

**(12) PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

**(11) Application No. AU 200126176 B2**  
**(10) Patent No. 775697**

(54) Title  
**Method for leaching nickeliferous laterite ores**

(51)<sup>7</sup> International Patent Classification(s)  
**C22B 023/00 C22B 003/44**  
**C22B 003/08 C22B 003/46**

(21) Application No: **200126176**

(22) Application Date: **2000.10.25**

(87) WIPO No: **WO01/32943**

(30) Priority Data

(31) Number	(32) Date	(33) Country
<b>09/432536</b>	<b>1999.11.03</b>	<b>US</b>

(43) Publication Date : **2001.05.14**

(43) Publication Journal Date : **2001.07.26**

(44) Accepted Journal Date : **2004.08.12**

(71) Applicant(s)  
**BHP Minerals International, Inc.**

(72) Inventor(s)  
**J. Carlos Arroyo; David A. Neudorf**

(74) Agent/Attorney  
**Griffith Hack,GPO Box 1285K,MELBOURNE VIC 3001**

(56) Related Art  
**US 4062924**  
**US 4410498**

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
10 May 2001 (10.05.2001)

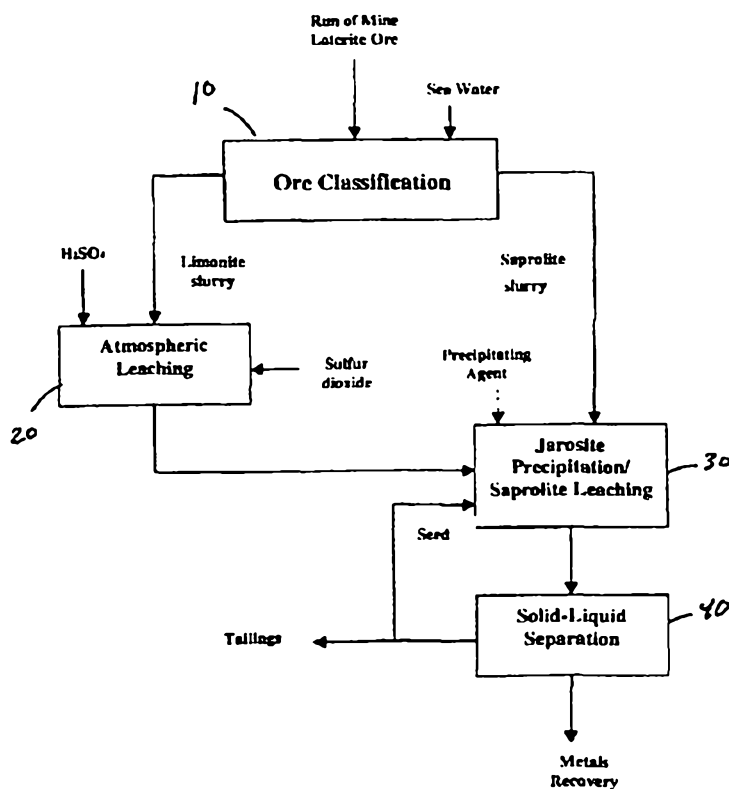
PCT

(10) International Publication Number  
WO 01/32943 A3

- (51) International Patent Classification<sup>7</sup>: C22B 23/00, 3/08, 3/44, 3/46 (74) Agent: NICHOLS, G., Peter; Brinks Hofer Gilson & Li-one, P.O. Box 10087, Chicago, IL 60610 (US).
- (21) International Application Number: PCT/US00/41555 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 25 October 2000 (25.10.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/432,536 3 November 1999 (03.11.1999) US (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant: BHP MINERALS INTERNATIONAL, INC. [US/US]; 204 Edison Way, Reno, NV 89502 (US).
- (72) Inventors: ARROYO, J., Carlos; 1601 Burnside Drive, Sparks, NV 89434 (US). NEUDORF, David, A.; 3285 Lapwing Lane, Reno, NV 89509 (US).
- Published:  
— with international search report

[Continued on next page]

(54) Title: ATMOSPHERIC LEACH PROCESS FOR THE RECOVERY OF NICKEL AND COBALT FROM LIMONITE AND SAPROLITE ORES  
METHOD FOR LEACHING NICKELIFEROUS LATERITE ORES



(57) Abstract: A process is provided for leaching nickeliferous laterite ores by hydrometallurgical methods at temperatures below the boiling point of the pulp and at atmospheric pressure from which high overall nickel and cobalt extractions are obtained. The high iron fraction of the laterite, referred to as limonite, is first contacted with a concentrated mineral acid to partially or completely dissolve the iron and nickel in solution. During this process, a reducing agent is used to keep the redox potential in solution below 1000 mV to enhance cobalt dissolution and more advantageously between 1000 and 900 mV to avoid reduction of ferric iron. Further mixing of the leach slurry in the presence of sodium, potassium, or ammonium will allow the formation of iron jarosite at ambient pressure. The resulting acid from iron hydrolysis is neutralized with the low iron fraction of the laterite ore (saprolite) dissolving nickel into solution. The resulting slurry can then be treated with conventional methods to recover nickel and cobalt from solution.

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## METHOD FOR LEACHING NICKELIFEROUS LATERITE ORES

### **BACKGROUND OF THE INVENTION**

The present invention relates to a hydrometallurgical process to recover nickel and cobalt from nickeliferous laterite ores and, in particular, to the atmospheric leaching of both limonite and saprolite ores with a mineral acid to dissolve nickel and cobalt wherein iron is rejected as jarosite.

The known reserves of nickel and cobalt in nickeliferous oxide ores, e.g., those referred to as laterites comprising limonite and saprolite ore, are far greater than the corresponding reserves in sulfide ores. An important disadvantage when processing laterite ores, however, is the inability to beneficiate these ores by conventional techniques.

