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**Hydrometallurgical process for a nickel oxide ore**

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(56) Related Art  
**JP 2002-121624 A**

## ABSTRACT

The hydrometallurgical process for a nickel oxide ore comprising a step (1) for obtaining an aqueous solution of crude nickel sulfate by High Pressure Acid Leach of a nickel oxide ore; a step (2) for obtaining a zinc free final solution formed; a step (3) for obtaining a waste solution; and a step (4) for scrubbing a hydrogen sulfide gas in exhaust gas, wherein utilization efficiency of hydrogen sulfide gas is enhanced while maintaining nickel recovery rate.

15 It is characterized in that at least one kind of the following operations (a) to (d) is adopted.

(a) to adjust total volume ( $m^3$ ) of the sulfurization reactor (B) in the above step (3), at a ratio of 0.2 to 0.9, relative to input mass (kg/h) of nickel to be introduced;

20 (b) to evaporate, under negative pressure, slurry in the above step (3), and to add hydrogen sulfide gas recovered to the above step (3);

(c) to reuse exhaust gas from the sulfurization reactor in the above step (3), and add it to the step (2); and

25 (d) to subject the waste solution in the above step (3) and exhaust gas in the above step (4) to countercurrent contact, then to introduce the exhaust gas to the scrubber again and to charge waste solution from the scrubber into the sulfurization reactor in the step (3).

Figure 1

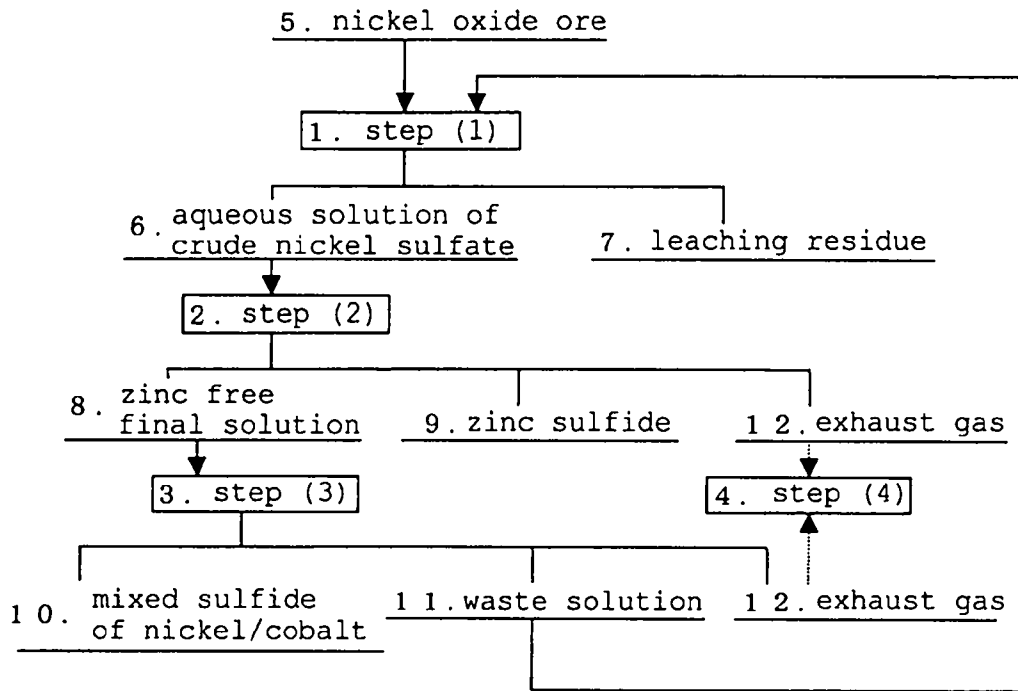
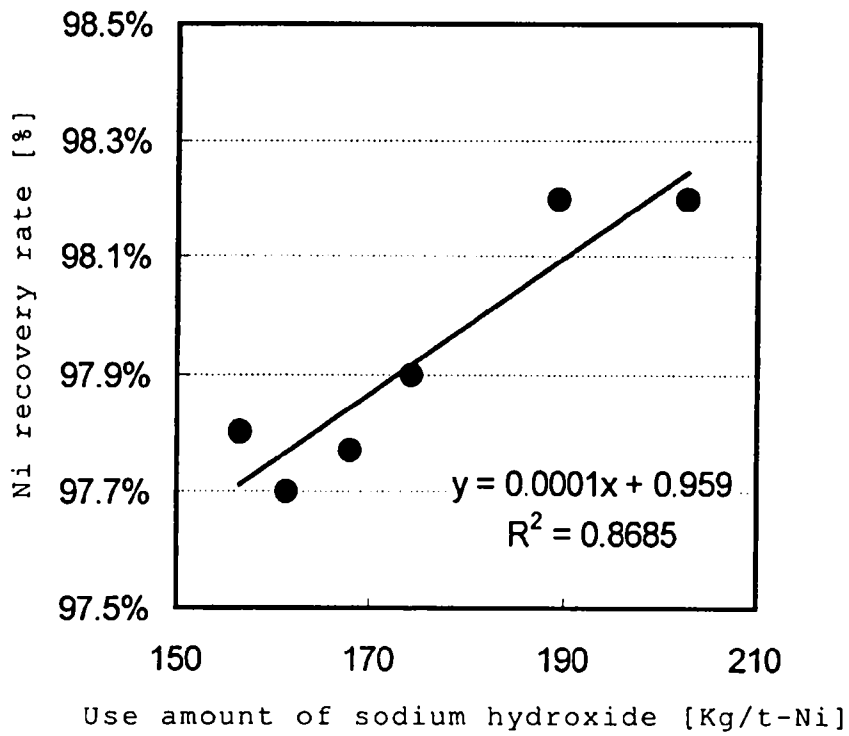


Figure 2



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Regulation 3.2

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*Patents Act 1990*

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# **COMPLETE SPECIFICATION STANDARD PATENT**

Invention Title:                    **Hydrometallurgical process for a nickel oxide ore**

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

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**HYDROMETALLURGICAL PROCESS FOR A NICKEL OXIDE ORE**

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

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The present invention relates to a hydrometallurgical process for a nickel oxide ore, and in more detail, the present invention relates to a hydrometallurgical process for a nickel oxide ore, which is capable of reducing use amount of hydrogen sulfide gas in a sulfurization step and use amount of an alkali to be used in exhaust gas treatment, and decreasing operation cost, by enhancement of utilization efficiency of hydrogen sulfide gas, while maintaining nickel recovery rate to a high yield of equal to or higher than 95%, and preferably equal to or higher than 98%, in a hydrometallurgical process for a nickel oxide ore including:

15

20

a step (1) for obtaining an aqueous solution of crude nickel sulfate by High Pressure Acid Leach of a nickel oxide ore, a step (2) for obtaining zinc sulfide and a zinc free final solution formed by introduction of the above aqueous solution of crude nickel sulfate into the inside of a sulfurization reactor (A), then the addition of hydrogen sulfide gas, a step (3) for obtaining a mixed sulfide of nickel/cobalt and a waste solution by introduction of the above zinc free final solution into the inside of a sulfurization reactor (B), then the addition of hydrogen sulfide gas, and a step (4) for scrubbing treatment of hydrogen sulfide gas in exhaust gas generating in the above steps (2) and (3).

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30

## 5 DESCRIPTION OF THE PRIOR ART

A High Pressure Acid Leach using sulfuric acid has been noticed in recent years, as the hydrometallurgical process for a nickel oxide ore. This method is composed of wet process steps throughout, without dry process treatment steps such as drying and roasting steps and the like, thus providing advantages not only in view of energy and cost saving but also in being capable of obtaining a mixed sulfide of nickel/cobalt having an enhanced nickel content of up to about 50% by weight.

15 As the High Pressure Acid Leach for obtaining the above mixed sulfide of nickel/cobalt, for example, there has been used a method including: a step (1) for obtaining an aqueous solution of crude nickel sulfate containing zinc as an impurity element, in addition to nickel and cobalt, by High Pressure Acid Leach of a nickel oxide ore, a step (2) for obtaining zinc sulfide and a zinc free final solution formed, by introduction of the above aqueous solution of crude nickel sulfate into the inside of a sulfurization reactor (A), then the addition of hydrogen sulfide gas, sulfurization of zinc contained in the aqueous solution of crude nickel sulfate, and then solid-liquid separation, a step (3) for obtaining a mixed sulfide of nickel/cobalt and a waste solution, by introduction of the above zinc free final solution into the inside of a sulfurization reactor (B), then the addition of hydrogen sulfide gas, sulfurization of nickel and cobalt contained in the zinc free final solution, and subsequently introduction of slurry formed into an evaporation apparatus for evaporation of hydrogen sulfide gas, and then solid-liquid separation, and a step (4)

5 for scrubbing treatment of hydrogen sulfide gas in exhaust gas generating in the above steps (2) and (3).

