsenic	As	3750 ppm
Silver	Ag	8 ppm

25 Samples of the concentrate were mixed with a sulphuric acid solution at a pulp density of 3% w/w to provide a pH range of 1.2 to 1.5. Nutrients included in the acid solution were ammonium sulphate at 200 mg/L, di-potassium hydrogen phosphate at 200 mg/L and magnesium sulphate heptahydrate



at 400 mg/L.

The acid level (pH) may vary from the start value and may either rise and then fall or fall from the outset. In most tests, the variation can be significant with the final pH often less than 1.0.

The slurry was inoculated with a thermotolerant bacteria culture designated MTC 1. The inoculated slurry was shaken in conical flasks at a temperature of 43°C. Samples were removed periodically and analysed for iron and arsenic extraction to determine the progress of the treatment.

The sample was treated by bacterial oxidation for 30 days to achieve 80% oxidation of the pyrite mineral. The solids weight loss due to the oxidation process was 52%. The solid residue was then separated from the residual acid solution. Leaching of the solid residue using alkaline cyanide solution recovered 92% of the gold. In comparison, cyanide leaching could recover only 74% of the gold from the concentrate in the untreated state. These results are summarised in Table 2. Table 2

Gold Recovery from Untreated and Oxidised Concentrate

<u>Sample</u>	<u>Iron Extracted</u> <u>(by weight)</u>	<u>Gold Recovered</u> <u>By Cyanide</u> <u>Leaching (by</u> <u>weight)</u>
Untreated	0%	74%
Bacterial Oxidation	80%	92%

The cyanide solution employed to recover the gold contained sodium cyanide at a concentration of 2 g/L.

The iron in the solution from the bacterial oxidation process can be removed by adjusting the pH to above 5.0 by the addition of lime, limestone, alkaline tailings or sodium hydroxide.

5 The results of this test show that gold encapsulated with pyrite (FeS) can be released from the sulphide lattice by at least partial oxidation of the sulphur and iron by the thermotolerant bacteria culture MTC 1 to render the gold accessible to cyanide solution.

10 EXAMPLE 2

A nickel sulphide ore designated N 1 was treated in accordance with the present invention. The ore contained both sulphidic nickel and non-sulphidic nickel minerals including violarite, lizardite and niccolite (NiAs).

15 Approximately 70% of the nickel was present as sulphidic nickel. Other minerals were siderite, goethite, pyrite, chlorite and quartz.

The ore had the following assay.

Table 3

20

Assay of Nickel Ore N 1

<u>Element</u>	<u>Symbol</u>	<u>Assay (by weight)</u>
Nickel	Ni	2.74%
Iron	Fe	18.7%

25 Samples of the ore were mixed with a sulphuric acid solution at a pulp density of 13% w/w to provide a pH range of 1.2 to 1.5. Nutrients included in the acid solution were ammonium sulphate at 200 mg/L, di-potassium hydrogen phosphate at 200 mg/L and magnesium sulphate heptahydrate at 400 mg/L.

The acid level (pH) may vary from the start value and may



either rise and then fall or fall from the outset. In most tests, the variation can be significant with the final pH often less than 1.0.

The slurry was inoculated with the thermotolerant bacteria culture designated MTC 1. The inoculated slurry was shaken in conical flasks at a temperature of 47°C. Samples were removed periodically and analysed for iron and nickel extraction to determine the progress of the treatment.

At the completion of the bacterial oxidation treatment, 17 days, the solution was removed from the residual solids and the residual solids washed with sulphuric acid solution to remove any residual nickel. The nickel recovery was 93% after the residual nickel was washed out of the solids residue.

The nickel could be recovered from the solution by raising the pH to a value of about 8.5, by the addition of lime or sodium hydroxide.

For comparison, the ore was also treated with iron (III) sulphate solution at pH 1.0 and 50°C for 24 hours to extract nickel. Only 16% of the nickel was recovered in this process.

These results are summarized in Table 4.

Table 4

Nickel Recovery from Ore N 1

<u>Treatment</u>	<u>Nickel in</u>	<u>Nickel</u>
<u>Method</u>	<u>Residue</u>	<u>Extraction</u>
(by weight)	(by weight)	
Iron (III)	2.03%	16%
Leaching		
Bacterial	0.60%	78%
Oxidation		



Bacterial                      0.19%                      93%  
 Oxidation  
 & Washing

The results of this test showed that base metals in ore as  
 5 sulphide minerals can be recovered by the action of the  
 thermotolerant bacteria culture MTC 1. The sulphidic  
 minerals were oxidised to release the nickel into the  
 acidic solution for conventional recovery.