A number of new hydrometallurgical processes are being developed for the extraction of nickel and cobalt from nickeliferous laterite ores. Many of these processes require the dissolution of the metal values with sulfuric acid at high temperature (245°-270° C) and pressure (525-785 psig), followed by solid-liquid separation and neutralization of residual free acid present at ambient pressure. This is the basic "Moa Bay Process", as described by J.R. Boldt and P.E. Queneau in "The Winning of Nickel", Methuen, London, 1967. In this process, the nickeliferous ore is first made into a pulp having a solids content of about 40% before leaching at high temperature and pressure. During pressure leaching most metals dissolve and iron and aluminum are rejected by hydrolysis to hematite and alunite, respectively. After leaching, the pulp is cooled and

washed by counter current decantation and the solids are directed to tailing treatment. Excess acid is neutralized and the remaining iron and aluminum are precipitated as hydroxides with the addition of coral mud. Nickel and cobalt are subsequently recovered via sulfide precipitation.

Several variations of the high-pressure acid leach (HPAL) method have been devised with the aim of improving the process and economical aspects. For example, U.S. Patent 4,044,096 provides guidelines to optimize the high-pressure acid leaching of nickeliferous lateritic ores through a combination of operational steps to improve the economics and efficiency of leaching. The steps include scalping laterite ore to remove the coarse (high magnesium) fraction and thus lower the acid consumption.

The HPAL process is most amenable for high iron ores containing 40 wt% iron or higher. Lateritic ores with an iron content less than 40 wt % contain in general a higher amount of acid consuming magnesium and are therefore not economically suitable for direct high pressure leaching. U.S. Patent 3,804,613 teaches a method of high-pressure acid leaching of saprolite ore at relatively low acid/ore ratios by preconditioning the saprolite with leach liquor from the high-pressure leach step. No mention is made of concurrent limonite leaching.

U.S. Patent 3,991,159 teaches the use of saprolite ore to neutralize acid resulting from the high-pressure acid leach of limonite ore. Leaching of the saprolite fraction is carried out at high temperature (150° –250° C) and pressure for effective iron and aluminum rejection, but with relatively low nickel extraction from the saprolite ore. In another process, U.S. Patent 4,097,575 teaches saprolite ore roasting at 500°-750°

C under oxidizing conditions to increase its neutralization capacity before neutralization of HPAL liquors. This process suffers from the high capital cost needed for roasting facilities.

While the prior art HPAL methods obtain a high extraction of nickel and cobalt, they require the use of expensive equipment and sophisticated materials of construction to withstand the use of concentrated acid at the high temperatures needed (200°-300° C). Furthermore, part of the rejected iron and aluminum are in the form of hydroxides, which are difficult to deal with. Several alternatives to the HPAL process to recover nickel and cobalt from laterite ore have been proposed.

For example, U.S. Patent 4,062,924 describes a method for leaching limonite ores in acidic media at temperatures up to 110° C. and in the presence of hydrogen sulfide gas to precipitate dissolved nickel and cobalt. Most dissolved iron is also reduced to the divalent oxidation state however, consuming very high amounts of the reducing gas in addition to high acid consumption. U.S. Patent 4,065,542 teaches a similar method. In this process, ferrous iron produced by the method described above is used to leach metal values from manganiferous sea nodules. U.S. Patent 4,511,540 illustrates a way to recover nickel and cobalt from ores with a manganiferous matrix by leaching with sulfuric acid in the presence of sulfur dioxide gas at temperatures below the boiling point of the liquid solution. None of these processes includes the treatment of saprolitic ores.

In the process of U.S. Patent 3,793,432, limonite ore is leached with sulfuric acid at a pH below 1.5, while simultaneously adding alkaline iron-precipitating agents. The

process is carried out at atmospheric pressures, but requires leaching times in excess of 40 hours and usually from 60 to 100 hours for efficient nickel extraction and iron precipitation. No use of saprolite is made in this process. U.S. Patent 4,410,498 teaches a method to leach saprolite ore with sulfuric acid at atmospheric pressure, while adding a reducing agent to maintain the redox potential between 400 and 600 mV. In another process, described in U.S. Patent 5,571,308, nickel and cobalt are leached from saprolite ore by contact with a mineral acid at room temperature or in the temperature range of 60° -80° C. The leaching mode can be conducted by heap, vat, or agitation leaching.

We have now found an efficient and economical method to leach both limonite and saprolite ores in a single process at atmospheric pressure, to obtain high percent dissolution of nickel and cobalt and reject iron from the leach liquor as a jarosite compound at the same time. The method avoids the high capital costs associated with sophisticated autoclaves.

#### **SUMMARY OF THE INVENTION**

It is thus an object of the present invention to provide a hydrometallurgical method to significantly dissolve nickel and cobalt from limonite and saprolite ores at temperatures below the boiling point at atmospheric pressure. It is another object of this invention to provide a method to reject iron as jarosite from the laterite pregnant liquors. These and other objects will more clearly appear from the following disclosure and appended drawings.

According to the present invention there is provided a hydrometallurgical process to extract nickel and cobalt from a laterite ore that includes at least a limonite and a saprolite ore, the process comprises:

- 5           a.    producing a limonite ore pulp in water, wherein the pulp has a solids concentration between 5 and 35 wt.% and wherein the limonite ore contains less than 6 wt.% magnesium;
- 10           b.    leaching the pulp at a temperature below the boiling point and at atmospheric pressure by mixing with sulfuric acid to form a leach slurry, wherein iron, cobalt, and nickel are dissolved in solution and substantially all the sulfuric acid is consumed;
- 15           c.    adding an iron precipitating agent selected from the group consisting of sodium, potassium, ammonium ions, and mixtures thereof to the pulp or leach slurry and precipitating iron as a jarosite compound; and
- 20           d.    maintaining the leach slurry temperature between 85°C and the boiling point of the leach slurry and maintaining the leach slurry free acid concentration between 5 and 15 gpl by adding saprolite ore to neutralize at least a portion of the acid generated by jarosite precipitation, wherein magnesium, cobalt, and nickel are simultaneously dissolved from the saprolite ore to form a  
25   final leach slurry and the final concentration of iron in a liquid component of the final leach slurry is less than 3 gpl due to iron being precipitated as a jarosite compound.