Figure 1 shows an example of a process chart of a hydrometallurgical process for a nickel oxide ore according to a High Pressure Acid Leach.

10

In Figure 1, a nickel oxide ore 5 is firstly subjected to High Pressure Acid Leach using sulfuric acid to form leached slurry, in the step (1). Next, the leached slurry is subjected to solid-liquid separation, and after multi-stage washings, separated to a leachate containing nickel and cobalt, and a leaching residue 7. The above leachate is subjected to neutralization to form the neutralized precipitate slurry containing a trivalent iron hydroxide, and an aqueous solution 6 of crude nickel sulfate. After that, the aqueous solution 6 of crude nickel sulfate is subjected to the sulfurization step composed of the step (2) and the step (3), and separated to a zinc sulfide 9 and a zinc free final solution 8, and a mixed sulfide 10 of nickel/cobalt and a waste solution 11, respectively. A sulfurization reactor to be used in this sulfurization step, is usually composed of a closed-type reactor equipped with a supply port of a reaction starting solution, an outlet of slurry after the reaction, a charge hole of hydrogen sulfide gas, and an exhaust gas hole.

25

It should be noted that exhaust gas 12 containing hydrogen sulfide gas generating from the step (2) and the step (3) is introduced into a scrubber of a step (4), and it is subjected to contact with the alkaline aqueous solution for absorption of hydrogen sulfide gas. The resulting waste solution from the

30

5 scrubber obtained here is treated separately. Still more, a waste solution 11 is circulated to be used as a washing solution in solid-liquid separation in the step (1).

10 Here, the above step (1) is composed of a leaching step for obtaining leached slurry, by the addition of sulfuric acid into slurry of a nickel oxide ore and leaching at a high temperature of equal to or high than 200°C under high pressure using an autoclave, a solid-liquid separation step for separation to the leaching residue in leached slurry and a  
15 leachate containing nickel and cobalt, and a neutralization step for forming the neutralized precipitate slurry containing impurity elements such as iron, and a starting solution for a sulfurization reaction, by adjustment of pH of the leachate containing impurity elements, in addition to nickel and cobalt.

20

In addition, in the above steps (2) and (3), a sulfurization reaction is carried out by the addition of hydrogen sulfide gas into the aqueous solution of crude nickel sulfate containing zinc as an impurity element, in addition to nickel and cobalt,  
25 to form a metal sulfide. Therefore, enhancement of efficiency of the sulfurization reaction is important.

As for the enhancement of efficiency of this sulfurization reaction, the following sulfurization methods have been disclosed. For example, a method for controlling the  
30 sulfurization reaction of metals by using hydrogen sulfide gas as a sulfurizing agent and adjusting concentration of hydrogen sulfide in a vapor phase, and correctly controlling ORP or pH in a solution (for example, refer to Patent Literature 1), a



5 method for the addition of a sulfide seed crystal to promote  
the sulfurization reaction, as well as to suppress the adhesion  
of a generating sulfide onto the inner surface of the reactor  
(for example, refer to Patent Literature 2), and a method for  
separation of zinc preferentially, by adjustment of pH and ORP  
10 of the aqueous solution of nickel sulfate containing cobalt and  
zinc (for example, refer to Patent Literature 3) and the like.  
These conventional technologies are effective technologies to  
solve each of the problems, even in the above High Pressure Acid  
Leach.

15

Incidentally, as the operation method of the above step  
(3), for example, operation is carried out under control of  
operation conditions such as nickel concentration, introduction  
flow amount, temperature, pH of a reaction starting solution  
20 to be introduced into the sulfurization reactor, at  
predetermined values, by blowing the hydrogen sulfide gas having  
a hydrogen sulfide gas concentration of equal to or higher than  
95% by volume into the vapor phase inside the sulfurization  
reactor and controlling the inner pressure thereof at  
25 predetermined value, and also, if necessary, by the addition  
of the sulfide seed crystal. This way enabled to secure a nickel  
recovery rate of equal to or higher than 95%. However, in order  
to enhance the nickel recovery rate stably at a still higher  
level, it is considered to carry out the reaction in a state  
30 of more increased temperature and pressure inside the  
sulfurization reactor. This case raises problems of use amount  
of hydrogen sulfide gas, along with treatment cost of exhaust  
gas from a reaction system, or cost of a reaction apparatus,

5 therefore enhancement of utilization efficiency of hydrogen sulfide gas to be added to the sulfurization step is required, to solve these problems. However, there is no description, in the above conventional technology, on enhancement of utilization efficiency of hydrogen sulfide gas.

10

Still more, in a production facility of hydrogen sulfide gas to be used industrially in a plant of a hydrometallurgical process for such as a practical operation plant of the above High Pressure Acid Leach, it is advantageous, in view of production efficiency thereof, to produce and use gas having a hydrogen sulfide gas concentration of below 100% by volume. Therefore, in hydrogen sulfide gas to be added inside the sulfurization reactor, hydrogen of a raw material in the production step of hydrogen sulfide gas, or an inert component such as nitrogen commingling in the production step of hydrogen sulfide gas, is contained in an amount of about 2 to 3% by volume. That is, hydrogen or nitrogen is included as an inert component not involved in the sulfurization reaction.

Therefore, in continued implementation of the operation in the sulfurization step such as the above steps (2), (3), the above inert component is accumulated inside the sulfurization reactor, causing decrease in sulfurization reaction efficiency. Therefore, such an operation is carried out that gas inside the sulfurization reactor is periodically discharged outside the system. In this case, because not only the inert component but also residual hydrogen sulfide gas are discharged at the same time, as exhaust gas, loss of hydrogen sulfide gas generates. In addition, exhaust gas from the inside of this sulfurization

5 reactor essentially requires scrubbing treatment such as  
absorption of hydrogen sulfide gas, for example, by subjecting  
to contact with an alkaline aqueous solution, therefore increase  
in use amount of hydrogen sulfide gas increases use amount of  
the alkali. As countermeasures thereof, it is considered to  
10 decrease vapor phase pressure or concentration of hydrogen  
sulfide inside the sulfurization reactor, however, this  
countermeasures, as described above, raises a problem of making  
it difficult to secure a nickel recovery rate of equal to or  
higher than 95%, which is a minimal level necessary as efficiency  
15 of total operation, and preferably equal to or higher than 98%.

Under these circumstances, in a practical operation plant  
of the conventional High Pressure Acid Leach, a nickel recovery  
rate of equal to or higher than 95% in a mixed sulfide of  
20 nickel/cobalt, has been secured by the excess addition of use  
amount of hydrogen sulfide gas, in a degree of about 1.3 to 1.4  
time hydrogen sulfide amount required theoretically in view of  
the sulfurization reaction. Therefore, such a method has been  
required that is capable of reducing the use amount of hydrogen  
25 sulfide gas in the sulfurization step, and the use amount of  
the alkali to be used in exhaust gas treatment, and decreasing  
operation cost, while maintaining the nickel recovery rate of  
equal to or higher than 95%.

30 [Patent Literature 1] JP-A-2003-313617 (page 1 and page 2)  
[Patent Literature 2] JP-A-2005-350766 (page 1 and page 2)  
[Patent Literature 3] JP-A-2002-121624 (page 1 and page 2)

## 5 SUMMARY OF THE INVENTION

In view of the above conventional technological problems, it is an object of the present invention to provide a hydrometallurgical process for a nickel oxide ore, which is capable of reducing use amount of hydrogen sulfide gas in a sulfurization step and use amount of an alkali to be used in exhaust gas treatment, and decreasing operation cost, by enhancement of utilization efficiency of hydrogen sulfide gas, while maintaining nickel recovery rate to a high yield of equal to or higher than 95%, and preferably equal to or higher than 98%, in a hydrometallurgical process for a nickel oxide ore including: a step (1) for obtaining an aqueous solution of crude nickel sulfate by High Pressure Acid Leach of a nickel oxide ore, a step (2) for obtaining zinc sulfide and a zinc free final solution formed by introduction of the above aqueous solution of crude nickel sulfate into the inside of a sulfurization reactor (A), then the addition of hydrogen sulfide gas, a step (3) for obtaining a mixed sulfide of nickel/cobalt and a waste solution by introduction of the above zinc free final solution into the inside of a sulfurization reactor (B), then the addition of hydrogen sulfide gas, and a step (4) for scrubbing treatment of hydrogen sulfide gas in exhaust gas generating in the above steps (2) and (3).