EXAMPLE 3

10 A gold bearing arsenopyrite - pyrite concentrate was  
 treated according to the present invention. This  
 concentrate was designated AP 1. The major sulphide  
 minerals were pyrite, 30% by weight and arsenopyrite, 35%  
 by weight. Other minerals present were calcite, quartz and  
 15 chlorite. The gold was present almost completely in the  
 arsenopyrite.

The concentrate had the following assay.

Table 5

Assay of Arsenopyrite Concentrate AP 1

20	<u>Element</u>	<u>Symbol</u>	<u>Assay</u> (by weight)
	Gold	Au	80 ppm
	Arsenic	As	16.7%
	Iron	Fe	28.1%
	Sulphur	S	30.0%
25	Nickel	Ni	1.5%

Samples of the concentrate were mixed with a sulphuric acid  
 solution at a pulp density of 3% w/w to provide a pH range  
 of 1.0 to 1.3. Nutrients included in the acid solution  
 were ammonium sulphate at 200 mg/L, di-potassium hydrogen



phosphate at 400 mg/L and magnesium sulphate heptahydrate at 400 mg/L.

The acid level (pH) may vary from the start value and may either rise and then fall or fall from the outset. In most tests, the variation can be significant with the final pH often less than 1.0.

The slurry was inoculated with the thermotolerant bacteria culture designated MTC 1. The inoculate slurry was shaken in conical flasks at a temperature of 40°C. Samples were removed periodically and analysed for iron and arsenic extraction to determine the progress of the treatment.

The sample was treated by bacterial oxidation for 12 days to achieve 90% break down of the arsenopyrite mineral. The solids weight loss due to the oxidation process was 30%.

The residual solids were then separated from the acid solution. Leaching of the separated solid residue using alkaline cyanide solution recovered 95% of the gold. In comparison, cyanide leaching could recover only 21% of the gold from the concentrate in the untreated state. These results are summarised in Table 6.

Table 6

Gold Recovery from Untreated and Oxidised Concentrate

<u>Sample</u>	<u>Arsenic</u> <u>Extracted</u> <u>(by weight)</u>	<u>Gold Recovered</u> <u>by Cyanide</u> <u>Leaching (by</u> <u>weight)</u>
Untreated	0%	21
Bacterial Oxidation	90%	95

The cyanide solution employed to recover the gold contained

sodium cyanide at a concentration of 2 g/L.

The arsenic and iron in the solution from the bacterial oxidation process can be removed by adjusting the pH to above 5.0 by the addition of lime, limestone, alkaline  
5 tailings or sodium hydroxide.

The results of this test show that gold encapsulated with arsenopyrite (FeAsS) can be released from the sulphide lattice by at least partial oxidation of the arsenic, sulphur and iron by the thermotolerant bacteria culture MTC  
10 1 to render the gold accessible to cyanide solution.

#### EXAMPLE 4

A gold bearing arsenopyrite - pyrite concentrate was treated according to the present invention. This concentrate was designated AP 2. The major sulphide  
15 minerals were pyrite, 90% by weight and arsenopyrite 9% by weight. Other minerals present were calcite, quartz and chlorite. The gold was distributed in both the arsenopyrite and the pyrite.

The concentrate had the following assay.

20

Table 7

#### Assay of Arsenopyrite - Pyrite Concentrate AP 2

<u>Element</u>	<u>Symbol</u>	<u>Assay (by weight)</u>
Gold	Au	54 ppm
Arsenic	As	4.2%
25 Iron	Fe	35.7%
Sulphur	S	40.0%

Samples of the concentrate were mixed with a sulphuric acid solution at a pulp density of 10% w/w to provide a pH range of 1.0 to 1.3. Nutrients included in the acid solution



were ammonium sulphate at 200 mg/L, di-potassium hydrogen phosphate at 400 mg/L and magnesium sulphate heptahydrate at 400 mg/L.

The acid level (pH) may vary from the start value and may  
5 either rise and then fall or fall from the outset. In most tests, the variation can be significant with the final pH often less than 1.0.

The slurry was inoculated with the thermotolerant bacteria culture designated MTC 1. The inoculated slurry was shaken  
10 in conical flasks at a temperature of 53°C. Samples were removed periodically and analysed for iron and arsenic extraction to determine the progress of the treatment.