30           According to the present invention there is also provided a hydrometallurgical process to extract nickel and cobalt from a laterite ore that includes at least a limonite and a saprolite ore, the process comprises:

- 35           a.    producing a limonite ore pulp in water, wherein the pulp has a solids concentration between 5 and 35 wt.% and wherein the limonite ore contains less than 6 wt.% magnesium;



b. leaching the pulp at a temperature below the boiling point and at atmospheric pressure by mixing with sulfuric acid to form a leach slurry, wherein iron, cobalt, and nickel are dissolved in solution and

5 substantially all the sulfuric acid is consumed;

c. maintaining the redox potential of the leach slurry between 1000 and 900 mV versus standard hydrogen electrode (SHE) with sulfur dioxide gas, wherein reduction of ferric iron is substantially avoided and

10 cobalt dissolution is enhanced;

d. adding an iron precipitating agent selected from the group consisting of sodium, potassium, ammonium ions, and mixtures thereof to the pulp or leach slurry and precipitating iron as a jarosite compound;

15 e. forming a final leach slurry by maintaining the leach slurry temperature between 85°C, and the boiling point of the leach slurry while maintaining the leach slurry free acid concentration between 5 and 15 gpl and at a pH of 1.0 to 1.8 by adding saprolite ore to neutralize  
20 at least a portion of the acid generated by jarosite precipitation, wherein magnesium, cobalt, and nickel are simultaneously dissolved from the saprolite ore and the final concentration of iron in a liquid component of the final leach slurry is less than 3 gpl due to iron being  
25 precipitated as a jarosite compound;

f. subjecting the final leach slurry to solid-liquid separation to form a pregnant leach liquor; and recovering nickel and cobalt from the pregnant leach liquor.

30 According to the present invention there is also provided a process of adding at least a portion of the jarosite compound to the leach slurry prior to adding the saprolite to serve as a seeding surface to enhance precipitation of iron as jarosite.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 shows a schematic flow sheet for the atmospheric leaching of limonite ore with a mineral acid and a reducing agent. Iron is subsequently rejected from the leach solution as insoluble jarosite by the addition of alkali metal or ammonium ions and saprolite ore is leached with acid produced by jarosite formation.

FIG. 2 is a variation of the flow sheet in FIG. 1 where seawater is used to pulp both limonite and saprolite ores prior to atmospheric leaching with sulfuric acid. Cobalt dissolution during limonite leaching is enhanced with additions of sulfur dioxide gas. Sodium present in seawater becomes the main source of iron precipitating agent.

FIG. 3 illustrates the effect of oxidation potential on cobalt dissolution and iron reduction from the trivalent to the divalent oxidation state during limonite atmospheric leaching.

**DETAILED DESCRIPTION OF THE INVENTION**

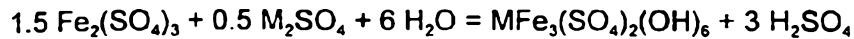
The present invention provides a single process to effect the dissolution of nickel and cobalt from both nickeliferous laterites, namely limonite and saprolite ores. The term limonite refers to the high iron (at least 25 wt.% Fe) and low magnesium (0.5 to 6 wt.% Mg) fraction contained within nickeliferous laterite ores. Similarly, the term saprolite denotes the low iron (5-20 wt% Fe) and high magnesium (at least 8 wt.% Mg) fraction contained within nickeliferous laterite ores. It should be stressed that these composition ranges are in no way limiting, but represent ranges more advantageously used in this process.

Referring now to FIG. 1, limonite and saprolite ores are first separated or classified 10. For example, the ores may be classified by pulping and screening, or mined selectively as to end up with two distinctive ore compositions (limonite and saprolite) as described above. The limonite ore is first pulped with water to a solids concentration between about 5 and about 35 wt.% and more advantageously to a solids content around 25 wt.% and then contacted with sulfuric acid ( $H_2SO_4$ ) 20 at a temperature below the boiling point of the pulp at atmospheric pressure while maintaining the redox potential below 1000 mV versus standard hydrogen electrode ("SHE") and more advantageously above 900 mV by the addition of a reducing agent to enhance cobalt dissolution.

The pulp is agitated (e.g., by stirring) for a period of time at the specified temperature to significantly effect the dissolution of nickel, cobalt and iron from the ore. At the end of the first leaching period, a precipitating agent is introduced into the pulp 30 to precipitate all of the iron. The precipitating agent is selected from the group consisting of alkali metal (Na or K), ammonium ions and mixtures thereof. The iron is precipitated as a jarosite. The amount of precipitating agent is at least the stoichiometric amount needed to precipitate all the iron. Optionally, a portion of the precipitated jarosite may be recycled by adding it with the iron precipitating agent to act as a seed.

The pulp is kept at a temperature above 90° C. and preferentially at the boiling point to promote iron precipitation as jarosite, whereby the resulting acid is neutralized with saprolite ore additions to maintain the free acid concentration in the range between

5 and 15 gpl and dissolve magnesium and nickel from the saprolite ore. The jarosite precipitation reaction may be described as follows:



where M is Na, Li, K, or  $\text{NH}_4$ . The pulp can then be treated according to conventional methods 50 to recover nickel and cobalt from the iron depleted solution.