The present inventors have intensively studied on enhancement of utilization efficiency of hydrogen sulfide gas in a hydrometallurgical process for a nickel oxide ore for recovering each of zinc, nickel and cobalt as a sulfide by High Pressure Acid Leach of a nickel oxide ore, and by the addition

5 of hydrogen sulfide gas to an aqueous solution of crude nickel sulfate containing zinc as an impurity element, in addition to nickel and cobalt, to attain the above object, and found that use amount of hydrogen sulfide gas in a sulfurization step, and use amount of an alkali to be used in exhaust gas treatment can  
10 be reduced, and operation cost can be decreased, by enhancement of utilization efficiency of hydrogen sulfide gas, while maintaining nickel recovery rate to a high yield of equal to or higher than 95%, and preferably equal to or higher than 98%, by adoption of at least one kind of the following operations  
15 (a) to (d), and have thus completed the present invention:  
(a) to adjust a total volume ( $m^3$ ) of the sulfurization reactor (B) to be used, so that a ratio of 0.2 to 0.9 ( $m^3/kg/h$ ) is attained relative to input mass per unit hour ( $kg/h$ ) of nickel contained in the zinc free final solution to be introduced, in the above  
20 step (3);  
(b) to evaporate under negative pressure, in evaporation of hydrogen sulfide gas dissolved in a solution of the slurry in the above step (3), and to add the recovered hydrogen sulfide gas into the inside of the sulfurization reactor (B) of the above  
25 step (3);  
(c) to reuse the hydrogen sulfide gas containing inert components from the sulfurization reactor (B), which gas is accumulated in the gas phase part thereof, by pressure control inside the sulfurization reactor (B), in the above step (3),  
30 and add it into the inside of the sulfurization reactor (A) of the above step (2), and  
(d) to subject the waste solution in the above step (3) and exhaust gas scrubbed in the above step (4) to countercurrent

5 contact, and to introduce the resulting exhaust gas to the scrubber again, and to subject it to contact with the alkaline aqueous solution for absorption of hydrogen sulfide gas, and to charge the resulting waste solution from the scrubber into the sulfurization reactor (B) in the above step (3).

10

That is, according to a first aspect of the present invention, there is provided a hydrometallurgical process for a nickel oxide ore including: a step (1) for obtaining an aqueous solution of crude nickel sulfate containing zinc as an impurity element, in addition to nickel and cobalt, by High Pressure Acid Leach of a nickel oxide ore, a step (2) for obtaining zinc sulfide and a zinc free final solution formed, by introduction of the above aqueous solution of crude nickel sulfate into the inside of a sulfurization reactor (A), then the addition of hydrogen sulfide gas, sulfurization of zinc contained in the aqueous solution of crude nickel sulfate, and then solid-liquid separation, a step (3) for obtaining a mixed sulfide of nickel/cobalt and a waste solution, by introduction of the above zinc free final solution into the inside of a sulfurization reactor (B), then the addition of hydrogen sulfide gas, sulfurization of nickel and cobalt contained in the zinc free final solution, and subsequently introduction of slurry formed into an evaporation apparatus for evaporation of hydrogen sulfide gas, and then solid-liquid separation, and a step (4) for obtaining an exhaust gas scrubbed and a waste solution from a scrubber, by introduction of exhaust gas from the above sulfurization reactor (A), sulfurization reactor (B) or evaporation apparatus into the scrubber, and subjecting it to

- 5 contact with an alkaline aqueous solution for absorption of hydrogen sulfide gas;
- characterized in that at least one kind of the following operations (a) to (d) is adopted:
- (a) to adjust total volume ( $m^3$ ) of the sulfurization reactor (B) to be used, so that a ratio of 0.2 to 0.9 ( $m^3/kg/h$ ) is attained, relative to input mass per unit hour ( $kg/h$ ) of nickel, contained in the zinc free final solution to be introduced, in the above step (3);
- 10 (b) to evaporate, under negative pressure, in evaporation of hydrogen sulfide gas dissolved in a solution from slurry generating in the above step (3), and to add hydrogen sulfide gas recovered into the inside of the sulfurization reactor (B) of the above step (3);
- 15 (c) to reuse the hydrogen sulfide gas containing inert components from the sulfurization reactor (B), which gas is accumulated in the gas phase part thereof, by pressure control inside the sulfurization reactor (B), in the above step (3), and add it into the inside of the sulfurization reactor (A) of the above step (2), and
- 20 (d) to subject the waste solution in the above step (3) and exhaust gas scrubbed in the above step (4) to countercurrent contact, and to introduce the resulting exhaust gas to the scrubber again, and to subject it to contact with the alkaline aqueous solution for absorption of hydrogen sulfide gas, and
- 25 to charge the resulting waste solution from the scrubber, into the sulfurization reactor (B) in the above step (3).
- 30

In addition, according to a second aspect of the present

5 invention, there is provided the hydrometallurgical process for a nickel oxide ore in the first aspect of the present invention, characterized in that, in the above operation (a), the ratio is 0.6 to 0.9 (m<sup>3</sup>/kg/h).

10 In addition, according to a third aspect of the present invention, there is provided the hydrometallurgical process for a nickel oxide ore in the first aspect of the present invention, characterized in that, in the above operation (a), the sulfurization reactor (B) comprises three or four units of  
15 reactors connected in series.

In addition, according to a fourth aspect of the present invention, there is provided the hydrometallurgical process for a nickel oxide ore in the first aspect of the present invention,  
20 characterized in that, in the above operation (b), the above negative pressure is equal to or higher than -70 kPaG.

In addition, according to a fifth aspect of the present invention, there is provided the hydrometallurgical process for  
25 a nickel oxide ore in the first aspect of the present invention, characterized in that, in the above operation (d), the above alkaline aqueous solution is an aqueous solution of sodium hydroxide, and use amount of sodium hydroxide is adjusted at 180 to 200 kg per 1 ton of input mass of nickel contained in  
30 the zinc free final solution to be introduced to the above step (3).

BRIEF DESCRIPTION OF THE DRAWINGS



5 Figure 1 is a drawing showing an example of a process chart of a hydrometallurgical process for a nickel oxide ore, according to a conventional High Pressure Acid Leach.

Figure 2 is a drawing showing relation between ratio of use amount of sodium hydroxide in a scrubber relative to input mass (t) of nickel contained in a zinc free final solution to be introduced to the step (3), and nickel recovery rate.

Figure 3 is a drawing showing relation between reactor volume relative to Ni load ( $m^3/kg/h$ ), and reaction pressure of a sulfurization reactor.

15 Figure 4 is a drawing showing relation between nickel recovery rate and reactor volume relative to Ni load ( $m^3/kg/h$ ).

NOTATION

- 1 step (1)
- 20 2 step (2)
- 3 step (3)
- 4 step (4)
- 5 nickel oxide ore
- 6 aqueous solution of crude nickel sulfate
- 25 7 leaching residue
- 8 zinc free final solution
- 9 zinc sulfide
- 10 mixed sulfide of nickel/cobalt
- 11 waste solution
- 30 12 exhaust gas

DETAILED DESCRIPTION OF THE INVENTION

The hydrometallurgical process for a nickel oxide ore of

5 the present invention is capable of reducing use amount of  
hydrogen sulfide gas in a sulfurization step, and use amount  
of an alkali to be used in exhaust gas treatment, and decreasing  
operation cost, by enhancement of utilization efficiency of  
hydrogen sulfide gas, while maintaining nickel recovery rate  
10 to a high yield of equal to or higher than 95%, and preferably  
equal to or higher than 98%, in the hydrometallurgical process  
for a nickel oxide ore using the above High Pressure Acid Leach,  
and thus industrial value thereof is extremely large.

15 Explanation will be given below in detail on the  
hydrometallurgical process for a nickel oxide ore of the present  
invention.

The hydrometallurgical process for a nickel oxide ore of  
the present invention is characterized in that at least one kind  
20 of the following operations (a) to (d) is adopted, in a  
hydrometallurgical process for a nickel oxide ore including:  
a step (1) for obtaining an aqueous solution of crude nickel  
sulfate containing zinc as an impurity element, in addition to  
nickel and cobalt, by High Pressure Acid Leach of a nickel oxide  
25 ore,

a step (2) for obtaining zinc sulfide and a zinc free final  
solution formed, by introduction of the above aqueous solution  
of crude nickel sulfate into the inside of a sulfurization  
reactor (A), then the addition of hydrogen sulfide gas,  
30 sulfurization of zinc contained in the aqueous solution of crude  
nickel sulfate, and then solid-liquid separation, a step (3)  
for obtaining a mixed sulfide of nickel/cobalt and a waste  
solution, by introduction of the above zinc free final solution

5 into the inside of a sulfurization reactor (B), then the addition  
of hydrogen sulfide gas, sulfurization of nickel and cobalt  
contained in the zinc free final solution, and subsequently  
introduction of slurry formed into an evaporation apparatus for  
evaporation of hydrogen sulfide gas, and then solid-liquid  
10 separation, and a step (4) for obtaining an exhaust gas scrubbed  
and a waste solution from a scrubber, by introduction of exhaust  
gas from the above sulfurization reactor (A), sulfurization  
reactor (B) or evaporation apparatus into the scrubber, and  
subjecting it to contact with an alkaline aqueous solution for  
15 absorption of hydrogen sulfide gas.

