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(71) Applicant(s)

Sumitomo Metal Mining Company Limited
(Incorporated in Japan)
11-3 5-chome Shinbashi, Minato-ku, Tokyo, Japan

(72) Inventor(s)

Susumu Makino
Naoyuki Tsuchida
Masaki Imamura
Kazuyuki Takaishi
Yoshitomo Ozaki

(74) Agent and/or Address for Service

Withers & Rogers
4 Dyer's Buildings, Holborn, LONDON, EC1N 2QP,
United Kingdom

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(54) Abstract Title

Solvent extraction of nickel sulfate

(57) The method of purifying nickel sulfate uses a multi-stage, counter-current, organic solvent extraction system composed of a least two extractors connected in series, and comprises a first extraction step of feeding a crude nickel sulfate solution that contains impurities of essentially sodium and ammonium into a second-stage extractor, followed by processing therein the crude nickel sulfate solution with an organic extractant having been fed into the second-stage extractor from the first-stage extractor, within a pH range falling between 6.5 and 7.0 in a manner of counter-current extraction reaction therebetween to thereby extract a part of nickel existing in the crude nickel sulfate solution into the organic extractant; and a second extraction step of transferring the nickel-containing organic phase, while transferring the crude nickel sulfate solution, which has been processed in the first extraction step and from which a part of nickel has been removed, to the first-stage extractor, followed by further processing therein the thus-transferred crude nickel sulfate solution with a fresh organic extractant, within pH range falling between 5.5 and 6.5 in a counter-current extraction reaction therebetween to thereby extract the remaining part of nickel still existing in the crude nickel sulfate solution into the organic extractant. In the method, the nickel-containing organic phase as separated in the second extraction step is divided into two portions, one of these portions being used as the organic extractant to be fed into the second-stage extractor and the other being transferred to a by-pass, organic phase-scrubbing step of scrubbing it to remove sodium and ammonium from the thus-transferred, nickel-containing organic phase.

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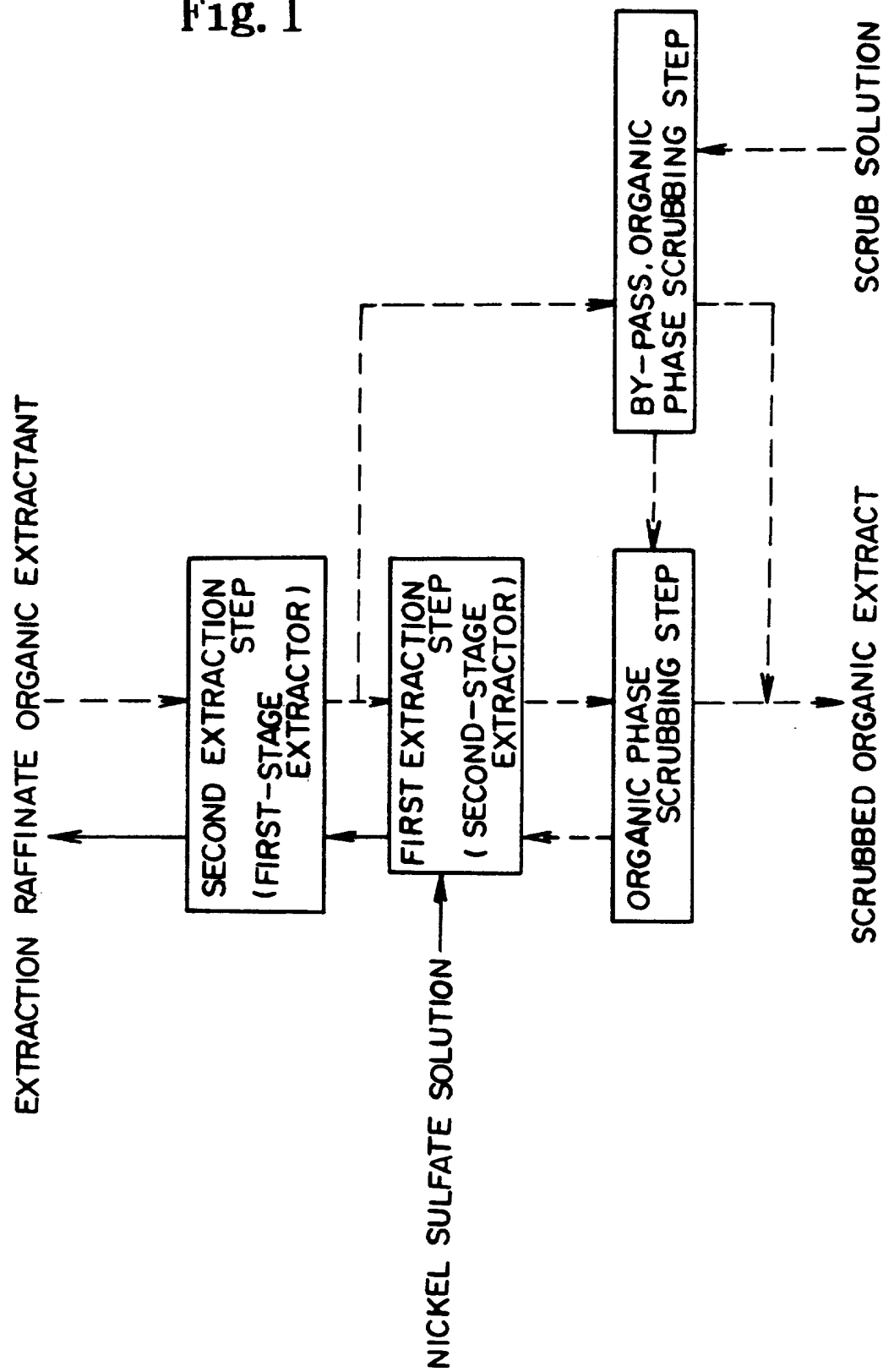