FIG. 2 shows another embodiment of the present invention. In this embodiment, limonite is pulped in seawater at the ore separation stage or after selectively mining 10 at solids density of 20 wt. %. The limonite slurry is leached 20 at atmospheric pressure with an amount of sulfuric acid to dissolve most or all of the iron, nickel, cobalt and magnesium present in the ore. Sulfur dioxide gas as the reducing agent is injected into the pulp during the course of limonite leaching to maintain the redox potential below 1000 mV and more advantageously above 900 mV to enhance cobalt dissolution while minimizing reduction of ferric iron to ferrous iron. The sodium content in seawater becomes the main source of iron precipitating agent with only a small amount of additional precipitating agent required in the subsequent simultaneous precipitation of jarosite and saprolite leaching stage 30. Precipitation of jarosite is promoted by maintaining the temperature at or close to the boiling point of the pulp and by recycling jarosite crystals previously produced in the same way to act as a seed surface. The pulp can then be treated according to conventional methods 50 to recover the nickel and cobalt.

The following examples illustrate, but do not limit, the present invention. Unless otherwise indicated, all parts and percentages are by weight. In all the experiments the

same apparatus was used, which consisted of a glass reactor equipped with baffles, agitator motor with speed controller and marine impeller, heating mantle and thermostat, thermometer and condenser. Samples were withdrawn with a 10 cc. syringe as needed and the liquid titrated after filtering to determine free acid concentration. Solid samples were usually returned to the reactor. In most cases, sulfur dioxide gas was dispensed from a cylinder via a solenoid valve and a glass frit inside the reactor. The redox potential in solution was measured with a platinum probe vs. Ag/AgCl reference electrode, but all values reported are vs. the standard hydrogen electrode.

### Example 1

This example illustrates the atmospheric leaching of limonite ore with sulfuric acid at atmospheric pressure. A sample of limonite ore, having the composition shown in Table 1, was pulped at 15 wt. % solids in deionized water and leached with sulfuric acid between 90° and 95° C, while stirring at 800 rpm. At the start of leaching, the redox potential of the solution was recorded and sulfur dioxide gas was used to control the potential at the specified value.

**Table 1 – Chemical composition of limonite ore sample (wt. %).**

Ni	Fe	Mg	Co	Al	Cr	Si	Mn	Zn
1.85	35.23	4.1	0.096	3.40	1.52	6.67	0.73	0.05

**Table 2 – Results from the atmospheric leaching of limonite ore.**

Test ID	Leach Time (hrs)	Eh (mV)	Initial Ore wt (g)	Wt. loss (%)	Residue composition (%)					Dissolution (%)	
					Ni	Fe	Mg	Co	Mn	Ni	Co
1	3	1100*	100	66.2	0.94	18.40	3.40	0.176	1.26	83	37
2	3	900	292	68.5	0.43	13.5	4.48	0.02	0.04	92	93

\* No sulfur dioxide used.

These results show that limonite ore is effectively leached with sulfuric acid at close to the boiling point of the solution at atmospheric pressure. The difference in final nickel dissolution between test 1 and test 2 obeys to the smaller amount of acid added in test 1 (1.05 g acid/g ore) relative to test 2 (1.15 g acid/g ore). This data also illustrates the effect of sulfur dioxide to keep the redox potential below 1000 mV on the dissolution of cobalt. In test 1, the redox potential was that measured in solution without sulfur dioxide gas addition and the final cobalt dissolution was of the order of 37%. In test 2, the redox potential was controlled at about 900 mV with sulfur dioxide additions resulting in better than 90% cobalt dissolution. Very similar manganese dissolution numbers can be calculated from the data in this example in agreement with the notion that cobalt is mainly associated with manganese (IV) minerals (asbolite). The reduction of Mn(IV) to Mn(II) is necessary to dissolve asbolite efficiently.

### Example 2

This example demonstrates the leaching of limonite ore followed by simultaneous jarosite precipitation and saprolite leaching, all under atmospheric pressure conditions. Limonite ore (286 g) was first mixed with synthetic seawater

containing 24.5 gpl NaCl and 4.7 gpl  $\text{MgCl}_2$  to form a 20 wt% solids pulp. The pulp was subsequently leached with sulfuric acid (acid/ore ratio of 1.2) for 3 hours at 95° C, while stirring at 800 rpm. No sulfur dioxide gas was added in this test and the measured redox potential was about 1200 mV. At the end of limonite leaching, when the free sulfuric acid concentration was of the order 10 gpl, 40 g of jarosite containing solids (used as seed) and 37 g of anhydrous sodium sulfate (make-up sodium precipitating agent) were added to the pulp. The jarosite containing solids were previously obtained in a similar test and consisted of natro-jarosite crystals as well as limonite and saprolite leach residues. The free sulfuric acid concentration in solution was controlled between 5 and 15 gpl with manual additions of dry saprolite ore. The average chemical composition of limonite ore, saprolite ore and jarosite seed used in this test are shown in Table 3. Saprolite additions continued until the free acid concentration in solution remained at around 5 gpl for a total of 235 g.

**Table 3- Chemical composition of limonite, saprolite and jarosite containing residue that was used as a seed (wt. %).**

Sample	Ni	Fe	Mg	Co	Al	Cr	Si	Mn	Zn
Limonite	1.85	35.7 0	4.00	0.091	3.32	1.53	6.55	0.748	0.053
Saprolite	2.01	8.29	16.30	0.025	1.03	0.483	20.5	0.181	0.01
Seed	0.47	23.5	2.25	0.044	1.47	1.08	10.7	0.322	0.02

**Table 4- Results from the atmospheric leaching of limonite followed by simultaneous jarosite precipitation and saprolite leaching.**

Final residue composition (wt. %)					Pregnant solution (g/l)			
Weight (g)	Ni	Fe	Mg	Co		Ni	Fe	Na
600	0.33	19.6	2.5	0.025				
	Overall metal dissolution (wt. %)				After limonite leach	4.2	82.3	19.7
	Ni	Fe	Mg	Co	At end of test	6.7	0.25	7.3
	80	0.2	70	55				

The results from this test, given in Table 4, show that about 82 gpl of iron was present in solution at the end of limonite leaching, confirming that the limonite ore was efficiently leached. Iron and sodium concentrations decreased to about 0.25 and 7.3 gpl, respectively at the end of the test due to natro-jarosite precipitation. Acid released by iron hydrolysis to jarosite was used to dissolve magnesium and nickel from saprolite ore. Therefore, overall nickel and cobalt dissolution from both limonite and saprolite ore at the end of the test was 80 and 55%, respectively. The amount of sodium used in the test for jarosite precipitation corresponded to approximately a molar ratio of sodium to iron of 0.6 or slightly less than twice the stoichiometric amount of sodium needed for complete precipitation of iron. X-ray diffraction performed on the final residue confirmed the presence of natro-jarosite. The total time for jarosite formation in this test was of the order of 15 hours.



