Phosphorus Speciation in Sludge from Nickel Electroplating

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The recycling of secondary resources to close material cycle loops should reduce the consumption of natural resources and thus help to reduce the environmental impact. For recycling, it is crucial to consider not only the nickel (Ni) content in the secondary resources, such as Ni plating waste liquids and sludge, but also the impurity levels, particularly the phosphorus (P) concentration. This study characterized the P species in three sludges from Ni electroplating processes using P K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The Ni and P concentrations in the sludges ranged from 11 to 41% and 2,800 to 24,000 ppm, respectively, depending on the type of sludge. The P K-edge XANES analysis identified phosphates and organic P as the major P species in the sludges, and hypophosphite and phosphite species as minor species. These findings provide detailed knowledge that should help to control P in Ni electroplating sludge.

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1. Introduction

Materials that contain nickel (Ni) are becoming increasingly useful because of their physical and other properties; however, the demand for Ni and other metal resources has grown rapidly and there have been reports of environmental problems accompanying its extraction and refining.^{1,2)} Studies have examined the impact of extraction and refining on the loss of animal and plant habitat,³⁾ as well as on biodiversity,⁴⁾ and there have been case reports from Ni ore- and ferronickel/Ni metal-producing countries of encroachment on nature protection zones,⁵⁾ inappropriate environmental management at production facilities accompanied by heavy metal pollution,^{6,7)} and emissions, including sulfur oxides and mining waste.⁸⁾ The production of substances such as ferronickel requires large amounts of energy and many greenhouse gases are emitted.^{9,10)}

Recycling secondary resources to close the loop in the material cycle should reduce the consumption of natural resources and thus contribute to reducing the environmental impact. For recycling, it is critical to consider not only the Ni content in secondary resources, such as Ni plating waste liquids and sludge, but also the impurity level, particularly the phosphorus (P) concentration. Phosphorus is normally considered an undesirable impurity in steel production because it has detrimental effects on the mechanical properties of steel. The market typically requires that the P content of ferronickel be less than 0.02%.¹¹⁾

Waste water from Ni plating contains high concentrations of Ni and P.¹²⁾ This waste water is treated by oxidation, neutralization, and settling, and is finally separated into solid and liquid phases. The residual solid phase, called sludge, contains Ni and P. Recently, several technologies have been developed for recycling Ni and P removal from waste water from Ni plating.¹³⁾ Phosphorous speciation might influence

to improve understanding of the P removal technology from the sludge. However, basic information on the P species in sludge has not been reported because they are found in lower concentrations than other main elements, such as Ni.

Phosphorus K-edge X-ray absorption near-edge structure (XANES) spectroscopy is a nondestructive, element-selective method for identifying low-concentration P species in a complex matrix and can distinguish inorganic and organic forms.¹⁴⁾ Recently, P K-edge XANES spectroscopy has been applied to environmental samples, such as marine sediment,¹⁴⁾ minerals,¹⁵⁾ soil,¹⁶⁾ and poultry litter.¹⁷⁾ P K-edge XANES spectroscopy of the sludge from Ni electroplating should produce new insights into the P species in sludge and help control P levels in waste.

In this study, we characterized the P species in sludges from Ni electroplating using P K-edge XANES spectroscopy and quantified the elements in sludge samples.

2. Experimental Procedure

2.1 Sludge samples from plating processes

Three sludge samples were collected from industrial plating sites in Japan. Sludge A was sampled as dewatered cake from a settling tank after several treatments with Ni electroplating solution. This sludge had been treated by (i) washing with water, (ii) adjusting the pH to 3, (iii) mixing with other water discharged from defatting and acid-washing processes, (iv) precipitation by adjusting the pH to 10, (v) agglomeration, and (vi) settling. Sludge B was sampled as dewatered cake from a settling tank after electroplating processes involving several metals, including Ni, chromium, and copper. Sludge C was sampled from a mixing tank containing waste water from several electroplating processes before the precipitation process.

Many chemicals are used in the treatment of wastewater from Ni electroplating, including hydrosulfate, ferric chloride (FeCl₃), caustic soda (NaOH), lime hydrate [Ca(OH)₂],

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polymer coagulant, and defatting agents. In this study, we divided the sludge samples into two types: “separate” and “mixed”. “Separate” referred to sludge collected only from Ni electroplating processes. “Mixed” indicated sludge collected from several plating processes. Sludge A was separate type and sludges B and C were mixed type (Table 1).

2.2 Quantification of elements in sludge samples

The concentrations of elements in the sludge samples were quantified on a dry basis in instrumental analyses. We measured the moisture content of the sludge samples after drying the samples at 110°C for 2 hours. The moisture content was defined as the percentage decrease in the original weight according to the Ministry of Environment Notification No.13 (Japan) standard.