Fig. 1

METHOD OF SOLVENT EXTRACTION OF NICKEL SULFATE**FIELD OF THE INVENTION**

The present invention relates to a method of two-stage solvent extraction for removing ammonia, sodium and other impurities from an aqueous solution of nickel.

BACKGROUND OF THE INVENTION

Regarding the industrial uses of nickel, for example, nickel sulfate is popularly used not only in ordinary electroplating but also in electroless nickel plating for computer hard discs. Recently, in addition, nickel sulfate is being much used as the material of nickel for secondary batteries.

For some of those uses, the amount of impurities such as ammonia, sodium, and others existing in a crude nickel sulfate solution is often required to be minimized as much as possible. To purify nickel sulfate, organic solvent extraction has heretofore been employed. The method of organic solvent extraction using an acid extractant requires a neutralizer both for removing the impurities from the starting crude solution by extracting them into the extractant and for extracting nickel therefrom into the extractant. As the neutralizer, in general, sodium hydroxide is popularly used, as being easy to handle. Using sodium hydroxide as the neutralizer, however, involves introduction of sodium into the organic phase. As a result, even when the purified nickel sulfate solution is concentrated

to give crystals of nickel sulfate, it is extremely difficult to prevent the crystals from being contaminated with sodium.

More concretely, for example, in the conventional method of removing cobalt, calcium and other impurities from a crude nickel sulfate solution through solvent extraction using an acid extractant, mostly used is an organic acid extractant such as an alkyl phosphonic acid or its ester as the acid extractant. In this, however, sodium or sodium hydroxide that is used as a pH-adjusting neutralizer shall naturally remain in the organic phase, resulting in that the crystals of nickel sulfate as formed from the purified nickel sulfate solution shall naturally contain sodium. On the other hand, when nickel is extracted from a crude nickel sulfate solution into such an organic acid extractant through solvent extraction, a large amount of sodium shall be extracted into the organic phase. Even when the resulting extract is stripped with a mineral acid such as sulfuric acid, most sodium moves into the strip solution, resulting in that the crystals of nickel sulfate to be obtained shall be contaminated with sodium.

Accordingly, in the solvent extraction method using an organic acid extractant for purifying nickel, the nickel-containing, organic phase must be scrubbed completely to separate and remove the sodium component from the organic phase. However, this scrubbing is uneconomical and disadvantageous, as it requires a large amount of scrub solution and as the nickel loss in the scrub raffinate is great. In addition, the

scrubbing is troublesome since it requires the treatment of the scrub raffinate.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an advantageous method of purifying a nickel sulfate solution through solvent extraction, in which sodium, ammonia and other impurities in the organic phase separated are economically removed to efficiently give a high-purity nickel sulfate solution.

The invention that attains the object as above is characterized by a method of solvent extraction of nickel sulfate, which uses a two-stage, counter-current, organic solvent extraction system composed of two extractors as connected in series, and which comprises a first extraction step of feeding a crude nickel sulfate solution that contains impurities of essentially sodium and ammonium into a second-stage extractor, followed by processing therein the crude nickel sulfate solution with an organic extractant having been fed into the second-stage extractor from the first-stage extractor, within a pH range falling between 6.5 and 7.0 in a manner of counter-current extraction reaction therebetween to thereby make a part of nickel existing in the crude nickel sulfate solution extracted out into the organic extractant, and a second extraction step of transferring the nickel-containing, organic phase to an organic phase-scrubbing step of scrubbing it to remove sodium and ammonium from the thus-transferred,

nickel sulfate solution, which has been processed in the first extraction step and from which a part of nickel has been removed, to the first-stage extractor, followed by further processing therein the thus-transferred crude nickel sulfate solution with a fresh organic extractant, in a pH range of 5.5 to 6.5 in a manner of counter-current extraction reaction therebetween to thereby make the remaining part of nickel still existing in the crude nickel sulfate solution extracted out into the organic extractant, and in which the nickel-containing organic phase as separated in the second extraction step is divided into two portions, and one of these portions is used as the organic extractant to be fed into the second-stage extractor while the other is transferred to a by-pass, organic phase-scrubbing step of scrubbing it to remove sodium and ammonium from the thus-transferred, nickel-containing organic phase.