### Example 3

Limonite ore (284 g) was first mixed with synthetic seawater containing 24.5 gpl NaCl and 4.7 gpl  $\text{MgCl}_2$  to form a 20 wt% solids pulp. The pulp was subsequently leached with sulfuric acid (acid/ore ratio of 1.2) for 3 hours at 95° C, while stirring at 800 rpm. The redox potential in solution was controlled between 900 and 830 mV with additions of sulfur dioxide gas. At the end of limonite leaching, when the free sulfuric acid concentration was of the order 10 gpl, 40 g of jarosite containing solids (used as seed) and 5 g of sodium chloride (make-up sodium precipitating agent) were added to the pulp. The jarosite containing solids were previously obtained in a similar test and consisted of natro-jarosite crystals as well as limonite and saprolite leach residues. The free sulfuric acid concentration in solution was controlled between 5 and 15 gpl with manual additions of dry saprolite ore. The average chemical composition of limonite ore, saprolite ore and jarosite seed used in this test are shown in Table 3. Saprolite additions continued until the free acid concentration in solution remained at around 5 gpl for a total of 236 g.

**Table 5- Results from the atmospheric leaching of limonite followed by simultaneous jarosite precipitation and saprolite leaching.**

Final residue composition (wt. %)					Pregnant solution (g/l)				
Weight (g)	Ni	Fe	Mg	Co		Ni	Fe	Fe <sup>+2</sup>	Na
545	0.32	20.7	2.7	0.005					
	Overall metal dissolution (wt. %)				After Limonite leach	4.1	82.3	-	11.4
	Ni	Fe	Mg	Co	At end of test	6.5	3.8	3.3	0.06
	83	1.7	71	90					

These results (see Table 5) show that iron produced during atmospheric leaching of limonite ore was hydrolyzed in the second part of the test, whereby the acid produced from hydrolysis was used to dissolve nickel and magnesium from saprolite ore. Overall nickel and cobalt dissolution from both limonite and saprolite ores was of the order of 83 and 90%, respectively, with the high cobalt dissolution in this test due to the addition of sulfur dioxide gas during limonite leaching. Iron and sodium concentrations decreased to about 3.8 and 0.06 gpl, respectively, at the end of the test due to natro-jarosite precipitation. Iron obtained after atmospheric leaching of limonite ore was precipitated in this test with about the stoichiometric amount of sodium needed for complete iron precipitation. The only source of sodium in the test was sodium chloride salt and the total time for jarosite precipitation was 18 hours. Although a relatively high total iron concentration remained in solution at the end of the test, most of this iron existed in the divalent state, which can not precipitate as jarosite.

**Example 4**

Limonite ore (281 g) was first mixed with deionized water to form a 20 wt% solids pulp. The pulp was subsequently leached with sulfuric acid (acid/ore ratio of 1.2) for 3 hours at 95° C, while stirring at 800 rpm. The redox potential in solution was controlled at 900 mV with additions of sulfur dioxide gas. At the end of limonite leaching, when the free sulfuric acid concentration was of the order 10 gpl, 40 g of jarosite containing solids (used as seed) and 44 g of sodium sulfate precipitating agent were added to the pulp. The jarosite containing solids were previously obtained in a similar test and consisted of natro-jarosite crystals as well as limonite and saprolite leach residues. The free sulfuric acid concentration in solution was controlled between 5 and 15 gpl with manual additions of dry saprolite ore. The average chemical composition of limonite ore, saprolite ore and jarosite seed used in this test are shown in Table 3. Saprolite additions continued until the free acid concentration in solution remained at around 5 gpl for a total of 236 g.

**Table 6- Results from the atmospheric leaching of limonite followed by simultaneous jarosite precipitation and saprolite leaching.**

Final residue composition (wt. %)					Pregnant solution (g/l)				
Weight (g)	Ni	Fe	Mg	Co					
601	0.29	20.2	2.4	0.007		Ni	Fe	Fe <sup>+2</sup>	Na
	Overall metal dissolution (wt. %)				After Limonite leach	4.0	79	-	12.1
	Ni	Fe	Mg	Co	At end of test	6.5	1.43	1.22	3.2
	82	1.2	70	89					

Results from this test show that the process is equally effective in fresh deionized water and that jarosite precipitation can be carried out with sodium sulfate as the only source of sodium. Iron and sodium concentrations decreased to about 1.43 and 3.2 gpl, respectively at the end of the test due to natro-jarosite precipitation. Iron obtained after atmospheric leaching of limonite ore was precipitated in this test with only slightly more than the stoichiometric amount of sodium needed for complete iron precipitation. Total time for jarosite precipitation was 17 hours. Final nickel and cobalt dissolution from both limonite and saprolite ore was 82 and 89%, respectively. The reason for the high cobalt dissolution was the addition of sulfur dioxide gas during limonite leaching. Most remaining iron in solution at the end of the test was in the divalent oxidation state.

#### Example 5

Limonite ore batches (280 g) were leached with sufficient sulfuric acid at 90° C and 800 rpm to dissolve all the iron, magnesium and nickel contained within the ore. The composition of the feed ore is given in Table 1. The pulp was leached for 3 hours and the redox potential in solution was monitored and adjusted to different values with addition of sulfur dioxide gas. At the end of the leaching time, the solid residues were chemically analyzed to determine their respective composition.