We measured concentrations of elements after drying of sludges. The P and Ni in sludges A and B were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES: ICPE-9000; Shimadzu, Kyoto, Japan) after acid digestion of the sludges with nitric acid (HNO₃). When HNO₃ was insufficient for the digestion, sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) were added and heated at an appropriate temperature on a hotplate.

Using wave-dispersive X-ray fluorescence (WDXRF) (XRF-1800; Shimadzu), the P, Ni, calcium (Ca), and magnesium (Mg) in sludges A to C were measured using a fundamental parameter method in a vacuum after making a sample disk.

The carbon contents of sludges A to C were quantified using a carbon/sulfur analysis instrument (CS-230SP; LECO, St. Joseph, MI, USA), which comprises a high-frequency induction heating furnace and infrared absorption analysis instrument. For this, a 0.1–0.2-g sludge sample was placed in a ceramic crucible. A mixture of powdered iron (0.8 g), tin (0.3 g), and tungsten (0.7 g) was used as an accelerator. An iron ore tailings sample (C: 1.88 ± 0.04%) was used as a standard sample, and the calibration curve for carbon (range: 0–120 mg) showed good linearity ($R^2 > 0.99$).

2.3 P K-edge X-ray absorption near edge structure (XANES) spectroscopy

We performed P K-edge XANES measurement of the dried sludge samples at the beamline BL-11B, Photon Factory (Tsukuba, Japan). Powdered sludge samples were mounted on carbon tape and the P K-edge XANES spectra were collected in total fluorescence yield (TFY) mode in a

vacuum, with 2140–2180 eV as the P K-edge energy range. The XANES spectra of P in different inorganic and organic reference compounds were collected to identify the chemical state of P. The inorganic P references were hydroxylapatite [HAP; Ca₅(PO₄)₃OH], octacalcium phosphate [OCP, Ca₈H₂(PO₄)₆·5H₂O], dicalcium phosphate dehydrate (DCPA, CaHPO₄·2H₂O), beta-calcium phosphate [β -Ca₃(PO₄)₂], calcium phosphite monohydrate (CaHPO₃·H₂O), calcium hypophosphite [Ca(H₂PO₂)₂], newberyite (MgHPO₄·3H₂O), sodium phosphate dodecahydrate (Na₃PO₄·12H₂O), and polyphosphate sodium (Na-polyPO₄). The organic P references were triphenyl phosphate (TPP) and adenosine triphosphate disodium (ATP-Na₂). These organic references involve the bonding of P with organic structures.

We used linear combination fitting (LCF) of XANES spectra to determine the major species using REX 2000 software (ver. 2.5.5; Rigaku, Tokyo, Japan). The linear combination fit for the experimental spectra was calculated using the residual value with the following formula:

$$R = \frac{\sum (\text{XANES}_{\text{measured}} - \text{XANES}_{\text{calculated}})^2}{\sum (\text{XANES}_{\text{measured}})^2}.$$

3. Results and Discussions

3.1 Elemental compositions of sludges

The concentrations of the elements (dry base) in the sludge samples from Ni electroplating are shown in Table 1. Sludges A, B, and C had P concentrations of 2,800, 6,100, and 24,000 ppm, respectively. The P concentration in sludge C from the mixing tank was one order of magnitude higher than that in sludges A and B. The Ni concentration in sludge A (41%) was higher than that in the two mixed sludges (11%). Ca, Mg, and C were found in all sludges because these elements are generally used as additives in the Ni electroplating process. Carbon contents (1.9–8.8%) were enough to react with P by quantitative measurement (Table 1).

3.2 Phosphorus speciation in sludges

Two major P species, *i.e.*, phosphates and organic phosphorous, were identified by analyzing the P K-edge XANES spectra of the sludge samples (Fig. 1). The post-edge structure of P K-edge can be used as a fingerprint region to identify the chemical condition of P.

The post-edge dip structure of sludge A at 2,154 eV was similar to that of organic P and MgHPO₄·3H₂O, as shown by label ‘a’ in Fig. 1. LCF identified the major P species in sludge A as 55% organic phosphorous and 32% MgHPO₄·3H₂O (Table 2). This suggests that the P in sludge A was mainly bonded to organics and Mg. A minor proportion of the P (13%) was identified as HAP.