(a) to adjust a total volume ( $m^3$ ) of the sulfurization reactor  
(B) to be used, so that a ratio of 0.2 to 0.9 ( $m^3/kg/h$ ) is attained  
relative to input mass per unit hour ( $kg/h$ ) of nickel contained  
in the zinc free final solution to be introduced, in the above  
20 step (3);

(b) to evaporate under negative pressure, in evaporation of  
hydrogen sulfide gas dissolved in a solution from slurry  
generating in the above step (3), and to add the recovered  
hydrogen sulfide gas into the inside of the sulfurization  
25 reactor (B) of the above step (3);

(c) to reuse the hydrogen sulfide gas containing inert  
components from the sulfurization reactor (B), which gas is  
accumulated in the gas phase part thereof, by pressure control  
inside the sulfurization reactor (B), in the above step (3),  
30 and add it into the inside of the sulfurization reactor (A) of  
the above step (2), and

(d) to subject the waste solution in the above step (3) and  
exhaust gas scrubbed in the above step (4) to countercurrent

5 contact, and to introduce the resulting exhaust gas to the scrubber again, and to subject it to contact with the alkaline aqueous solution for absorption of hydrogen sulfide gas, and to charge the resulting waste solution from the scrubber into the sulfurization reactor (B) in the above step (3).

10

The hydrometallurgical process for a nickel oxide ore, which is a base in the method of the present invention, includes the following steps (1) to (4).

a step (1): to obtain an aqueous solution of crude nickel sulfate containing a zinc as an impurity element, in addition to nickel

15

and cobalt, by High Pressure Acid Leach of a nickel oxide ore;

a step (2): to obtain a zinc sulfide and a zinc free final solution formed, by introduction of the above aqueous solution of crude nickel sulfate into the inside of a sulfurization reactor (A),

20

then the addition of hydrogen sulfide gas, sulfurization of zinc contained in the aqueous solution of crude nickel sulfate, and then solid-liquid separation;

a step (3): to obtain a mixed sulfide of nickel/cobalt and a waste solution, by introduction of the above zinc free final

25

solution into the inside of a sulfurization reactor (B), then the addition of hydrogen sulfide gas, sulfurization of nickel and cobalt contained in the zinc free final solution, and subsequently introduction of slurry formed into an evaporation apparatus for evaporation of hydrogen sulfide gas, and then

30

solid-liquid separation; and

a step (4): to obtain an exhaust gas scrubbed and a waste solution from a scrubber, by introduction of exhaust gas from the above sulfurization reactor (A), sulfurization reactor (B) or

5 evaporation apparatus into the scrubber, and subjecting it to contact with an alkaline aqueous solution for absorption of hydrogen sulfide gas.

10 The above step (1) is a step for obtaining an aqueous solution of crude nickel sulfate containing zinc as an impurity element, in addition to nickel and cobalt, by High Pressure Acid Leach of a nickel oxide ore.

15 The above step (1), in detail, is composed of a leaching step for obtaining leached slurry, by the addition of sulfuric acid into slurry of a nickel oxide ore and leaching at a high temperature of equal to or high than 200°C under high pressure using an autoclave, a solid-liquid separation step for separation to the leaching residue in leached slurry and a leachate containing nickel and cobalt, and a neutralization step  
20 for forming the neutralized precipitate slurry containing impurity elements such as iron, and a starting solution for a sulfurization reaction scrubbed most parts of the impurity elements, by adjustment of pH of the leachate containing impurity elements, in addition to nickel and cobalt. Here, the  
25 High Pressure Acid Leach is not especially limited, and is one, for example, composed of operation to prepare the ore slurry by making the slurry of a nickel oxide ore; and leaching operation to obtain a leachate containing nickel and cobalt, by adding the sulfuric acid to the ore slurry transferred, still more  
30 blowing high pressure air as an oxidizing agent and high pressure steam as a heating source, stirring under control at predetermined temperature and pressure, and forming leached slurry composed of a leaching residue and a leachate. Here

5 leaching is carried out under pressure formed by predetermined  
temperature, for example, 3 to 6 MPaG, therefore, a reactor for  
high-temperature and high-pressure (autoclave) is used, which  
is capable of enduring these conditions. In this way, a leaching  
rate of each of nickel and cobalt of equal to or higher than  
10 90%, and preferably equal to or higher than 95% is obtained.

The above nickel oxide ore is so-called a lateritic ore  
such as limonite and saprolite. Nickel content in the above  
lateritic ore is usually 0.5 to 3.0% by mass, and is contained  
15 as a hydroxide or a silicic bittern (magnesium silicate) mineral.  
In addition, iron content is 10 to 50% by mass, and iron is  
contained mainly as a trivalent hydroxide (goethite,  $\text{FeOOH}$ ),  
however, divalent iron is partially contained in the silicic  
bittern mineral.

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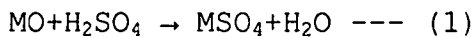
The above slurry concentration is not especially limited,  
because it depends largely on properties of a nickel oxide ore  
to be treated, however, the leached slurry of higher  
concentration is preferable, and usually adjusted at about 25  
25 to 45% by mass. That is, the leached slurry with a concentration  
lower than 25% by mass requires a large apparatus to obtain the  
same residence time in leaching, and also the addition amount  
of an acid increases for adjustment of the residual acid  
concentration. In addition, the resulting leachate has lower  
30 nickel concentration. In contrast, the leached slurry with a  
concentration over 45% by mass increases viscosity (yield  
stress) of slurry itself, and causes a problem of difficult  
transfer (frequent pipe clogging, high energy requirement etc.),

5 although it requires smaller facility scale.

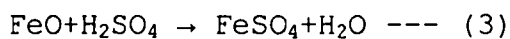
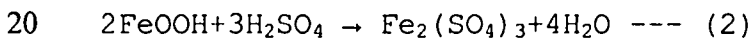
In the above leaching operation, nickel and cobalt and the like are leached as a sulfate and leached iron sulfate is fixed as hematite, by the leach reaction and the high-temperature hydrolysis represented by the following formulae (1) to (5).  
 10 However, because fixation of iron ions does not entirely proceed, the divalent and trivalent iron ions are usually contained, besides nickel and cobalt and the like, in a liquid part of the resulting leached slurry.

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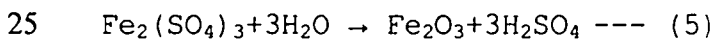
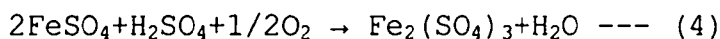
[leaching reaction]



(wherein M represents Ni, Co, Fe, Zn, Cu, Mg, Cr, Mn or the like.)



[high-temperature hydrolysis]



Temperature to be used in the above leaching operation is not especially limited, however, it is preferably 220 to 280°C, and more preferably 240 to 270°C. That is, iron is fixed as hematite mostly by carrying out the reaction in this temperature  
 30 range. In the temperature below 220°C, iron dissolves and remains in the reaction solution, due to low rate of the high-temperature thermal hydrolysis, resulting in increase in

5 load in the subsequent neutralization step for removing the iron,  
which makes it very difficult to separate the iron from nickel.  
In contrast, the temperature over 280°C is not suitable, because  
not only selection of a material of a reactor to be used for  
High Pressure Acid Leach is difficult but also cost of steam  
10 for raising temperature increases, although the  
high-temperature thermal hydrolysis itself is promoted.

Amount of sulfuric acid to be used in the above leaching  
operation is not especially limited, and an excess amount is  
15 used so as to leach iron in an ore, for example, the amount of  
200 to 500 kg per ton of the ore is used, the addition amount  
of sulfuric acid over 500 kg per one ton of the ore, is not  
preferable, due to increased cost of the sulfuric acid. It  
should be noted that pH of the resulting leachate is preferably  
20 adjusted at 0.1 to 1.0, considering filterability of the  
leaching residue containing hematite generated in the  
solid-liquid separation step.

The above step (2) is a step for obtaining zinc sulfide  
25 and the zinc free final solution formed, by introduction of the  
aqueous solution of crude nickel sulfate containing zinc as an  
impurity element in addition to nickel and cobalt into the inside  
of the sulfurization reactor (A), then the addition of hydrogen  
sulfide gas, sulfurization of zinc contained in the relevant  
30 aqueous solution of crude nickel sulfate, and then solid-liquid  
separation.

It should be noted that this step is one to prevent the  
commingling of zinc into the mixed sulfide of nickel/cobalt



5 recovered in the subsequent step (3). Here conditions of the sulfurization reaction are not especially limited, and such conditions are used that zinc is sulfurized preferentially against nickel and cobalt, by the sulfurization reaction.

10 It should be noted that, in the case where zinc amount contained in the above aqueous solution of crude nickel sulfate is low in a degree not to raise a problem of quality thereof, when zinc is commingled to the mixed sulfide of nickel/cobalt to be formed in the later step, the step (2) may be omitted.

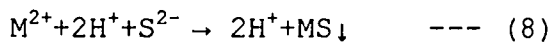
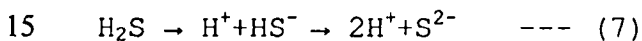
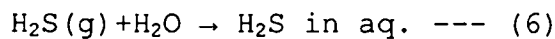
15 The above step (3) is one for obtaining the mixed sulfide of nickel/cobalt and the waste solution, by introduction of the zinc free final solution obtained in the above step (2) into the inside of the sulfurization reactor (B), then the addition of hydrogen sulfide gas, sulfurization of nickel and cobalt  
20 contained in the relevant zinc free final solution, subsequent introduction of slurry formed to the evaporation apparatus for evaporation of hydrogen sulfide gas, and then solid-liquid separation. It should be noted that evaporation of hydrogen sulfide gas from the slurry is carried out for scrubbing  
25 treatment of the waste solution.

In the above steps (2) and (3), the method for the addition of hydrogen sulfide gas into the inside of the sulfurization reactors (A) and (B), is not especially limited, however, the  
30 addition is carried out by blowing the solution introduced into the sulfurization reactors, into the upper space part (vapor part) or the solution of the sulfurization reactors, under stirring mechanically. It should be noted that as the

5 sulfurization reactors to be used, a closed-type reactor is preferable, which is equipped with a supply port of a reaction starting solution, a outlet of slurry after the reaction, a charge hole of hydrogen sulfide gas and an exhaust gas hole.

10 The sulfurization reaction to be used in the above steps (2) and (3), is represented by the following formulae (6) to (8):

[sulfurization reaction]



(wherein M represents Ni, Co, Zn or the like.)

Here, firstly, hydrogen sulfide gas added into the inside  
 20 of the sulfurization reactor requires a dissolving reaction of the hydrogen sulfide gas into water in the above formula (6), and dissolution of the hydrogen sulfide into water in the above formula (7). Here, concentration of dissolved hydrogen sulfide is generally proportional to pressure of hydrogen sulfide in  
 25 the vapor phase part, according to Henry's law. Therefore, in order to increase a vapor-liquid reaction rate, it is important to increase partial pressure of hydrogen sulfide in the vapor phase part. However, as described above, because the inert component is contained in hydrogen sulfide gas to be added,  
 30 accumulation of the inert component inside the sulfurization reactor decreases the reaction rate. Therefore, gas of the inert component accumulated was periodically discharged by pressure control inside the sulfurization reactor. That is,

5 supply of hydrogen sulfide gas into the inside of the  
sulfurization reactor took a system for controlling pressure  
inside the sulfurization reactor at 50 to 70% of supply pressure  
of hydrogen sulfide, and such a discharge system was taken that  
in the timing when pressure inside the sulfurization reactor  
10 increased to over control pressure by accumulating the inert  
component, vapor forming the vapor phase of the sulfurization  
reactor was discharged from a pressure control valve of the  
sulfurization reactor. Here, the inert component is  
accumulated in vapor forming the above vapor phase, and by  
15 discharging it from the sulfurization reactor, the above  
accumulation was eliminated, however, hydrogen sulfide was also  
discharged accompanying therewith.

Next, by the reaction of the above formula (8), the metal  
ion in the solution forms a sulfide and is precipitated, however,  
20 because zinc provides higher reaction rate as compared with  
nickel or cobalt by setting suitable conditions, separation of  
zinc is carried out preferentially firstly in the step (2).

In the sulfurization reaction to be used in the above step  
25 (3), seed crystal composed of a sulfide containing nickel and  
cobalt produced, may be charged into the sulfurization reactor  
(B), if necessary. Here, ratio of the seed crystal is not  
especially limited, however, it is preferable to be 150 to 200%  
by mass, relative to amount of nickel and cobalt to be charged  
30 into the sulfurization reactor (B). In this way, it is possible  
to promote the sulfurization reaction at lower temperature, and  
at the same time to suppress adhesion of a generated sulfide  
onto the inner surface of the reactor. That is, it is the result

5 of the facts that an easy deposition state is given by generation  
of nucleus formation of the sulfide at the surface of the seed  
crystal, and generation of a fine nucleus of the sulfide inside  
the reactor is suppressed thereby. In addition, by adjustment  
of particle size of the seed crystal, the resulting particle  
10 size can be controlled.

Temperature to be used in the above sulfurization reaction  
is not especially limited, however, 65 to 90°C is preferable.  
That is, generally the higher temperature promotes much more  
15 the sulfurization reaction itself, however, the temperature  
over 90°C raises many problems such as cost increase for raising  
the temperature, adhesion of a sulfide onto the reactor, due  
to high reaction rate.

20 The above step (4) is a step for obtaining a scrubbed exhaust  
gas and a waste solution from the scrubber, by introduction of  
exhaust gas from the sulfurization reactor (A) of the above step  
(2), the sulfurization reactor (B) of the above step (3), or  
the evaporation apparatus of the above step (3), and subjecting  
25 it to contact with the alkaline aqueous solution for absorption  
of hydrogen sulfide gas.

The scrubber to be used in the above step (4) is not  
especially limited, and for example, such a type is used, that  
30 carries out effectively contact between the alkaline aqueous  
solution and exhaust gas, such as a scrubbing tower.

In the smelting method of the present invention,

5 enhancement of utilization efficiency of hydrogen sulfide gas  
by adoption of at least one kind of operations of the above (a)  
to (d), has important technological significance, in the  
hydrometallurgical process for a nickel oxide ore including the  
above steps (1) to (4). In this way, although use amount of  
10 hydrogen sulfide gas was conventionally about 1.3 to 1.4 time  
hydrogen sulfide amount required theoretically in view of the  
sulfurization reaction (formulae (6) to (8)), it can be  
decreased down to below 1.3 time, preferably down to 1.05 to  
1.15 time. In addition, in the operations of (a) to (c), amount  
15 of the alkali to be used in exhaust gas treatment is also  
decreased, accompanying with decrease in use amount of hydrogen  
sulfide gas.

Explanation will be given below on operations thereof, as  
well as action effect thereof.

20

(1) Operation of (a)

Operation of the above (a) is one for adjusting the total  
volume ( $m^3$ ) of the sulfurization reactor (B) to be used in the  
step (3), in the hydrometallurgical process for a nickel oxide  
25 ore including the above steps (1) to (4), so that total volume  
becomes a ratio of 0.2 to 0.9 ( $m^3/kg/h$ ), preferably 0.6 to 0.9  
( $m^3/kg/h$ ), relative to input mass per unit hour ( $kg/h$ ) of nickel  
contained in the zinc free final solution to be introduced. In  
this way, by sufficient securing of reaction time of the  
30 sulfurization reaction, utilization rate of hydrogen sulfide  
gas is increased, as well as by promotion of sulfurization of  
nickel and cobalt, recovery rate is enhanced. It should be noted  
that use amount of hydrogen sulfide gas can be decreased to 1.1

5 to 1.2 time of hydrogen sulfide amount required theoretically  
in view of the sulfurization reaction.

That is, because sulfurization reaction rate of nickel and  
cobalt is lower as compared with zinc, countermeasures by  
10 increase in reaction temperature or control pressure is  
considered in order to enhance recovery rate, however, it is  
not preferable due to incurring cost increase for temperature  
increase or deterioration of utilization rate of hydrogen  
15 sulfide in exhaust gas. In addition, implementation of a  
high-pressure reaction requires enhancement of pressure-proof  
specifications of an apparatus, which causes increase in  
apparatus cost. Therefore, operational importance of the  
apparatus of the sulfurization step is to secure sufficient  
20 reaction time, for example, by adjusting the total volume ( $m^3$ )  
of the sulfurization reactor (B) to be used in the step (3),  
so that total volume becomes a ratio of 0.2 to 0.9 ( $m^3/kg/h$ ),  
relative to input mass per unit hour ( $kg/h$ ) of nickel contained  
in the zinc free final solution to be introduced, inner pressure  
25 of the sulfurization reactor (B) can be controlled at equal to  
or lower than 300 kPaG. In addition, by adjusting the total  
volume ( $m^3$ ) of the above sulfurization reactor (B) so that total  
volume becomes a ratio of 0.6 to 0.9 ( $m^3/kg/h$ ), relative to input  
mass per unit hour ( $kg/h$ ) of nickel contained in the zinc free  
30 final solution to be introduced, inner pressure of the  
sulfurization reactor (B) can be controlled at equal to or lower  
than 200 kPaG, and also a recovery rate of nickel of equal to  
or higher than 98% can be attained.

