



# A novel method for nickel recovery and phosphorus removal from spent electroless nickel-plating solution



Liuyun Li<sup>a,\*</sup>, Naoki Takahashi<sup>b</sup>, Keiichi Kaneko<sup>b</sup>, Tadaaki Shimizu<sup>a</sup>, Takayuki Takarada<sup>b</sup>

<sup>a</sup> Department of Chemistry and Chemical Engineering, Niigata University, 2-8050, Ikarashi, Niigata 950-2181, Japan

<sup>b</sup> Division of Environmental Engineering Science, Faculty of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan

## ARTICLE INFO

### Article history:

Received 29 September 2014

Received in revised form 30 March 2015

Accepted 26 April 2015

Available online 1 May 2015

### Keywords:

Electroless nickel-plating solution

Nickel recovery

Phosphorus removal

Ion exchange

Calcium precipitation

## ABSTRACT

A new approach to nickel recovery from spent electroless nickel-plating (ENP) solution was investigated using ion-exchange method with brown coal. Nickel ion-exchange was influenced by the solution pH, with the optimum values of pH 9.0–10.0, and was hindered by the anion species existing in the spent solution, especially for the high concentrations of phosphorus compounds. Calcium hydroxide precipitated most of the phosphorus from spent ENP solution, with the highest phosphorus removal efficiency of 98.2%. At the same time, pH control is required to prevent the co-precipitation of nickel hydroxide. Phosphorus removal with CaCO<sub>3</sub> and CaCl<sub>2</sub> showed strong pH dependence. The solution pH dropped with CaCl<sub>2</sub> addition. As a result, the formation of calcium sulphate occurred prior to that of P–Ca compounds. In contrast, CO<sub>3</sub><sup>2-</sup> anions from CaCO<sub>3</sub> dissolution reacted with the H<sup>+</sup> ions to neutralize the solution and decrease CaCO<sub>3</sub> solubility at last, the phosphorus removal reached its maximum of 51%. Combined use of calcium carbonate and calcium chloride improved phosphorus removal, maximizing the phosphorus removal efficiency at 94.8%, and enabling 62% of nickel in the ENP solution to be ion-exchanged into brown coal.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Electroless plating plays an important role in the industry and has been widely used owing to the low stresses in the deposits and ease of operation. In the electroless nickel plating (ENP) process, nickel metal is deposited by the chemical reduction of nickel ions by hypophosphite, aminoborane, or borohydride compounds [1,2]. The nickel and hypophosphite ions in solution decrease as the reaction proceeds, so nickel sulphate and sodium hypophosphite are normally added to the plating bath to replenish these ions. However, the accumulated phosphite, sulphate, sodium and other species lower the quality of deposited films and repeatedly used plating baths therefore need to be discarded [1].

Wastewater treatment following electroless nickel plating runs has been a subject of worldwide concern. Considering environmental protection and that the spent plating solution is a source of high amounts of dissolved nickel, many research groups have proposed and developed treatment technologies aimed at the removal and recovery of nickel. Such technologies include adsorption [3,4], electrodialysis [5,6], electrowinning [7,8], continuous solvent extraction [9] and precipitation [10]. The nickel recovery rate was in

some cases above 90% with current industrial recovery efficiency of less than 50% [1,8].

Ion exchange is considered as another environmentally friendly and cost-efficient technology for nickel recovery from spent ENP solution [11]. In particular, brown coal is cheap and has significant cation-exchange capacity because it contains functional groups (–COOH, –OH, etc.). Protons in the functional groups can exchange with cations and coordinate directly with metal ions [12]. Techniques for loading nickel onto brown coal have been studied and it has been found that approximately 9 wt% Ni can be exchanged into Loy Yang (LY) brown coal by ion-exchange [12]. Nickel particles disperse well in the coal matrix and the prepared Ni loading Loy Yang coal (LY–Ni) showed high performance during gasification of the coal matrix. Gasification rates of the LY coal were as high as 78.2% at the low gasification temperature of 500 °C and 100% at 700 °C in a steam/N<sub>2</sub> flow [13]. The LY–Ni char showed micro-porous textural characteristics and exhibited outstanding catalytic behaviour for the decomposition of biomass volatiles at relatively low temperatures of 500–650 °C. This temperature range is much lower than that of conventional methods (600–800 °C for catalytic gasification and 800–950 °C for non-catalytic gasification). More than 98% of the tarry materials were catalysed into light fuel gases and most of the N-containing compounds were catalytically reduced into non-toxic N<sub>2</sub> gas

\* Corresponding author. Tel./fax: +81 25 262 7376.

E-mail address: [liliuyun@eng.niigata-u.ac.jp](mailto:liliuyun@eng.niigata-u.ac.jp) (L. Li).

[12,14]. Nickel ion-exchanged brown coal prepared from spent ENP solution was therefore expected to provide high nickel recovery and a low-cost, high-performance catalyst preparation method.