In the organic phase-scrubbing step in the method of the invention, it is preferable that the nickel-containing organic phase as separated in the first extraction step is scrubbed with scrub solution that contains nickel in an amount of at least 10 g/liter. In the by-pass, organic phase-scrubbing step therein, it is preferable that the nickel-containing organic phase as separated in the second extraction step is washed with scrub solution that contains nickel in an amount of at least 0.6 times the amount of nickel existing in the phase.

It is also preferable that at least a part of the wash waste as discharged in the by-pass, organic phase-scrubbing step is used as the scrub solution in the organic phase-scrubbing step.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a flowchart illustrating the outline of one preferred embodiment of the invention, in which nickel is extracted in a two-stage, counter-current extraction system.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

In solvent extraction using an organic acid extractant where nickel is extracted into the extractant from a crude nickel sulfate solution containing impurities of essentially sodium and ammonium, generally used is an alkyl phosphonic acid or its ester, such as Cyanex 272, D2EHPA, PC88A or the like, as the extractant. In this, it is desirable that the pH of the extractant is kept between 5 and 7 in consideration of the residual loss of nickel in the extraction residue. If the extraction is carried out at a pH higher than that raffinate, a large amount of sodium, ammonium and other impurities that may be extracted out into the extractant at a pH higher than the pH range suitable for nickel extraction and the removal of those impurities from the resulting organic phase is difficult. However, we, the present inventors have tried a specific two-stage extraction of a nickel sulfate solution, using a specific two-stage, counter-current, organic solvent extraction system composed of two extractors as connected in series, while transferring a part of the nickel-containing organic phase having been extracted in the system to a by-pass scrubbing step in which the thus-transferred extract is

scrubbed to thereby remove therefrom sodium, ammonium and other impurities still existing in the phase, and have succeeded in efficiently removing those impurities from the nickel-containing organic phase.

Fig. 1 is a flowchart illustrating the outline of one typical embodiment of the invention for solvent extraction of nickel sulfate. As illustrated, a crude nickel sulfate solution containing sodium, ammonium and other impurities is subjected to two-stage counter-current extraction with an organic acid extractant, in which are used at least two extractors as connected in series, whereby almost all nickel having existed in the starting, crude nickel sulfate solution is extracted out into the organic extractant. Precisely, in the first extraction step of the system, a starting, crude nickel sulfate solution is fed into the second-stage extractor, in which the solution is processed with an organic extractant having been fed thereinto from the first-stage reactor in a manner of counter-current extraction reaction therebetween to thereby make a part of nickel existing in the crude nickel sulfate solution extracted out into the organic extractant.

In the second extraction step, the crude nickel sulfate solution, which has been processed in the first extraction step and from which a part of nickel has been removed, is transferred to the first-stage extractor, and is further processed therein with a fresh organic extractant in a manner of counter-current extraction reaction therebetween to thereby make the remaining part of nickel still existing in the crude nickel sulfate

solution extracted out into the organic extractant. The nickel extraction in the second-stage extractor in the first extraction step shall be carried out in a pH range of 6.5 to 7.0, while that in the first-stage reactor in the second extraction step shall be carried out in a pH range of 5.5 to 6.5.

The pH in the second extraction step is defined to fall between 5.5 and 6.5, or that is, defined to be lower than the pH range in the first extraction step. This is because, in the second extraction step in which a smaller amount of nickel is extracted into the organic acid extractant, nickel is favorably extracted at such a low pH value lower than 6.5 while effectively preventing the extraction of sodium and ammonium into the organic extractant.

A part of the nickel-containing organic phase having been separated in the second extraction step and having been discharged out from the first-stage extractor is transferred to the by-pass, organic extract-scrubbing step, while the remaining part thereof is circulated to the second-stage extractor. This is because, within a relatively high pH range, for example, within a pH range of 6.5 or higher, the increase in the concentration of nickel being extracted into the organic extractant inhibits the extraction of sodium and ammonium into the organic extractant. Therefore, a part of the nickel-containing organic phase is transferred to the by-pass, organic extract-scrubbing step, to thereby reduce the amount of the organic extractant to be fed into the second-stage extractor,

and the nickel extraction is carried out in the second-stage extractor in a pH range of 6.5 to 7.0 whereby the nickel concentration in the organic phase as separated in the first extraction step is increased while reducing the amount of sodium, ammonium and other impurities that may be in the organic phase.