The percent cobalt extraction as calculated from the chemical composition of solids residues was plotted as a function of the average redox potential in the tests. The extent of cobalt dissolution from limonite ore increased sharply when the redox potential decreased below 1000 mV, as shown in Figure 3. The percent cobalt

extraction (Co ext) did not significantly increase further below 1000 mV. Liquid samples were withdrawn during the experiments when variations in redox potential occurred and the concentration of ferrous iron in these samples is also shown as a function of potential in Figure 3. As can be seen from the graph, dissolved iron in solution started being reduced by sulfur dioxide gas below about 900 mV. Therefore, it is preferred to maintain the redox potential during limonite leaching between about 900 and about 1000 mV to maximize cobalt dissolution without reducing iron to the divalent oxidation state, which unnecessarily consumes sulfur dioxide gas and prevents precipitation of iron as jarosite in the subsequent step.

While there have been described what are presently believed to be the preferred embodiments of the invention, those skilled in the art will realize that changes and modifications may be made thereto without departing from the spirit of the invention. It is intended to claim all such changes and modifications that fall within the true scope of the invention.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A hydrometallurgical process to extract nickel and cobalt from a laterite ore that includes at least a limonite and a saprolite ore, the process comprises:
  - a. producing a limonite ore pulp in water, wherein the pulp has a solids concentration between 5 and 35 wt.% and wherein the limonite ore contains less than 6 wt.% magnesium;
  - b. leaching the pulp at a temperature below the boiling point and at atmospheric pressure by mixing with sulfuric acid to form a leach slurry, wherein iron, cobalt, and nickel are dissolved in solution and substantially all the sulfuric acid is consumed;
  - c. adding an iron precipitating agent selected from the group consisting of sodium, potassium, ammonium ions, and mixtures thereof to the pulp or leach slurry and precipitating iron as a jarosite compound; and
  - d. maintaining the leach slurry temperature between 85°C and the boiling point of the leach slurry and maintaining the leach slurry free acid concentration between 5 and 15 gpl by adding saprolite ore to neutralize at least a portion of the acid generated by jarosite precipitation, wherein magnesium, cobalt, and nickel are simultaneously dissolved from the saprolite ore to form a final leach slurry and the final concentration of iron in a liquid component of the final leach slurry is less than 3 gpl due to iron being precipitated as a jarosite compound.
2. The process of claim 1 wherein the solid density of the limonite ore pulp is between 15 and 25 wt.% solids.
3. The process of claim 1 or claim 2 includes maintaining the pH of the leach slurry between 1.0 and 1.8 with the addition of saprolite ore.
4. The process of any one of the preceding claims wherein the final concentration of iron in a liquid component of the final leach slurry is less than 0.5 gpl.

5. The process of any one of the preceding claims wherein the limonite ore is pulped in seawater that provides a source of iron precipitating agent.

6. The process of any one of the preceding claims  
5 comprises maintaining the redox potential of the leach slurry during the limonite leach step below 1000 mV versus standard hydrogen electrode (SHE).

7. The process of any one of the preceding claims  
10 comprises controlling the redox potential of the leach slurry during the limonite leach step by adding a reducing agent wherein cobalt dissolution is enhanced.

8. The process of claim 7 wherein sulfur dioxide gas is used as the reducing agent.

9. The process of any one of the preceding claims  
15 comprises adding at least a portion of the jarosite compound to the leach slurry prior to adding the saprolite to serve as a seeding surface to enhance precipitation of iron as jarosite.

10. The process of any one of the preceding claims  
20 comprises subjecting the final leach slurry to solid-liquid separation to form a pregnant leach liquor and a final leach residue.

11. The process of claim 10 wherein the solid-liquor  
25 separation is conducted by a process selected from the group consisting of counter current decantation, filtration or a combination thereof.

12. The process of claim 10 or claim 11 further  
comprises separating nickel and cobalt from the pregnant leach liquor.

13. The process of claim 12 wherein the separation  
30 is conducted by a process selected from the group consisting of sulfide precipitation with hydrogen sulfide gas, solvent extraction, ion exchange, or a combination thereof.

14. The process of claim 13 further comprises adding  
35 ion exchange resin to the final leach slurry wherein nickel and cobalt are loaded onto the resin.

15. The process of any one of the preceding claims wherein saprolite ore is added to the leach slurry in the form of a pulp.

16. The process of any one of the preceding claims  
5 wherein the saprolite ore is pulped in seawater that provides a source of the iron precipitating agent.

17. The process of any one of the preceding claims wherein the precipitating agent is added to the ore pulp.

18. The process of any one of the preceding claims  
10 wherein the precipitating agent is added to the leach slurry.

19. A hydrometallurgical process to extract nickel and cobalt from a laterite ore that includes at least a limonite and a saprolite ore, the process comprises:

15 a. producing a limonite ore pulp in water, wherein the pulp has a solids concentration between 5 and 35 wt.% and wherein the limonite ore contains less than 6 wt.% magnesium;

20 b. leaching the pulp at a temperature below the boiling point and at atmospheric pressure by mixing with sulfuric acid to form a leach slurry, wherein iron, cobalt, and nickel are dissolved in solution and substantially all the sulfuric acid is consumed;

25 c. maintaining the redox potential of the leach slurry between 1000 and 900 mV versus standard hydrogen electrode (SHE) with sulfur dioxide gas, wherein reduction of ferric iron is substantially avoided and cobalt dissolution is enhanced;

30 d. adding an iron precipitating agent selected from the group consisting of sodium, potassium, ammonium ions, and mixtures thereof to the pulp or leach slurry and precipitating iron as a jarosite compound;

35 e. forming a final leach slurry by maintaining the leach slurry temperature between 85°C, and the boiling point of the leach slurry while maintaining the leach slurry free acid concentration between 5 and 15 gpl and at a pH of 1.0 to 1.8 by adding saprolite ore to neutralize



at least a portion of the acid generated by jarosite precipitation, wherein magnesium, cobalt, and nickel are simultaneously dissolved from the saprolite ore and the final concentration of iron in a liquid component of the final leach slurry is less than 3 gpl due to iron being precipitated as a jarosite compound;

f. subjecting the final leach slurry to solid-liquid separation to form a pregnant leach liquor; and

g. recovering nickel and cobalt from the pregnant leach liquor.