The P K-edge XANES spectrum of sludge B was similar to that of sludge A, and LCF indicated that organic P (47%) and MgHPO₄·3H₂O (25%) were the dominant species (Table 2). Sludges A and B were collected from the same Ni-P plating facility, but were of different sample types (“separate” and “mixed”, respectively). This suggests that the major P species were not influenced by mixing with other dis-

Table 1 Concentrations of the elements (dry basis) found in Ni electroplating sludge.

	Sludge A	Sludge B	Sludge C
Separate or mix	Separate	Mixed	Mixed
Sampling point	Settling tank	Settling tank	Mixing tank
Moisture content (%)	84	79	77
P (ppm)	2800	6100	24000
Ni (%)	41	11	11
Ca (ppm)	3900	7500	92000
Mg (ppm)	85000	84000	8500
C (%)	1.9	8.8	4.8

charged water and deposits. Minor P species identified in sludge B were HAP and β - $\text{Ca}_3(\text{PO}_4)_2$ (Table 2).

Sludge C had a characteristic shoulder at 2,154 eV, which was derived from Ca phosphates such as β - $\text{Ca}_3(\text{PO}_4)_2$ and OCP ('b' in Fig. 1). The specific shoulder derived from Ca phosphates has been reported in P K-edge XANES spectroscopy studies using various P compounds.^{13,14} In addition, a small and broad peak around 2,162 eV was also seen for sludge C. This peak was similar to the peaks of β - $\text{Ca}_3(\text{PO}_4)_2$

and OCP ('c' and 'd' in Fig. 1, respectively). According to the LCF, Ca phosphates comprised 75% of the P chemical form and were the main P species in sludge C (Table 2).

The spectrum edge around 2,150 eV for the sludge samples had a broader shoulder than that of the phosphates and organic P, as shown in Fig. 1, implying the existence of other P species. Since the broader spectrum edge around 2,150 eV was partly derived from $\text{Ca}(\text{H}_2\text{PO}_2)_2$, a minor part of the P in sludges A and B existed as hypophosphite salts (Table 2). The edge structure of sludge C was distinct from that of the other sludges and showed a fit with phosphite salts, such as Ca phosphite monohydrate (Table 2).

In addition, a fairly broad peak at 2,164~2,176 eV was found in sludges A and B. This broad peak pattern has been reported for several organic P compounds.¹⁴ Phospholipid has a similarly broad structure. Organic residues were generally generated in the defatting process and mixed into the sludge. Therefore, phospholipid could form in the sludge phase.

It is noted that sampling point might influence to generate organic P species. Although all sludges contained carbon, organic P species were only identified in sludges A and B sampled from settling tank (Tables 1 and 2). However, organic P species were not identified in sludge C from mixing tank. Therefore, organic P species might generate in final residue from settling tank.

4. Conclusion

The P species in three sludges from Ni electroplating processes were characterized using P K-edge XANES spectroscopy. The Ni and P concentrations in the sludges ranged from 11–41% and 2,800–24,000 ppm, respectively, depending on the type (separate or mixed) and sampling point (settling or mixing tanks) of the sludge. Two major P species (phosphates and organic phosphorous) were identified in the sludges. Hypophosphite and phosphite species were identified as minor P forms. These detailed findings will help to improve the control of P in sludge from Ni electroplating.

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Fig. 1 Normalized P K-edge X-ray absorption near-edge structure (XANES) spectra of the sludge from nickel (Ni) electroplating: solid line, measured spectrum of the sludge sample; dashed line, spectrum of the standard material; circle, spectrum fitted using linear combination fitting.

Table 2 Phosphorus speciation of sludge from Ni electroplating determined by linear combination fitting of the P K-edge XANES spectra.

	Sludge A	Sludge B	Sludge C
Phosphates	55%	55%	91%
	MgHPO ₄ ·3H ₂ O (39%)	MgHPO ₄ ·3H ₂ O (25%)	β -Ca ₃ (PO ₄) ₂ (39%)
	HAP (16%)	HAP (21%)	OCP (39%)
		β -Ca ₃ (PO ₄) ₂ (9%)	Na-polyPO ₄ (13%)
Organic phosphorous	41%	43%	0%
	TPP (32%)	TPP (32%)	
	ATP-Na ₂ (9%)	ATP-Na ₂ (11%)	
Others	5%	3%	8%
	Ca(H ₂ PO ₂) ₂ (5%)	Ca(H ₂ PO ₂) ₂ (3%)	CaHPO ₃ ·H ₂ O (8%)
R value	0.111	0.114	0.062

HAP: Ca₅(PO₄)₃OH, OCP: Ca₈H₂(PO₄)₆·5H₂O, Na-polyPO₄: Polyphosphate sodium, TPP: triphenyl phosphate, ATP-Na₂: Adenosine triphosphate disodium

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