Specifically, in the method of the invention, a part of the organic phase having been separated in the second extraction step and having been discharged out from the first-stage extractor is transferred to the by-pass, organic phase-scrubbing step, while the remaining part thereof is circulated to the second-stage extractor. The method of the invention is better than any other conventional process not comprising such a specific circulation step in that the former produces two effects, one being a physical effect of reducing the amount of the organic extractant to be used in the two extraction steps in which the amount of impurities to be extracted into the extractant may increase, and the other being a chemical effect of increasing the nickel concentration in the organic phase to thereby reduce the amount of impurities that may be in the extract.

The organic phase having been transferred from the first extraction step to the organic phase-scrubbing step, and a part of the organic phase having been transferred from the second extraction step to the by-pass, organic phase-scrubbing step are both scrubbed with a nickel-containing scrub solution in the respective steps, whereby the impurities of sodium and ammonium existing in those organic phases are substituted with

nickel existing in the scrub solution, and are removed from the organic phase. We, the present inventors have found that, in order to enhance the substitution reaction, the nickel concentration in the scrub solution is preferably 0.6 times the nickel content of the organic phase, and is not smaller than 10 g/liter.

Where the organic phase is scrubbed under the defined condition, the scrub raffinate as discharged from the by-pass, organic phase-scrubbing step may be used as the scrub solution for scrubbing the organic phase having been separated in the first extraction step. This is because, since the organic phase to be transferred from the second extraction step to the by-pass, organic phase-scrubbing step is one having been processed with a relatively large amount of an organic extractant at a relatively low pH value for nickel extraction, it has a relatively low nickel content of falling between 1 and 5 g/liter or so, while containing sodium, ammonium and impurities in an amount of from 1 to 2 g/liter or so. Therefore, in this by-pass scrubbing step, nickel existing in the scrubbing solution used may be substituted with those impurities without so much reducing the nickel content of the resulting scrub raffinate, and the scrub raffinate from this by-pass scrubbing step can be used in the organic phase-scrubbing step where the organic phase from the first extraction step is scrubbed.

For example, where an organic phase containing sodium and ammonium impurities in an amount of 2 g/liter and having been transferred into the by-pass scrubbing step is scrubbed with

an aqueous nickel sulfate solution having a nickel content of 20 g/liter in a ratio of 1/1, the reduction in the nickel concentration in the scrub raffinate of the aqueous solution, due to the substitution reaction, may be at most about 2.5 g/liter, and the scrub raffinate from this by-pass scrubbing step still has a nickel content of not smaller than 10 g/liter that may be well used as a scrubbing solution in the organic phase-scrubbing step. The impurity concentration in the scrub raffinate from the by-pass scrubbing step, which is used as the scrubbing solution in the organic phase-scrubbing step, shall increase in some degree, but does not interfere with the scrubbing with that scrub solution in the organic phase-scrubbing step since the substitution reaction between the impurities in the organic phase and nickel in the scrub solution occurs predominantly in the organic phase-scrubbing step.

Accordingly, in the method of the invention, sodium and ammonium can be effectively removed from the organic phase even when a small amount of a scrub solution is used as a whole. The nickel-containing scrub solution for use in the invention may be the purified nickel sulfate solution to be obtained from the organic phase having been separated through extraction of the invention, or may be prepared from nickel sulfate crystals to be obtained from the purified nickel sulfate solution.

In the illustrated embodiment for organic solvent extraction, used is a counter-current extraction system which comprises two extractors as connected in series, which, however, is not limitative. Apart from this, also employable herein is

any other multi-stage extraction system comprising more than two extractors as connected in series, in which nickel is extracted from a crude nickel sulfate solution in one or more intermediate-stage extractors, while a part of the organic phase from the previous extractor is transferred into a bypass, organic phase-scrubbing step.

Now, the invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

Example 1:

Herein made was an experiment of nickel extraction from an aqueous phase containing nickel, sodium and ammonium into an organic acid extractant, using a two-stage, counter-current mixer-settler system comprising two mixer-settlers as connected in series, in which the mixer zone of each mixer-settler had an effective capacity of 0.5 liters and the settler zone thereof had a capacity of 3.1 liters (mixer-settler is hereinafter referred to as settler), according to the method of the invention (Example of the invention) and to a conventional method (Comparative Example). This is to demonstrate how and to what degree sodium and ammonium are prevented from being extracted into the extractant.

The amount of the aqueous phase fed into the system was 1.3 liters/hr, and the amount of nickel fed into the aqueous phase was 38 g/hr while that of sodium fed thereinto was about 34 g/hr. The ammonia concentration in the aqueous phase was 1.0 g/liter. As the organic acid extractant, used herein was

PC-88A (manufactured by Dai-hachi Chemical Co.) as diluted with Cleansol G (manufactured by Nippon Petroleum Co.) to have a concentration of 20 % (v/v), and its amount fed into the system was 2.6 liters/hr.