20. The process of claim 19 comprises maintaining the redox potential of the leach slurry during the limonite leach below 1000 mV versus standard hydrogen electrode (SHE).

21. The process of claim 19 or claim 20 comprises controlling the redox potential by adding a reducing agent wherein cobalt dissolution is enhanced.

22. The process of claim 21 wherein sulfur dioxide gas is used as the reducing agent.

23. The process of any one of claims 19 to 22 wherein the limonite ore is pulped in seawater that provides the primary source of iron precipitating agents.

24. The process of any one of claims 19 to 23 wherein saprolite ore is added to the leach slurry in the form of a pulp.

25. The process of any one of claims 19 to 23 wherein the saprolite ore is pulped in seawater that provides a source of the iron precipitating agent.

26. The process of any one of the preceding claims comprises adding at least a portion of the jarosite compound to the leach slurry prior to adding the saprolite to serve as a seeding surface to enhance precipitation of iron as jarosite.

27. A hydrometallurgical process to extract nickel and cobalt from a laterite ore that includes at least a limonite and a saprolite ore, the process comprises:

a. producing a limonite ore pulp in water,

wherein the pulp has a solids concentration between 5 and 35 wt.% and wherein the limonite ore contains less than 6 wt.% magnesium;

5       b.    leaching the pulp at a temperature below the boiling point and at atmospheric pressure by mixing with sulfuric acid to form a leach slurry, wherein iron, cobalt, and nickel are dissolved in solution and substantially all the sulfuric acid is consumed;

10       c.    maintaining the redox potential of the leach slurry between 1000 and 900 mV versus standard hydrogen electrode (SHE) with sulfur dioxide gas, wherein reduction of ferric iron is substantially avoided and cobalt dissolution is enhanced;

15       d.    separating the leach slurry into a leach solution and a leach residue by a solid-liquid separation;

      e.    adding an iron precipitating agent selected from the group consisting of sodium, potassium, ammonium ions, and mixtures thereof to the pulp or leach solution and precipitating iron as a jarosite compound;

20       f.    forming a final leach slurry by maintaining the leach slurry temperature between 85°C, and the boiling point of the leach slurry while maintaining the leach slurry free acid concentration between 5 and 15 gpl and at a pH of 1.0 to 1.8 by adding saprolite ore to neutralize at  
25   least a portion of the acid generated by jarosite precipitation, wherein magnesium, cobalt, and nickel are simultaneously dissolved from the saprolite ore and the final concentration of iron in a liquid component of the final leach slurry is less than 3 gpl due to iron being  
30   precipitated as a jarosite compound;

      g.    subjecting the final leach solution to solid-liquid separation to form a pregnant leach liquor; and

35       h.    recovering nickel and cobalt from the pregnant leach liquor.

28.       The process of claim 27 wherein the limonite ore is pulped in seawater that provides the primary source of

iron precipitating agents.

29. The process of claim 27 or claim 28 wherein  
saprolite ore is added to the leach slurry in the form of  
a pulp.

5 30. The process of any one of claims 27 to 29  
wherein the saprolite ore is pulped in seawater that  
provides a source of the iron precipitating agents.

31. The process of any one of claims 27 to 30  
comprises adding at least a portion of the jarosite  
10 compound to the leach slurry prior to adding the saprolite  
to serve as a seeding surface to enhance precipitation of  
iron as jarosite.

15 Dated this 6th day of May 2003  
BHP MINERALS INTERNATIONAL, INC.  
By their Patent Attorneys  
GRIFFITH HACK  
Fellows Institute of Patent and  
20 Trade Mark Attorneys of Australia