It is, however, recognized that nickel ion exchange is always obstructed by anions in the ENP solution. Dihydrogen phosphite ( $\text{H}_2\text{PO}_3^-$ ) particularly accumulates after nickel plating operations. Chemical precipitation targeting the removal of P from wastewater, has been a well-established practice since the 1950s [15]. Chemical precipitation may occur spontaneously, but is unusually initiated by the addition of a di- or trivalent metal ion, e.g., magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), aluminium ( $\text{Al}^{3+}$ ), or ferric iron ( $\text{Fe}^{3+}$ ). The choice of the metal ion is important because recovered P that is too tightly metal-bound cannot readily be reused in industrial and agricultural applications [15]. Although P removal using aluminium- and iron-based precipitation is quite common in wastewater treatment [16–19], it is less appealing for recovery efforts because P recovery from these solids appears to be difficult, and aluminium is toxic to many plants and some soil organisms. Fe–P compounds are generally considered unavailable to plants, although a fraction of the insoluble P may eventually become bioavailable depending on hydration or aging [20]. Magnesium- and calcium-based precipitations are common means of P removal owing to their relatively low cost and ease of handling [21–23], with the products most commonly recycled as fertilizer.

In this study, calcium hydroxide, calcium chloride and calcium carbonate were selected to investigate phosphorus removal from spent ENP solution. The extents of P removals with the various compounds were compared. The treated solution was subsequently employed in the nickel loading brown coal process to evaluate nickel recovery performance. As a fundamental study, nickel recovery from the original spent ENP solution and water diluted spent ENP solutions are also discussed.

## 2. Materials and methods

An original spent ENP solution was used in this work, provided by Hohsen Precision Co., Ltd, Japan. Table 1 shows the composition of the spent ENP solution. Nickel loading brown coal was prepared by mixing Loy Yang (LY, Victoria, Australia; 45–75  $\mu\text{m}$ ) brown coal and nickel solutions. Table 2 shows the proximate and ultimate analyses of the naturally dried LY coal.

Calcium hydroxide, calcium chloride and calcium carbonate were selected to evaluate phosphorus removal from the spent ENP solution. The reagents were supplied by Wako Pure Chemical Industries, Ltd. The phosphorus removal procedure is shown in Fig. 1. A dose of the Ca compound(s) was mixed into 25 ml spent ENP solution and the Ca/P ratios were varied. Detailed information is given in Section 3.3. After 3 h of stirring, precipitates and solution were filtrated. The solution was used for Ni recovery by LY coal, and part of it was analysed by atomic absorption spectrophotometry and ion chromatography to determine the nickel and phosphorus concentrations. Phosphorus removal efficiency (a measurement of the amount of P removed by the calcium compounds, expressed as a percentage) was estimated by the change in concentration of the phosphite ion in the spent ENP solutions before and after mixing with the calcium compounds.

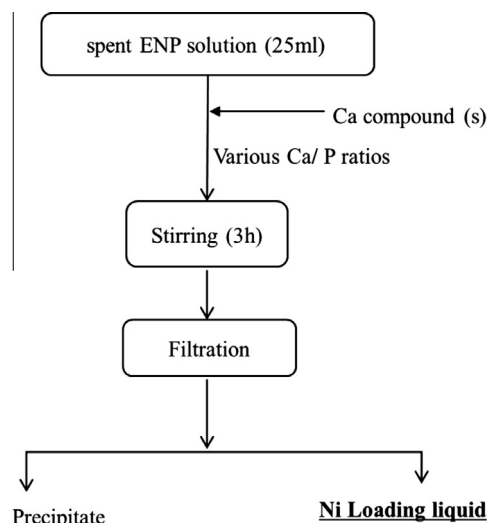
The preparation procedure for the nickel-loaded brown coal is schematically illustrated in Fig. 2. A 29% ammonia solution was

**Table 1**  
Composition of the spent electroless nickel plating solution.

Element	Ni	P	S	F	Cl	pH
Concentration (g/L)	4.82	59.18	12.40	16.50	0.28	4.9

**Table 2**  
Proximate and ultimate analyses of Loy Yang brown coal.

Proximate analysis (wt%)				Ultimate analysis (wt%, dry, ash free)				
Moisture	Fixed carbon	Volatile matter	Ash	C	H	N	S	O (by diff.)
13.6	42.0	51.8	0.7	62.5	5.7	0.6	0.2	31.0



**Fig. 1.** Procedure for phosphorus removal by Ca compounds.

first added to the original spent ENP solution or P-removal treated solution (Fig. 1) for pH adjustment. A basic nickel loading solution with pH values around 9.0–10.0 was prepared. A dose of LY coal was then immersed in the nickel solution to allow ion exchange to take place. The nickel/coal mass ratio (the ratio of mass of nickel in the loading solution to the mass of LY coal) was 1/10. After stirring the mixture for about 3 h, the ion-exchanged coal was filtered and washed repeatedly until no further nickel was detected in the rinse water. Following drying, preparation for the nickel loading LY coal (LY–Ni) was completed. Nickel recovery efficiency (measurement of the amount of nickel recovered by LY coal, expressed as a percentage) was estimated by the change in mass of nickel in the spent ENP solutions before and after LY–Ni preparation. For the tests with aqueous  $\text{NiSO}_4$  solution, a 55 mmol/L  $\text{NiSO}_4$  solution was used as the nickel loading liquid.

Nickel and calcium concentrations were measured by atomic absorption spectrophotometry (AA-6400F, Shimadzu, Kyoto, Japan) after adequate dilution with distilled water. Major anions of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and phosphorus were quantified by ion chromatography (TCD, Eluent solution: 1.0 mM  $\text{NaHCO}_3$  – 3.2 mM  $\text{Na}_2\text{CO}_3$ ; ICA-2000, TOA DKK, Tokyo, Japan). X-ray diffraction (XRD) (M03XHF<sup>22</sup>, Mac Science Co., Ltd, Cu K $\alpha$  radiation, 40 kV, 30 mA) was employed for characterization of the precipitates.

## 3. Results and discussion

### 3.1. