

SYNERGISTIC EFFECT OF Ni EXTRACTION AND ITS APPLICATION FOR WASTE SOLUTION IN Ni NON - ELECTRIC PLATING

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Abstract

Waste solution from the Ni non-electric plating process contains 4.0kg/m³ Ni (II), 0.1kg/m³ Fe (III), 0.01kg/m³ Zn (II), 48kg/m³ SO₄²⁻, 98kg/m³ HPO₃²⁻ and 31kg/m³ lactic acid as a typical composition. Solvent extraction, cementation, ion exchange resin and precipitation methods may be used for the treatment of this kind of solution. In this study, solvent extraction of Ni (II) is investigated using two kinds of extractant in order to clarify the relation between extraction percent age and pH for various extractant mixtures. As Ni ions have an octahedral structure with ligands, the synergistic effect for Ni extraction may be effected by using two types of extractants.

1. Introduction

In recent years, with the development of the electronics industry, mechanical engineering and so on, various new surface treatments have been devised. Non-electric nickel plating is a typical surface treatment technology used in the production of electronic goods, precision instrument parts, etc. Nickel ions and reduction agents, such as formaldehyde and sodium phosphinate, are consumed by the deposition of nickel based on chemical reduction on an object, while non-electric nickel plating proceeds. In order to maintain a fixed composition of the plating liquor¹⁾, it is therefore necessary to add nickel sulfate and reduction agents intermittently.

Although the composition of plating liquor is precisely controlled during the nickel plating process, the accumulation of water-soluble salts such as phosphorous acid and sodium sulfate takes place with an increase in operation cycles. Therefore, periodical discharge of the plating liquor must be conducted so as not to accumulate various water-soluble salts. Most of the plating waste liquors are treated by the precipitation method using such materials as metal hydroxide and sulfate, since sea dumping has been prohibited by the London Dumping Convention of 1996²⁾. The establishment of the process to recycle useful ingredients such as nickel, phosphinic acid and organic acid, is desirable from the viewpoint of environmental protection and resources preservation.

Precipitation, ion exchange resin, adsorption, solvent extraction and so on are used as

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separation methods for the various materials in solution. Solvent extraction, which has a superior separation ability for metal ions at high concentrations, is useful for processing metal plating waste liquor. Some studies of the separation and recovery of nickel ions have reported that solvent extraction maybe applied to plating waste liquor, but the proposed methods need the addition of alkali for pH regulation during the extraction stage⁹. If a nickel recovery process is to prove economical, it is important to extract nickel ions efficiently without adjusting pH in a nickel recovery process. The objective of this study is to clarify the mechanism and phenomena for synergistic extraction of nickel ions. Synergistic extraction was applied in order to extract nickel ions efficiently from the plating waste liquor without pH regulation. The synergistic extraction of nickel ions from an aqueous solution was investigated by using various extractant mixtures.

2. Experimental

Two kinds of extractant and one diluent were used as an organic phase. The main extractants are di-2-ethylhexyl phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) and versatic acid 10 (VA10). One of the extractants shown in Table 1 was selected as the second component of the extractant mixture in the organic phase. Kerosene was used as a diluent. The aqueous phase was 0.005 mol/dm³ of nickel sulfate solution, and the pH adjustment of the aqueous phase was carried out by using sodium hydroxide and hydrochloric acid.

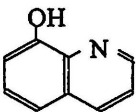
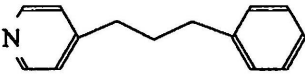
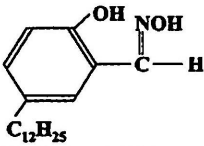
| Name | Structural formula | M.W. |
|---|---|-------|
| Organophosphorus compound | | |
| Tri-n-butyl phosphate (TBP) | $[C_4H_9-O]_3P=O$ | 266.3 |
| Trioctyl phosphate (TOP) | $[C_8H_{17}-O]_3P=O$ | 434.6 |
| Trioctyl phosphine oxide (TOPO) | $[C_8H_{17}]_3P=O$ | 386.6 |
| Nitrogen containing compound | | |
| 8-Quinolinol |  | 154.2 |
| 4-Phenylpropyl pyridine (4-PPP) |  | 197.3 |
| LIX860 _® (5-dodecylsalicylaldoxime) |  | 305.2 |

Table 1. Structural formula of organic compounds

The same volume, 15 cm³, of the organic and aqueous phases was put in a centrifuge tube, and then the tube was shaken by a vertical-type shaker for 60 min. The phase separation was carried out by centrifuge. The nickel ion concentration in aqueous solution was measured by atomic absorption spectrophotometry (AA-6800, Shimadzu) to calculate the extraction amount from the material balance before and after the extraction operation.

3. Results and Discussion

The synergistic effect takes place by adding neutral organophosphorus compounds, such as tri-n-butyl phosphate (TBP) and tri-n-octyl phosphorous oxide (TOPO), to the main extractants of carboxylic acid and acidic alkyl phosphoric ester, and TBP and TOPO coordinate to the extracted species formed between metal ions and main extractants^{4,6}.

The extraction experiments of nickel ions were carried out by using the organic mixtures of 0.1mol/dm³ main extractants and 0.1mol/dm³ additive extractants. The extractants used in this study were D2EHPA, PC-88A and VA10, and, as additive extractants TBP, TOPO and tri-n-octyl phosphate (TOP). The extraction curves of nickel ions are shown in Fig.1. That from the mixture of acidic extractant and neutral organophosphorus compound is very similar to the one in which only the acidic extractant was used. The combination giving the largest synergistic effect is the PC-88A – TOPO system, where the ΔpH_{50} was about 0.22. ΔpH_{50} means the difference between the pH of the extractant mixture and that of the main extractant on its own at 50% nickel extraction.

When the ΔpH_{50} value is large, it means that the synergistic effect is also large. That is, ΔpH_{50} indicates the degree of synergistic effect. The results show that the synergistic effect

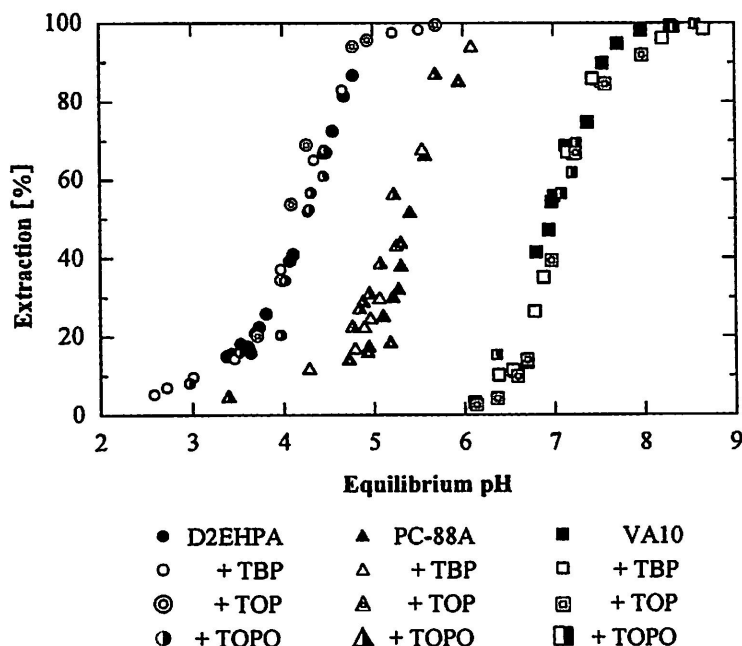


Fig.1 Extraction of nickel ions using mixtures of various acidic extractants and organophosphorus compounds

for nickel ions is very small when the neutral organophosphorus compound is used as the additive extractant.

Nitrogen containing compounds are known to be effective as the additive extractant for synergistic extraction of nickel ions⁷⁻¹⁰. Extraction of nickel ions was carried out using a nitrogen containing compound such as 8-quinolinol, 4-phenylpropyl pyridine (4-ppp) and LIX860 as an additive extractant. They have a nitrogen group as a donor ligand. The concentrations of acidic extractant and additive were prepared at 0.1 mol/dm³, respectively. The extraction of nickel ions with the mixtures of various acidic extractants and 8-quinolinol is shown in Fig.2. The extraction curves shift to the left side when using the mixture of

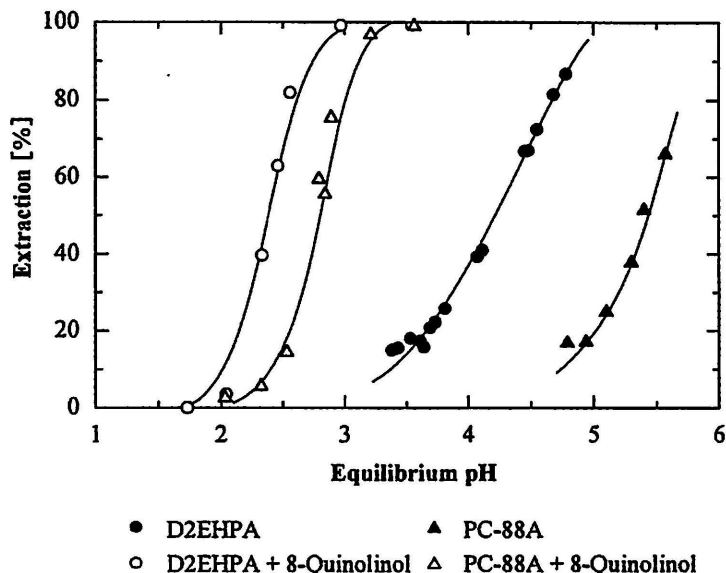


Fig.2 Extraction of nickel ions using mixtures of acidic extractants and 8-quinolinol

D2EHPA and 8-quinolinol, thus confirming that the synergistic effect takes place with the extractant mixture. The ΔpH_{50} value is 1.84 larger than that in the case of no additions. In using an extractant mixture of PC-88A and 8-quinolinol, a small amount of solid material forms at the interface of organic and aqueous phases regardless of the equilibrium pH. On the other hand, for the extractant mixture of VA10 and 8-quinolinol a large amount of solid forms at the interface in a wide pH range.

The additive extractant, 4-ppp, is added to D2EHPA, PC-88A and VA10 as a main extractant. The extraction curves obtained with mixtures of various acidic extractants and 4-ppp are shown in Fig.3. The pH_{50} for D2EHPA is located at pH 4.25, while the extraction curve obtained by using the extractant mixture falls to a lower pH than that with D2EHPA. The ΔpH_{50} value for the D2EHPA-4-ppp mixture is 1.29. For the D2EHPA-4-ppp mixture, the extraction curve shift caused by the addition of 4-ppp is large compared with the case of 8-quinolinol shown in Fig.2. The pH_{50} values for PC-88A and VA10 are pH 5.38 and 6.97, respectively. When the extractant mixtures of PC-88A and 4-ppp, and VA10 and 4-ppp are used, they exhibit a fairly big synergistic effect to give the ΔpH_{50} values of 1.63 and 1.52,

respectively.

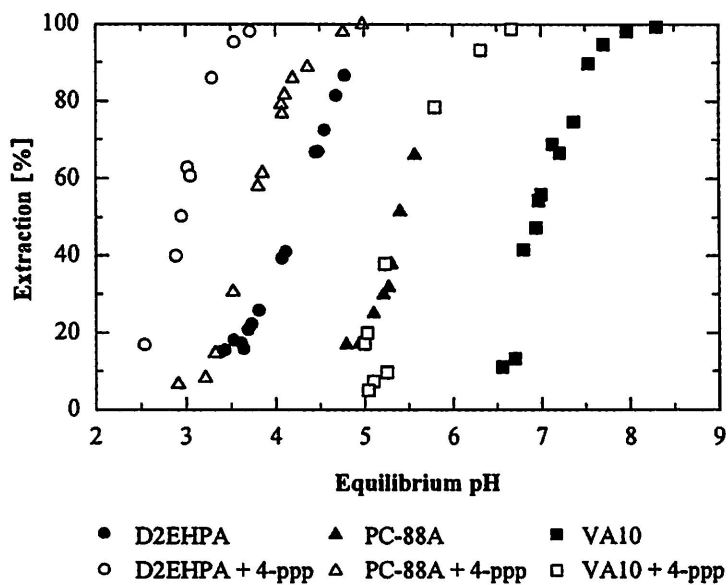


Fig.3 Extraction of nickel ions using mixtures of various acidic extractants and 4-ppp

The extraction of nickel ions was carried out using LIX860 as a nitrogen containing extractant. The extraction curves are shown in Fig.4. Nickel ions are extracted with LIX860 alone at a low pH 2.5-4.0. With the extractant mixtures of D2EHPA and LIX860, and PC-88A and LIX860, the extraction curve shifts to the lower pH side due to the synergistic effect.

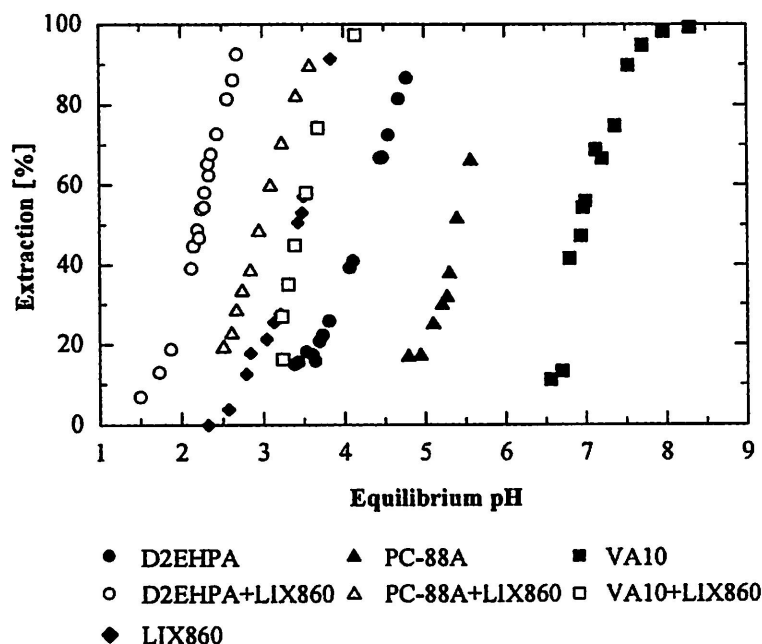


Fig.4 Extraction of nickel ions using the mixtures of various acidic extractants and LIX860

Using the two extractant mixtures of VA10 and LIX860, both extraction curves are identical. This mixture does not cause any synergistic effect. This result is explained by the small acid dissociation constant of VA10. VA10 does not have the function as an acidic extractant below pH 3.0, while LIX860 exhibits the extraction of nickel ions at the same pH.

The pH_{50} values for the main extractant and for the mixture and the ΔpH_{50} obtained from the above results are summarized in Table 2. The largest value of ΔpH_{50} in the extractant mixture is obtained for the mixture of PC-88A and TOPO to be about 0.22. On the other hand, when the extractant mixture of PC-88A and LIX860 is used for the extraction of nickel ions, the ΔpH_{50} value is at its highest. The extraction curve of nickel ions using the mixture of D2EHPA and LIX860 exhibits the lowest pH.

| Mixtures | pH_{50} (main extractant) | pH_{50} (mixture) | ΔpH_{50} |
|-------------------------------------|------------------------------------|----------------------------|------------------------|
| Organophosphorus compound | | | |
| D2EHPA+TBP | | 4.17 | 0.08 |
| +TOP | 4.25 | 4.25 | <0.01 |
| +TOPO | | 4.25 | <0.01 |
| PC-88A+TBP | | 5.32 | 0.06 |
| +TOP | 5.38 | 5.38 | <0.01 |
| +TOPO | | 5.16 | 0.22 |
| VA10+TBP | | 6.97 | <0.01 |
| +TOP | 6.97 | 6.97 | <0.01 |
| +TOPO | | 6.97 | <0.01 |
| Nitrogen containing compound | | | |
| D2EHPA+8-Quinolinol | 4.25 | 2.41 | 1.84 |
| +4-PPP | 4.25 | 2.96 | 1.29 |
| +LIX860 | 4.25 | 2.24 | 2.01 |
| PC-88A+4-PPP | 5.38 | 3.75 | 1.63 |
| +LIX860 | 5.38 | 2.78 | 2.60 |
| VA10+4-PPP | 6.97 | 5.45 | 1.52 |

Table 2. Extraction of nickel ions using various extractant mixtures

The pH of non-electric nickel plating liquor is ordinarily about 4. If an extractant mixture of D2EHPA-LIX860 is used, it is possible to obtain a high extraction of nickel ions from the nickel plating waste liquor without adjusting pH. Extraction and recovery of nickel ions from artificial waste liquor is examined by using the mixture of D2EHPA and LIX860. The plating waste liquor contains Ni (II), Fe (III) and Zn (II) as metal components. Before separating and recovering nickel ions, it is necessary to remove Fe (III) and Zn (II). The flow sheet for a nickel recovery process is shown in Fig.5. The mixture of D2EHPA and LIX860 is used for extraction of nickel ions after removal of Fe (III) and Zn (II) with D2EHPA or PC-88A. The metal concentration of non-electric plating waste liquor and the experimental results of extraction are shown in Table 3. In the first extraction stage, the extraction of Fe (III) and Zn (II) is about 100% with D2EHPA or PC-88A, but at the same time, about 10% of Ni (II) is extracted and lost. In the second extraction stage, Ni (II) extraction is about 40%.

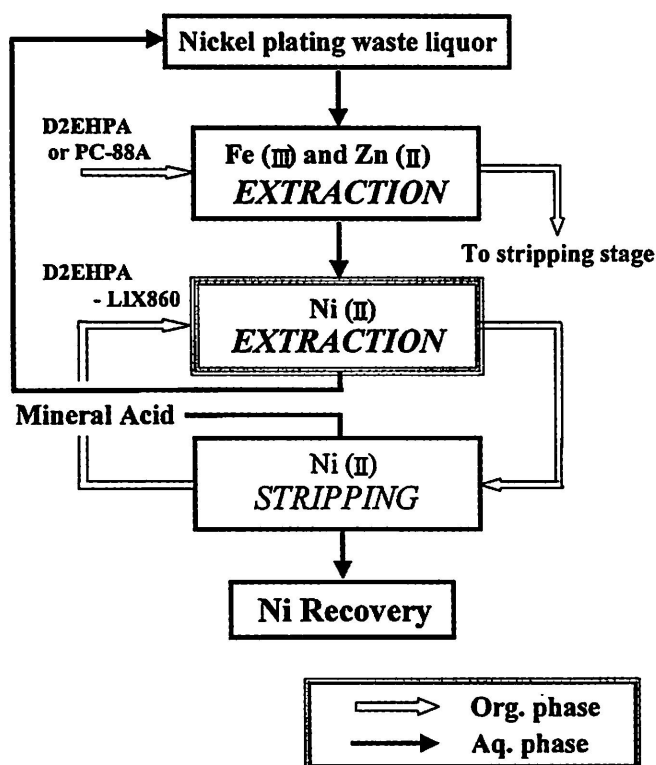


Fig.5 Flowsheet for nickel recovery process from nickel plating waste liquor

| Concentration of non-electric plating waste liquor [mg/dm ³] | | | | |
|--|----------------|------|-------|-------|
| | Ni | Fe | Zn | pH |
| Actual | 4000 | 90 | 8 | 4.64 |
| Artificial | 502.4 | 10.1 | 1.2 | 4.61 |
| First extraction stage of metal ions from waste liquor | | | | |
| Extractant | Extraction [%] | | | Eq.pH |
| | Ni | Fe | Zn | |
| D2EHPA | 11.8 | 100 | 100 | 2.62 |
| PC-88A | 9.52 | 100 | 100 | 2.99 |
| Second extraction stage of nickel with D2EHPA-LIX860 | | | | |
| Extractant in the first stage | Extraction [%] | | Eq.pH | |
| D2EHPA | 43.6 | | 2.28 | |
| PC-88A | 48.6 | | 2.35 | |

Table 3. Metal concentration of non-electric plating waste liquor and extraction of various metal ions in extraction stages

This extraction rate can be improved by changing phase ratio and extractant concentration. The stripping of Ni (II) from the mixture of D2EHPA and LIX860 loading Ni (II) is carried out by using sulfuric acid at various concentrations. Experimental results of stripping are shown in Fig.6. It is possible to strip 100% of Ni (II) with 0.1 mol/dm³ sulfuric acid.

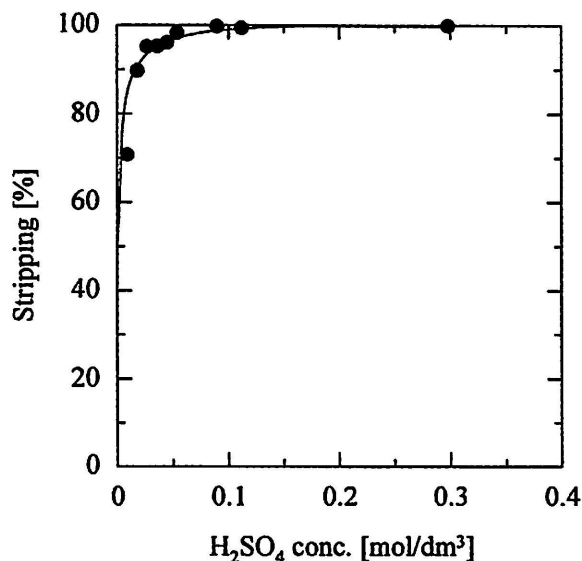


Fig.6 Stripping of nickel ions with sulfuric acid

4. Conclusions

The synergistic extraction of nickel ions was investigated by using extractant mixtures of acidic extractants with neutral organophosphorous compounds, and of acidic extractants with nitrogen-containing compounds.

The synergistic effect is not significant for the extractant mixture of acidic extractants and neutral organophosphorous compounds, while a large synergistic effect is seen when a mixture of the acidic extractant and nitrogen-containing compounds is used. Nickel ions can be extracted in the wide pH range of 3.0-8.0 without any pH adjustment by using the acidic extractant itself and the various extractant mixtures.

It is possible to extract Ni (II) from artificial waste liquor using the mixture of D2EHPA and LIX860 without pH adjustment. Ni (II) can be stripped with 0.1 mol/dm³ sulfuric acid from the Ni (II)-loading mixtures of D2EHPA and LIX860

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