5

Although the operation of the above (a) can be attained, for example, by scale up of the sulfurization reactor (B), extreme scale up of the sulfurization reactor itself raises problems in view of uniform dispersion of hydrogen sulfide gas into a solution, cost of stirring power and capital investment, and thus it is not especially limited, however, it is preferable industrially to use 3 or 4 units of reactors connected in series. It should be noted here that supply of hydrogen sulfide gas into each of the reactors connected in series is preferably carried out separately so that inner pressure of each of the reactors is controlled at predetermined value. In addition, slurry inside each of the reactors connected in series is transferred in continuous flow from the first stage, to which the zinc free final solution is charged, to the last stage, from which slurry after completion of the reaction is extracted.

(2) Operation of (b)

Operation of the above (b) is one for the addition of recovered hydrogen sulfide gas into the inside of the sulfurization reactor (B) of the above step (3), by evaporation under negative pressure, in evaporation of hydrogen sulfide gas dissolved in a solution, from slurry generated in the above step (3), in the hydrometallurgical process for a nickel oxide ore including the above steps (1) to (4). That is, it is one for recovering the dissolved hydrogen sulfide gas from slurry after completion of the sulfurization reaction by evaporation, to repeatedly re-utilize it in the sulfurization reactor (B). In this way, effective utilization is possible to maintain

5 concentration of hydrogen sulfide dissolved in a solution, which  
is required to progress the sulfurization reaction. Therefore,  
it becomes possible not only to decrease charge amount of new  
hydrogen sulfide gas but also to extremely decrease load of the  
scrubbing apparatus for scrubbing hydrogen sulfide gas from the  
10 above waste solution. In this way, it is possible to decrease  
use amount of hydrogen sulfide gas down to about 1.1 to 1.2 time  
of hydrogen sulfide amount required theoretically in view of  
the sulfurization reaction.

15 The operation of the above (b) is attained, for example,  
by introducing slurry after completion of the sulfurization  
reaction, from the sulfurization reactor to a reactor which is  
maintained at a lower pressure state than that of the  
sulfurization reactor, preferably at a negative pressure state,  
20 by a pressure decreasing fan or the like, and evaporating the  
dissolved hydrogen sulfide gas, and then transferring it to the  
sulfurization reactor by a gas compression apparatus or the like,  
after removing steam from the evaporated gas by a cooling  
apparatus or the like.

25

In the operation of the above (b), the above pressure is  
not especially limited, as long as it is a negative pressure  
of equal to or lower than 0 kPaG, however, the negative pressure  
is preferably equal to or higher than -70 kPaG. That is, the  
30 negative pressure lower than -70 kPaG causes a problem of  
pressure resistance of a reactor to be used in the sulfurization  
reactor.



## 5 (3) Operation of (c)

Operation of the above (c) is one for reusing, from the relevant sulfurization reactor (B), hydrogen sulfide gas containing inert components such as hydrogen, nitrogen or the like accumulated in the gas phase part thereof, by pressure control inside the sulfurization reactor (B) to be used in the above step (3), and adding them into the sulfurization reactor (A) of the above step (2), in the hydrometallurgical process for a nickel oxide ore including the above steps (1) to (4). In this way, it becomes possible to effectively utilize hydrogen sulfide gas containing the inert components, which was conventionally discharged periodically outside the system, as low concentration hydrogen sulfide gas, for the sulfurization reaction of zinc in the sulfurization reactor (A), and thus utilization rate of hydrogen sulfide gas is enhanced, as well as use amount of the alkali in the scrubbing treatment can be saved and decreased. In this way, it becomes possible to decrease use amount of hydrogen sulfide gas down to about 1.1 to 1.2 time of hydrogen sulfide amount required theoretically in view of the sulfurization reaction.

25

In the operation of the above (c), reuse of hydrogen sulfide gas containing the inert components accumulated in the vapor phase part inside the sulfurization reactor (B), is not especially limited, however, it is carried out so that concentration of hydrogen or nitrogen in the vapor phase part is over predetermined value, as a guideline.

30

## (4) Operation of (d)

5           Operation of the above (d) is one for subjecting the waste  
solution in the above step (3) and exhaust gas scrubbed in the  
above step (4), to countercurrent contact, then introducing the  
resulting exhaust gas to the scrubber again to subject it to  
10           contact with the alkaline aqueous solution for absorption of  
hydrogen sulfide gas, and charging the resulting waste solution  
from the scrubber into the sulfurization reactor (B) in the above  
step (3). In this way, hydrogen sulfide contained in trace  
amount in the waste solution after evaporation treatment, is  
15           transferred into exhaust gas, and can be recovered in the waste  
solution from the scrubber, and thus can be utilized effectively  
as a sulfurizing agent. Here, it becomes possible to decrease  
use amount of hydrogen sulfide gas down to about 1.1 to 1.2 time  
of hydrogen sulfide amount required theoretically in view of  
the sulfurization reaction.

20

          The alkaline aqueous solution to be used in the operation  
of the above (d) is not especially limited, and an aqueous  
solution of sodium hydroxide is used preferably. Explanation  
will be given below on use amount of sodium hydroxide in the  
25           scrubber here and nickel recovery rate in the step (3).

          Figure 2 shows relation between ratio of use amount (kg)  
of sodium hydroxide in a scrubber, relative to input mass (t)  
of nickel contained in a zinc free final solution to be introduced  
to the step (3), and nickel recovery rate.

30

          It is found from Figure 2 that use amount of sodium hydroxide  
in the operation of (d) is not especially limited, however, it  
is preferable to be adjusted at 180 to 200 kg per 1 ton of input  
mass of nickel contained in the zinc free final solution to be

5 introduced to the step (3). In this way, a nickel recovery rate of equal to or higher than 98% is attained.

[Examples]

10 Explanation will be given below in further detail on the present invention with reference to Examples of the present invention, however, the present invention should not be limited to these Examples. It should be noted that analysis of metals used in Examples was carried out with an ICP emission spectrometry.

15

(Example 1)

20 Explanation will be given on the case of using the operation of (a) of the hydrometallurgical process for of the present invention. Firstly, according to the process chart shown in Figure 1, a zinc sulfide and a zinc free final solution were obtained in the step (2), from an aqueous solution of crude nickel sulfate produced from the step (1) of the High Pressure Acid Leach for a nickel oxide ore. It should be noted that the following explanation will relate to volume of a closed-type sulfurization reactor in obtaining a mixed sulfide of nickel/cobalt and a waste solution, by using the above zinc free  
25 final solution in the step (3).

30 As the aqueous solution of crude nickel sulfate, nickel, cobalt, iron and zinc were contained in concentrations of 3 to 4 g/L, 0.2 to 0.4 g/L, 1 to 2 g/L and 0.05 to 0.2 g/L, respectively, and pH was 3.5. In addition, as a closed-type sulfurization reactor of the step (3), three units of the closed-type sulfurization reactors, with a volume of 0.15 m<sup>3</sup> per one unit,

5 connected in series, were used.

By continuous introduction of hydrogen sulfide gas with 98% by volume produced in the hydrogen sulfide gas production facility into the inside of the above closed-type sulfurization reactor, operation of the sulfurization reaction was carried out to determine relation between ratio of total volume ( $m^3$ ) of the sulfurization reactor (B) relative to input mass per unit hour (kg/h) of nickel contained in the zinc free final solution to be introduced here, and reaction pressure of the sulfurization reactor, or nickel recovery rate. Results are shown each in Figure 3 and Figure 4. It should be noted that the nickel recovery rate was determined from ratio of nickel weight recovered as a sulfide, relative to nickel weight in the aqueous solution of crude nickel sulfate introduced into the sulfurization reactor, by operation of the sulfurization reaction.

Figure 3 shows relation between ratio of total volume ( $m^3$ ) of the sulfurization reactor (B) relative to input mass per unit hour (kg/h) of nickel contained in the zinc free final solution to be introduced ("reactor volume relative to Ni load ( $m^3/kg/h$ )" in this drawing), and reaction pressure of the sulfurization reactor, when the nickel recovery rate of 95 to 99% was obtained. It should be noted here that result is also shown at the same time in the case where a reactor with  $0.25 m^3$  was connected in front of the first unit of the above three units of the connected reactors, to form four units in total connected in series.

It is found from Figure 3 that by adjusting the reactor

5 volume relative to Ni load ( $\text{m}^3/\text{kg}/\text{h}$ ), so that volume becomes a  
ratio of 0.2 to 0.9, inner pressure of the sulfurization reactor  
(B) can be controlled at equal to or lower than 300 kPaG, and  
by adjusting the reactor volume relative to Ni load ( $\text{m}^3/\text{kg}/\text{h}$ ),  
so that volume becomes a ratio of 0.6 to 0.9 ( $\text{m}^3/\text{kg}/\text{h}$ ), inner  
10 pressure of the sulfurization reactor (B) can be controlled at  
equal to or lower than 200 kPaG.

Figure 4 shows relation between nickel recovery rate in  
the case where solution flow amount was changed variously under  
15 condition of the inner pressure of the sulfurization reactor  
fixed at constant value, and ratio of total volume ( $\text{m}^3$ ) of the  
sulfurization reactor (B) relative to input mass per unit hour  
(kg/h) of nickel contained in the zinc free final solution to  
be introduced ("reactor volume, relative to Ni load ( $\text{m}^3/\text{kg}/\text{h}$ )"  
20 in this drawing).

It is understood from Figure 4 that by setting the reactor  
volume relative to Ni load ( $\text{m}^3/\text{kg}/\text{h}$ ), to be equal to or higher  
than 0.6, a nickel recovery rate of equal to or higher than 98%  
can be obtained.

25 As described above, because sufficient nickel recovery  
rate can be obtained under condition of decreased inner pressure  
of the sulfurization reactor (B) to 300 kPaG, preferably equal  
to or lower than 200 kPaG, utilization rate of hydrogen sulfide  
gas increases. In this case, use amount of hydrogen sulfide gas  
30 was able to decrease down to 1.2 time of hydrogen sulfide amount  
required theoretically in view of the sulfurization reaction.

(Example 2)

5 Explanation will be given on the case using the operations  
of (a) and (d) of the hydrometallurgical process for of the  
present invention. Firstly, according to the process chart  
shown in Figure 1, a mixed sulfide of nickel/cobalt and a waste  
solution were obtained in the step (3), using the zinc free final  
10 solution after separation of zinc as a sulfide in the step (2)  
from the aqueous solution of crude nickel sulfate produced from  
the step (1) of the High Pressure Acid Leach for a nickel oxide  
ore. It should be noted that the following explanation will  
relate to the waste solution obtained in the step (3) and the  
15 waste solution from the scrubber obtained in the step (4).

The aqueous solution of crude nickel sulfate and the  
closed-type sulfurization reactor of the step (3) were similar  
as in Example 1. In addition, the reactor volume relative to  
Ni load ( $\text{m}^3/\text{kg}/\text{h}$ ) was adjusted at 0.6.

20 Here, the waste solution in the above step (3) and exhaust  
gas scrubbed in the above step (4) were subjected to contacting,  
in counter-flow, by using a scrubbing tower, and then the  
resulting exhaust gas was introduced again into the scrubber  
for absorption of hydrogen sulfide gas, by being subjected to  
25 contact with the aqueous solution of sodium hydroxide, and the  
resulting waste solution from the scrubber was charged into the  
sulfurization reactor (B) of the above step (3). It should be  
noted here that in the scrubber, the aqueous solution of sodium  
hydroxide, with a concentration of 25% by mass, was used, and  
30 use amount of sodium hydroxide was adjusted at 190 kg per 1 ton  
of input mass of nickel contained in the zinc free final solution  
to be introduced to the step (3).

In this case, use amount of hydrogen sulfide gas was able

5 to decrease down to 1.06 time of hydrogen sulfide amount required theoretically in view of the sulfurization reaction. In addition, nickel recovery rate was 98%.

(Example 3)

10 Explanation will be given on the case of using the operations of (a) and (b) of the hydrometallurgical process for of the present invention. Firstly, according to the process chart shown in Figure 1, a mixed sulfide of nickel/cobalt and a waste solution were obtained in the step (3), using the zinc  
15 free final solution after separation of zinc as a sulfide in the step (2) from the aqueous solution of crude nickel sulfate produced from the step (1) of the High Pressure Acid Leach for a nickel oxide ore. It should be noted that the following explanation will relate to the waste solution obtained in the  
20 step (3).

The aqueous solution of crude nickel sulfate and the closed-type sulfurization reactor of the step (3) were similar as in Example 1. In addition, the reactor volume relative to Ni load ( $\text{m}^3/\text{kg}/\text{h}$ ) was adjusted at 0.6.

25 Here, slurry discharged from the sulfurization reactor at the final stage was introduced into a reactor maintained at a negative pressure state of -68 kPaG by a pressure decreasing fan, and hydrogen sulfide gas dissolved in the solution was evaporated, and then charged to the sulfurization reactor (B)  
30 by a compressor, after removing steam from the evaporated gas by cooling.

In this case, use amount of hydrogen sulfide gas was able to decrease down to 1.08 time of hydrogen sulfide amount required

5 theoretically in view of the sulfurization reaction. In addition, nickel recovery rate was 98%.

(Example 4)

Explanation will be given on the case using the operations  
10 of (a) and (c) of the hydrometallurgical process for of the present invention. Firstly, according to the process chart shown in Figure 1, a mixed sulfide of nickel/cobalt and a waste solution were obtained in the step (3), using the zinc free final solution after separation of zinc as a sulfide in the step (2)  
15 from the aqueous solution of crude nickel sulfate produced from the step (1) of the High Pressure Acid Leach for a nickel oxide ore. It should be noted that the following explanation will relate to the exhaust gas obtained in the step (3).

The aqueous solution of crude nickel sulfate and the  
20 closed-type sulfurization reactor of the step (3) were similar as in Example 1. In addition, the reactor volume relative to Ni load ( $\text{m}^3/\text{kg}/\text{h}$ ), was adjusted at 0.6

Here, exhaust gas extracted from the sulfurization reactor was charged inside the sulfurization reactor of the step (2).  
25 In this case, use amount of hydrogen sulfide gas was able to decrease down to 1.07 time of hydrogen sulfide amount required theoretically in view of the sulfurization reaction. In addition, nickel recovery rate was 98%.

30 From the above, it is understood that, in Examples 1 to 4, by adoption of at least one kind of the above (a) to (d), in the hydrometallurgical process for a nickel oxide ore including the above steps (1) to (4), use amount of hydrogen



5 sulfide gas can decrease down to 1.05 to 1.2 time of hydrogen sulfide amount required theoretically in view of the sulfurization reaction, which was conventionally 1.3 to 1.4 time.

10 As is clear from the above, the hydrometallurgical process for a nickel oxide ore of the present invention, is suitable as the hydrometallurgical process for a nickel oxide ore, which is capable of enhancing utilization efficiency of hydrogen sulfide gas, while maintaining nickel recovery rate to a high  
15 yield in the mixed sulfide of nickel/cobalt, in the hydrometallurgical process for a nickel oxide ore using the above High Pressure Acid Leach.

5 THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A hydrometallurgical process for a nickel oxide ore comprising:

10 a step (1) for obtaining an aqueous solution of crude nickel sulfate containing zinc as an impurity element, in addition to nickel and cobalt, by High Pressure Acid Leach of a nickel oxide ore;

15 a step (2) for obtaining zinc sulfide and a zinc free final solution formed, by introduction of the above aqueous solution of crude nickel sulfate into the inside of a sulfurization reactor (A), then the addition of hydrogen sulfide gas, sulfurization of zinc contained in said aqueous solution of crude nickel sulfate, and then solid-liquid separation;

20 a step (3) for obtaining a mixed sulfide of nickel/cobalt and a waste solution, by introduction of the above zinc free final solution into the inside of a sulfurization reactor (B), then the addition of hydrogen sulfide gas, sulfurization of nickel and cobalt contained in said zinc free final solution, and subsequently introduction of slurry formed into an evaporation apparatus for evaporation of hydrogen sulfide gas, and then solid-liquid separation; and

25 a step (4) for obtaining an exhaust gas scrubbed and a waste solution from a scrubber, by introduction of exhaust gas from the above sulfurization reactor (A), sulfurization reactor (B) or evaporation apparatus into the scrubber, and subjecting it to contact with an alkaline aqueous solution for absorption of hydrogen sulfide gas;

30 characterized in that at least one kind of the following

5 operations (a) to (d) is adopted:

(a) to adjust a total volume ( $m^3$ ) of the sulfurization reactor (B) to be used, so that a ratio of 0.2 to 0.9 ( $m^3/kg/h$ ) is attained relative to input mass per unit hour ( $kg/h$ ) of nickel contained in the zinc free final solution to be introduced, in the above  
10 step (3);

(b) to evaporate under negative pressure, in evaporation of hydrogen sulfide gas dissolved in a solution of said slurry in the above step (3), and to add the recovered hydrogen sulfide gas into the inside of the sulfurization reactor (B) of the above  
15 step (3);

(c) to reuse the hydrogen sulfide gas containing inert components from said sulfurization reactor (B), which gas is accumulated in the gas phase part thereof, by pressure control inside the sulfurization reactor (B), in the above step (3),  
20 and add it into the inside of the sulfurization reactor (A) of the above step (2), and

(d) to subject the waste solution in the above step (3) and exhaust gas scrubbed in the above step (4) to countercurrent contact, and to introduce the resulting exhaust gas to the  
25 scrubber again, and to subject it to contact with the alkaline aqueous solution for absorption of hydrogen sulfide gas, and to charge the resulting waste solution from the scrubber into the sulfurization reactor (B) in the above step (3).

30 2. The hydrometallurgical process for a nickel oxide ore according to claim 1, characterized in that, in the above operation (a), the above ratio is 0.6 to 0.9 ( $m^3/kg/h$ ).

- 5 3. The hydrometallurgical process for a nickel oxide ore according to claim 1, characterized in that, in the above operation (a), the sulfurization reactor (B) comprises three or four units of reactors connected in series.
- 10 4. The hydrometallurgical process for a nickel oxide ore according to claim 1, characterized in that, in the above operation (b), the above negative pressure is equal to or higher than -70 kPaG.
- 15 5. The hydrometallurgical process for a nickel oxide ore according to claim 1, characterized in that, in the above operation (d), the above alkaline aqueous solution is an aqueous solution of sodium hydroxide, and use amount of sodium hydroxide is adjusted at 180 to 200 kg per 1 ton of input mass of nickel  
20 contained in the zinc free final solution to be introduced into the above step (3).

Figure 1

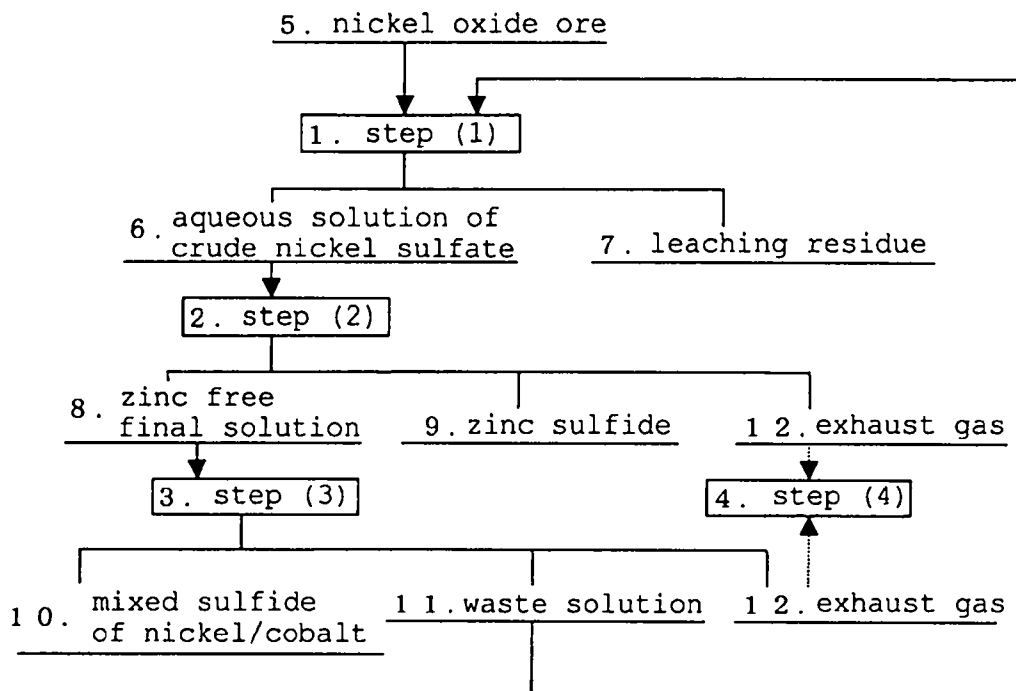


Figure 2

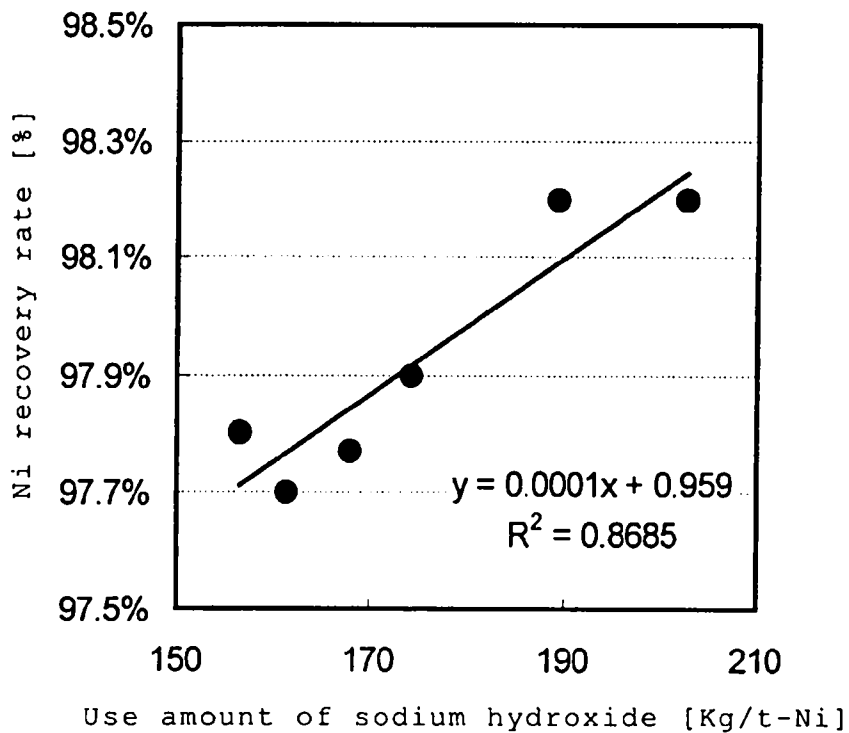


Figure 3

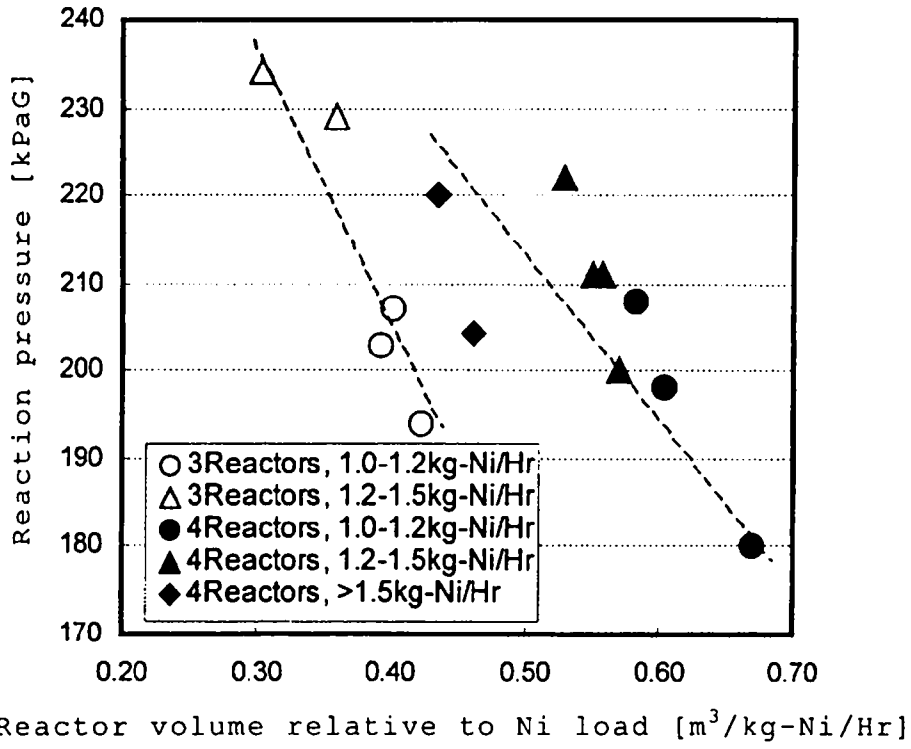


Figure 4