FIGURE 1

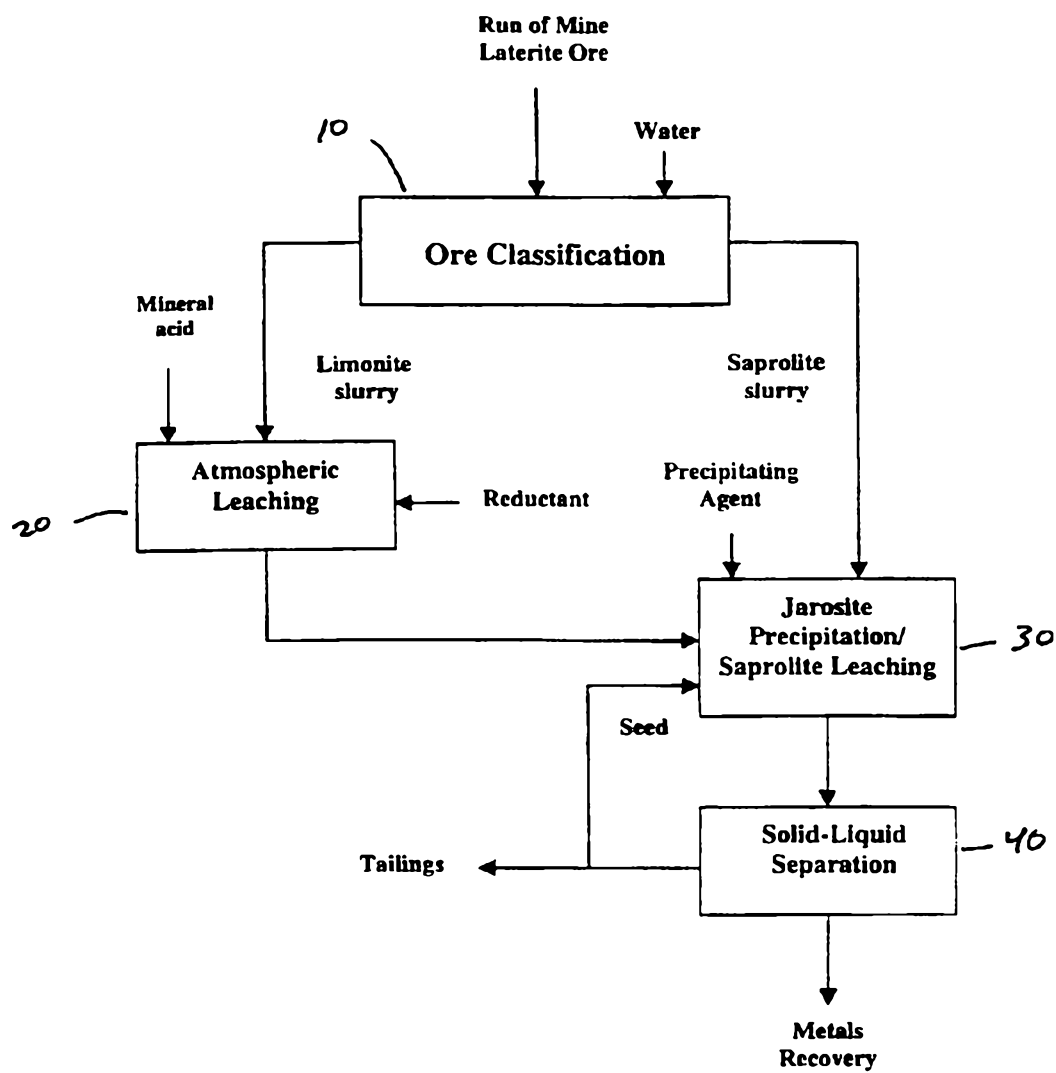


FIGURE 2

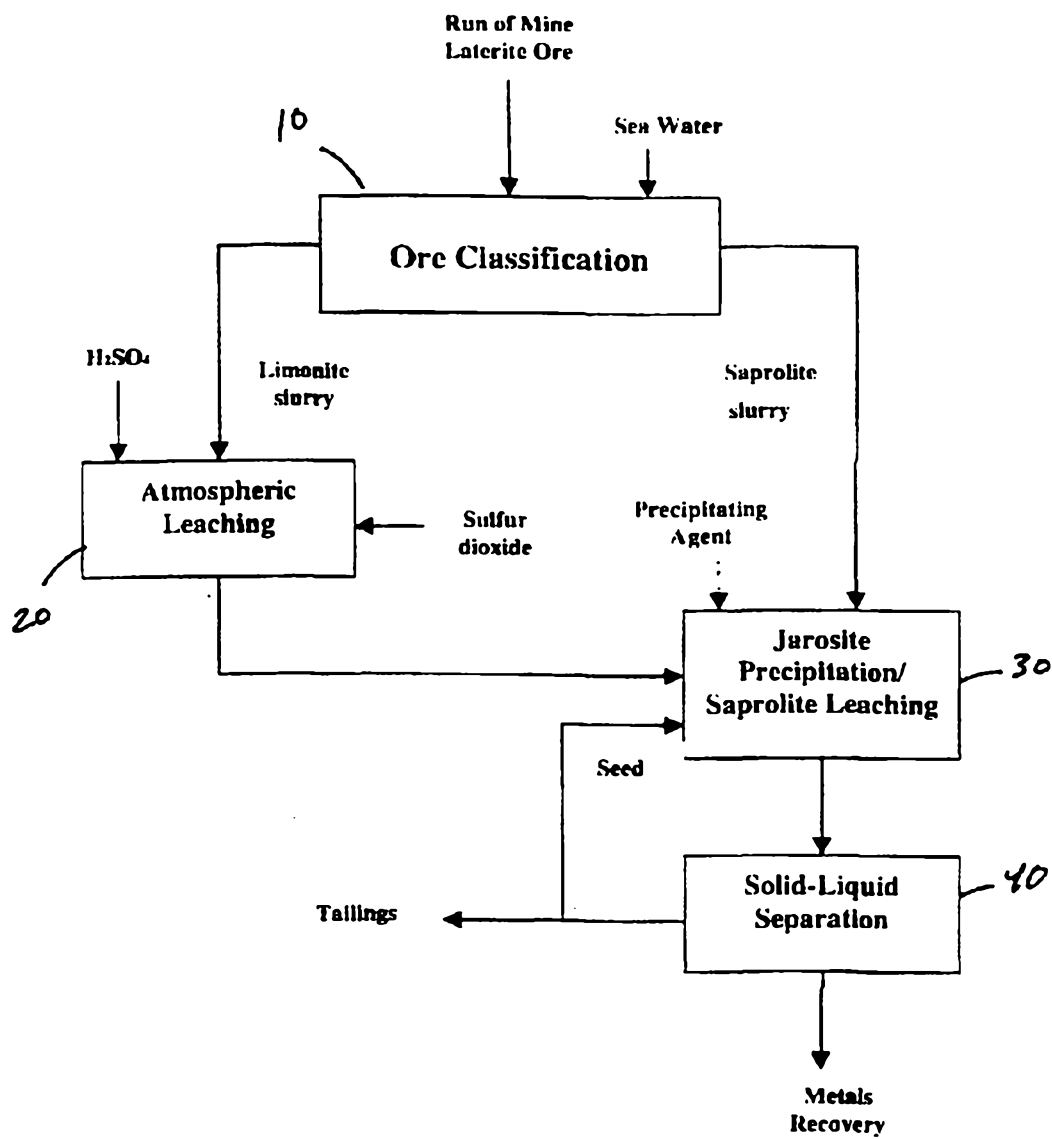


FIGURE 3