The sample was treated by bacterial oxidation for 12 days to achieve 90% oxidation of the arsenopyrite mineral and an  
15 additional 21 days for 70% pyrite oxidation as well as arsenopyrite oxidation. The weight loss due to the oxidation process was 25% for the arsenopyrite and 78% for the 100% arsenopyrite plus 70% pyrite. The solids residue was then separated from the acid solution.

20 Leaching of the solid residue using alkaline cyanide solution recovered 79% of gold for the oxidation of 90% arsenopyrite and 87% for complete oxidation of the arsenopyrite and 70% of the pyrite. In comparison, cyanide leaching could recover only 53% of the gold from the  
25 concentrate in the untreated state. These results are summarised in Table 8.

Table 8

Gold Recovery from Untreated and Oxidised Concentrate

<u>Sample</u>	<u>Arsenic</u>	<u>Iron</u>	<u>% Gold</u>
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<u>Recovered</u>	<u>Extracted</u>	<u>Extracted</u>	<u>(by</u>
<u>weight)</u>	<u>(by weight)</u>	<u>(by weight)</u>	<u>)</u>
5 Untreated	0%	0%	
53%			
Bacterial Oxidation	90%	25%	
79%			
Bacterial Oxidation	100%	70%	
10 87%			

The cyanide solution employed to recover the gold contained sodium cyanide at a concentration of 2 g/L.

The arsenic and iron in the solution from the bacterial oxidation process can be removed by adjusting the pH to  
 15 above 5.0 by the addition of lime, limestone, alkaline tailings or sodium hydroxide.

The results of this test show that gold encapsulated with arsenopyrite (FeAsS) and in pyrite (FeS<sub>2</sub>) can be released from the sulphide lattice by at least partial oxidation of  
 20 the arsenic, sulphur and iron by the thermotolerant bacteria culture MTC 1 to render the gold accessible to cyanide solution. This example also shows that the MTC 1 culture is able to operate according to the invention at 53°C.

25 The thermotolerant bacteria culture MTC 1 was isolated from a coal mine in Western Australia. Sludge and water samples



from the mine which contained acidophilic, thermotolerant bacteria were taken and used to inoculate volumes of a modified 9K medium containing yeast extract. The modified 9K medium had the following composition:-

<u>Basal Salts</u>	<u>Concentration</u>
$(\text{NH}_4)_2\text{SO}_4$	0.2 g/L
$\text{K}_2\text{HPO}_4$	0.2 g/L
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.4 g/L
$\text{FeSO}_4$	to 9.000 mg/L iron
$\text{H}_2\text{SO}_4$ to reduce pH to 1.2	

The samples were incubated at 30°C in a mineral salts solution containing 400mg/L  $(\text{NH}_4)_2\text{SO}_4$ , 200 mg/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 100mg/L  $\text{K}_2\text{HPO}_4$ , 100mg/L KCl, and pyrite 1.0 g/L at a pH of 2.0. Growth was observed after 7 days. These samples were then sub cultured in modified 9K medium without yeast extract.

Modifications and variations such as would be apparent to a skilled addressee are deemed within the scope of the present invention.



## CLAIMS

- 5 1. A process for recovering metals from particulate refractory precious or base metal containing sulphide material characterised in that it comprises contacting the sulphide material with an aqueous solution at a temperature in the range from 25 to 55°C, the aqueous solution containing a thermotolerant bacteria culture having an optimum growth temperature of 40 to 45°C and capable of promoting oxidation of the sulphide material at a temperature in the range from 25 to 55°C, separating the oxidised residue from the aqueous liquid and treating the oxidised residue and/or the aqueous liquid to recover metal therefrom.
- 10 2. A process according to claim 1, characterised in that the aqueous solution is acidic.
3. A process according to claim 2, characterised in that the aqueous solution has a pH in the range from 0.5 to 2.5.
4. A process according to any one of claims 1 to 3, characterised in that the thermotolerant bacteria is acidophilic.
- 15 5. A process according to any one of the preceding claims, characterised in that the thermotolerant bacteria is aerobic.
6. A process according to claim 5, characterised in that the aqueous liquid is aerated during the operation of the process.
- 20 7. A process according to any one of the preceding claims, characterised in that the thermotolerant bacteria is capable of autotrophic growth.
8. A process according to any one of the preceding claims, characterised in that no CO<sub>2</sub> is supplied to the thermotolerant bacteria during the operation of the process other than that available from ambient air.
- 25 9. A process according to any one of the preceding claims, characterised in that the aqueous liquid contains sodium chloride in an amount up to 20 grams per litre.