The organic extractant was fed into the first-stage settler, while the aqueous phase containing nickel, sodium and ammonium was into the second-stage settler, and the two were reacted in the settler of each stage in a manner of continuous counter-current extraction reaction. In Example of the invention, a part of the organic phase as separated in the first-stage settler was transferred to a by-pass scrubbing step at a flow rate of 1 liter/hr, while the other part thereof was transferred to the second-stage settler at a flow rate of 1.6 liters/hr. Being different from this, in Comparative Example, all the organic phase separated in the first-stage settler was transferred to the second-stage settler in the manner of conventional solvent extraction.

The data of Example of the invention, including the pH value, the flow rate, the nickel, sodium and ammonium concentration, the amount of sodium and ammonium as extracted into the organic extractant (sodium and ammonium contamination), and the amount of nickel as extracted into the organic extractant (nickel recovery) in each extraction stage, are shown in Table 1; and those of Comparative Example are in Table 2.

Table 1

Example of the Invention	pH	Flow Rate (liter/hr)	Ni (g/liter)	Na (g/liter)	NH ₃ (g/liter)	Ni Recovery (%)	Na Contamination (%)	NH ₃ Contamination (%)
Organic Phase in 1st-stage settler	5.5	2.56	1.90	0.96	0.08	-	3.0	8.0
Aqueous Phase in 1st-stage settler		1.63	0.55	16.8	0.44	97.6	-	
Organic Phase in 2nd-stage settler	7.0	1.6	22.4	1.08	0.05		5.2	15.5
Aqueous Phase in 2nd-stage settler		1.3	3.61	2.11	0.58	-	-	

Table 2

Comparative Example	pH	Flow Rate (liter/hr)	Ni (g/liter)	Na (g/liter)	NH ₃ (g/liter)	Ni Recovery (%)	Na Contamination (%)	NH ₃ Contamination (%)
Organic Phase in 1st-stage settler	5.5	2.56	2.00	0.86	0.06	-	-	-
Aqueous Phase in 1st-stage settler		1.64	0.57	15.0	0.34	97.6	-	-
Organic Phase in 2nd-stage settler	7.0	2.56	14.6	2.01	0.12	-	15.7	29.4
Aqueous Phase in 2nd-stage settler		1.3	3.80	2.12	0.44	-	-	-

In Example of the invention, the amount of nickel in the aqueous phase fed into the system was 29 g/liter, and the amount of nickel in the extraction raffinate was reduced to 0.55 g/liter as a result of the counter-current, two-stage extraction. In other words, the nickel recovery was 97.6 % as in Table 1. The amount of sodium that contaminated the final organic phase was 3.0 %, which was in the by-pass organic phase, and 5.2 %, which was in the organic phase from the second-stage settler, totaling 8.2 %. The amount of ammonia contaminated the same totaled 23.5 %.

On the other hand, in Comparative Example of the conventional counter-current, two-stage extraction with no by-pass step, the nickel extraction was 97.6 % as in Table 2, which is the same as that in Example of the invention, but the amount of sodium and ammonium contaminated the final organic phase was 15.7 % and 29.4 %, respectively. Thus, it is obvious that the amount of sodium and ammonium that contaminated the final organic phase was smaller in Example of the invention than that in Comparative Example. This means the significant effect of the invention that prevents the contamination of the organic phase with sodium and ammonia.

Example 2:

Using the same system and according to the same process as in Example 1, herein made was another experiment according to the method of the invention (Example of the invention) and to a conventional method (Comparative Example). This is to demonstrate the influence of the flow rate of the aqueous phase

fed into the system on the nickel recovery and on the sodium and ammonium contamination.

In this experiment, the amount of nickel, sodium and ammonium fed into the settler was the same as that in Example 1, but the amount of the aqueous phase fed thereinto was 2.3 liters/hr or 3.31 liter/hr, which was larger than that in Example 1. The other conditions for this experiment were the same as those in Example 1, and the data were obtained also in the same manner as in Example 1 except that the pH of the aqueous phase was measured herein. The data of Example of the invention are shown in Table 3, and those of Comparative Example are in Table 4.

Table 3

Example of the Invention	pH	Flow Rate (liter/hr)	Ni (g/liter)	Na (g/liter)	NH ₃ (g/liter)	Ni Recovery (%)	Na Contamination (%)	NH ₃ Contamination (%)
Organic Phase in 1st-stage settler		2.56	2.23	0.62	0.06	-	1.92	5.56
Aqueous Phase in 1st- stage settler	5.5	2.63	0.52	10.8	0.31			
Organic Phase in 2nd-stage settler		1.56	21.8	0.65	0.03	96.4	3.17	5.15
Aqueous Phase in 2nd- stage settler	7.0	2.30	2.77	9.92	0.37			

Table 4

Comparative Example	pH	Flow Rate (liter/hr)	Ni (g/liter)	Na (g/liter)	NH ₃ (g/liter)	Ni Recovery (%)	Na Contamination (%)	NH ₃ Contamination (%)
Organic Phase in 1st-stage settler		2.56	2.34	0.57	0.05	-	-	
Aqueous Phase in 1st-stage settler	5.5	2.63	0.57	10.0	0.26			
Organic Phase in 2nd-stage settler		2.56	14.1	1.25	0.08	96.0	10.0	21.2
Aqueous Phase in 2nd-stage settler	7.0	2.30	2.87	8.98	0.31			

From the data in Tables 3 and 4, it is known that, in both Example of the invention and Comparative Example, the increase in the amount of the aqueous phase fed into the settler resulted in slight decrease in the nickel recovery but improved the removal of sodium and ammonium. In particular, in Example of the invention, the total sodium and the total ammonium having contaminated the by-pass organic phase and the second-stage organic phase were 5.1 % and 10.7 %, respectively, which were much smaller than those in Comparative Example.

In another experiment of Example of the invention, the amount of the aqueous phase fed into the first-stage settler was varied to 3.31 liters/hr, and the other conditions were the same as above. The data of this experiment are shown in Table 5.

Table 5

Example of the Invention	pH	Flow Rate (liter/hr)	Ni (g/liter)	Na (g/liter)	NH ₃ (g/liter)	Ni Recovery (%)	Na Contamination (%)	NH ₃ Contamination (%)
Organic Phase in 1st-stage settler		2.56	0.57	0.45	0.04		1.4	4.23
Aqueous Phase in 1st- stage settler	5.5	3.62	2.31	7.85	0.23			
Organic Phase in 2nd-stage settler		1.56	21.0	0.46	0.03	94.7	2.23	4.58
Aqueous Phase in 2nd- stage settler	7.0	3.30	2.33	6.92	0.27			

As in Table 5, when the amount of the aqueous phase fed into the first-stage settler was increased while the other conditions were not varied, the total sodium and the total ammonium having contaminated the organic phase were 3.6 % and 8.8 %, respectively, which were further lower than those in Table 4, but the nickel recovery decreased with the increase in the amount of the aqueous phase fed into the settler. The series of these experiments made herein verifies that the nickel recovery greatly depends on the pH in the extraction reaction, especially on the pH in the first-stage settler. That is, it verifies that, when the pH of the aqueous phase in the first-stage settler is low to be 5.5 so that the first-stage extraction is carried out such a low pH value, the nickel recovery is greatly lowered.

Example 3:

Using the same system and according to the same process as in Example 1, except that the amount of nickel fed to the system was varied to 37 g/liter and that the pH in the first-stage settler was varied to 6.0, 6.5 or 7.0, herein made was still another experiment according to the method of the invention (Example of the invention) and to a conventional method (Comparative Example). This is to demonstrate the influence of the pH value in the settler on the nickel recovery and on the sodium contamination. The data obtained are shown in Table 6.

Table 6

pH in 1st-stage settler	Example of the Invention		Comparative Example	
	Ni	Na	Ni	Na
	Recovery Contamination (%)	Recovery Contamination (%)	Recovery Contamination (%)	Recovery Contamination (%)
6.0	99.4	11.5	99.4	15.8
6.5	99.9	19.4	99.9	16.0
7.0	100	23.2	100	16.0

From the data in Table 6, it is known that the increase in the pH value resulted in the increase in the nickel recovery in both Example of the invention and Comparative Example, while resulting in the great increase in the sodium contamination only in Example of the invention but not in Comparative Example. This is because, since the pH in the second-stage settler in this experiment was set at 7.0 like in the other experiments, the sodium contamination in Comparative Example where the organic phase from the first-stage settler was not transferred to the by-pass step greatly depended on the pH value in the second-stage settler and was therefore not changed so much, while, in Example of the invention where a part of the organic phase from the first-stage settler was transferred to the by-pass step, the pH value in the first-stage settler had a great influence on the sodium contamination, resulting in that the sodium contamination in Example of the invention would have increased with the increase in the pH value in the first-stage settler.

However, the data in Example 2 indicate that the sodium contamination in the organic phase from the first-stage settler decreases with the increase in the aqueous phase as fed into

the settler. Having noted this, we carried out another experiment where the flow rate of the aqueous phase into the first-stage settler was increased up to 3.3 liters/hr but the other conditions including the amount of nickel fed into the system were the same as above. The data of this experiment are shown in Table 7.

Table 7

pH in 1st-stage settler	Example of the Invention			Comparative Example		
	Ni Recovery (%)	Na Contami- nation (%)	NH ₃ Contami- nation (%)	Ni Recovery (%)	Na Contami- nation (%)	NH ₃ Contami- nation (%)
6.0	98.6	5.5	10.3	98.4	7.3	16.2
6.5	99.8	10.7	14.1	99.8	7.4	16.4
7.0	99.8	13.6	18.9	99.9	7.4	16.3

From the data in Table 7, it is known that the increase in the flow rate of the aqueous phase fed into the system resulted in the decrease in the sodium and ammonium contamination in the organic phase, as in Table 3, while the sodium contamination and also the ammonium contamination in the organic phase did not influenced by the pH change in the first-stage settler, as in Table 6. However, it is further known therefrom that, in Example of the invention, the sodium contamination in the organic phase decreased with the increase in the flow rate of the aqueous phase, as in Comparative Example, but increased only a little with the increase in the pH value in the first-stage settler. That is, the increase in the sodium contamination in Example of the invention was much lowered in this experiment.

This means that, in Example of the invention, if the pH in the first-stage settler is lowered to be not higher than 6.5, preferably to fall between 5.5 and 6.5, the impurity contamination in the organic phase can be totally reduced more than in Comparative Example.

Example 4:

Herein made was an experiment to demonstrate the influence of the nickel concentration in scrub solution on the removal of sodium from organic extracts. In this experiment, 200 ml of an organic phase and 200 ml of nickel-containing scrub solution, and stirred for 10 minutes until phase equilibrium. The nickel and sodium concentration in the organic phase used herein was controlled by reacting the same organic extractant as in Example 1 with a solution of nickel sulfate at a pH of 6.5 to 7.5. Sodium hydroxide was used as the neutralizer to control the sodium concentration in the organic phase. Prior to the phase equilibrium in the mixture of the organic phase and the scrub solution, the nickel concentration in the scrub solution was controlled with nickel sulfate (NiSO_4) added thereto, while the sodium concentration therein was with sodium sulfate (Na_2SO_4) also added thereto. Table 8 shows various phase-equilibrated conditions of the organic phase and the scrub solution both having a varying nickel concentration and a varying sodium concentration.

Table 8

Ni Ratio (A/O)	Organic Phase		Aqueous Phase		Na Distribution (O/A)
	Ni (g/liter)	Na (g/liter)	Ni (g/liter)	Na (g/liter)	
0.04	15.1	1.38	0.58	5.51	0.25
0.58	12.6	0.51	7.36	7.97	6.4×10^{-2}
0.89	12.5	0.007	10.3	0.168	4.2×10^{-2}
1.32	12.4	0.001	16.4	0.022	4.5×10^{-2}
0.34	23.6	0.037	8.08	0.522	7.1×10^{-2}
0.60	19.4	0.019	11.6	0.945	2.0×10^{-2}
1.3×10^{-3}	7.64	5.66	0.010	6.59	0.86
7.0×10^{-2}	8.58	4.93	0.060	16.0	0.31

From Table 8, it is known that the nickel ratio (A/O) in the phase-equilibrated system greatly depends on the sodium distribution (O/A). This means that, in the phase-equilibrated condition, if the nickel concentration in the aqueous phase is 0.6 times (A/O) that in the organic phase and if the nickel content of the aqueous phase is not smaller than 10 g/liter, the removal of sodium from the organic phase is promoted.

Example 5:

Based on the data obtained in the series of experiments made hereinabove, we made herein a pilot test of two-stage counter-current extraction of the present invention, using the same two-stage counter-current mixer-settler system as in

Example 1 and according to the flowchart illustrated in Fig. 1. Table 9 shows the composition of the crude nickel sulfate solution processed herein and the composition of the scrub solution used herein. As the organic acid extractant, used herein was PC-88A.

Table 9

Element (g/liter)	Crude Nickel Sulfate Solution	Scrub Solution
Ni	55.7	18.0
Cu	0.61	-
Zn	0.78	-
Ca	0.75	-
NH ₃	3.3	-
Na	6.7	0.01

The flow rate of the nickel sulfate solution fed to the second-stage settler was 0.3 liters/hr, and that of the organic extractant fed into the first-stage settler was 2.6 liters/hr. The pH in the first extraction step (in the second-stage settler) was 7.0, and that in the second extraction step (in the first-stage settler) was 5.5. The flow rate of the organic phase to be transferred into the by-pass step from the second extraction step (that is, from the first-stage settler) was 1.6 liters/hr.

Two mixer-settlers were provided for the by-pass scrubbing step of scrubbing the organic phase from the second extraction step and for the scrubbing step of scrubbing the organic phase from the first extraction step, and the flow rate of the scrub solution introduced into those was 1.0 liter/hr. Under the

counter-current solvent extraction of nickel was carried out according to the method of the invention, and the data of the test are shown in Table 10. Apart from this, another test of conventional, two-stage, counter-current solvent extraction of nickel (Comparative Example) was carried out under the same condition as above except that the nickel concentration in the starting nickel sulfate solution was 56.5 g/liter, that the nickel concentration in the scrub solution was 17.6 g/liter, and that no by-pass scrubbing was effected. The data of Comparative Example are shown in Table 11. In Comparative Example, no by-pass scrubbing of the organic phase from the second extraction step was carried out. In this, therefore, the settler for the by-pass scrubbing was not provided.

Table 10

Liquid in each step (g/liter)	Ni	Cu	Zn	Ca	NH ₃	Na
Extraction Raffinate	0.52	<0.001	<0.001	<0.001	0.44	18.8
Organic Phase	16.9	0.11	0.15	0.14	0.05	1.08
Organic Phase in By-pass Step	1.90	<0.001	<0.001	0.01	0.08	0.96
Scrubbed Organic Phase	19.7	0.11	0.15	0.15	0.002	0.002
Scrub Raffinate	12.2	<0.001	<0.001	<0.001	0.78	2.53
By-pass Scrubbed Organic Phase	3.13	<0.001	<0.001	0.01	0.008	0.003

Table 11

Liquid in each step (g/liter)	Ni	Cu	Zn	Ca	NH ₃	Na
Extraction Raffinate	0.58	<0.001	<0.001	<0.001	0.34	17.6
Organic Phase	9.84	0.11	0.15	0.14	0.12	5.10
Scrubbed Organic Phase	13.3	0.11	0.15	0.15	0.007	0.015
Scrub Raffinate	8.15	<0.001	<0.001	<0.001	0.30	2.53

As is obvious from the data in Table 10 and Table 11, the nickel recovery was almost the same in Example of the invention and in Comparative Example, but the sodium and ammonium contamination in the organic phase obtained in Example of the invention greatly differs from that obtained in Comparative Example. Precisely, based on the nickel content (100 %) of the nickel sulfate separated from the organic phase, the sodium content and the ammonium content of the organic phase were both not larger than 100 ppm in Example of the invention, but were larger than 1000 ppm and larger than 500 ppm, respectively, in Comparative Example. Even though the crystallization of nickel sulfate from the organic phase is taken into consideration, it is obvious that the process of Comparative Example requires an increased amount of scrub solution in the scrubbing step and requires a large amount of nickel to be put in the scrubbing solution in order to promote the scrubbing of the organic phase.

As has been described in detail hereinabove, according to the method of the present invention for solvent extraction of nickel with an organic acid extractant, the sodium and ammonium contamination in the organic phase obtained is much reduced with ease, and, in addition, the amount of scrub solution to be used for scrubbing the organic phase can be reduced significantly. Thus, the method of the invention has the advantage of being economical in industrial purification of nickel sulfate.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent

to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

1. A method of solvent extraction of nickel sulfate, using a two-stage, counter-current, organic solvent extraction system composed of two extractors connected in series, the method comprising a first extraction step of feeding crude nickel sulfate solution that contains impurities of essentially sodium and ammonium into a second-stage extractor, followed by processing therein the crude nickel sulfate solution with an organic extractant having been fed into the second-stage extractor from a first stage-extractor, in a pH range of 6.5 to 7.0 in a counter-current extraction reaction therebetween to thereby extract part of the nickel from the crude nickel sulfate solution into the organic extractant; and a second extraction step of transferring the nickel-containing, organic phase to an organic phase-scrubbing step to remove sodium and ammonium from the thus-transferred, nickel-containing organic phase, while transferring the crude nickel sulfate solution, which has been processed in the first extraction step and from which a part of nickel has been removed, to the first-stage extractor, followed by further processing therein the thus-transferred crude nickel sulfate solution with fresh organic extractant, within a pH range falling between 5.5 and 6.5 in a counter-current extraction reaction therebetween to thereby extract the remaining part of nickel still existing in the crude nickel sulfate solution into the organic extractant; and in which the nickel-containing organic phase as separated in the second extraction step is divided into two portions, one of these portions being used as the organic extractant to be fed into the second-stage extractor and the other being transferred to by a by-pass, organic phase-scrubbing step to remove sodium and ammonium from the thus-transferred, nickel-containing organic phase.

2. A method of solvent extraction of nickel sulfate as claimed in claim 1, wherein, in said organic phase-scrubbing step, the nickel-containing organic phase as separated in the first extraction step is scrubbed with scrub solution that contains nickel in an amount of at least 10 g/liter.

3. A method of solvent extraction of nickel sulfate as claimed in claim 1 or claim 2, wherein, in said by-pass, organic phase-scrubbing step, the nickel-containing organic phase as separated in the second extraction step is scrubbed with scrub solution that contains nickel in an amount of at least 0.6 times the amount of nickel existing in said phase.

4. A method of solvent extraction of nickel sulfate as claimed in any preceding claim, wherein at least a part of the scrub raffinate as discharged in the by-pass, organic phase-scrubbing step is used as the scrub solution in the organic phase-scrubbing step.



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Claims searched: 1-4

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C1A (APD2B,APD2S,APD2Y,APDT)

Int Cl (Ed.6): C22B 3/32,23/00

Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	NONE	

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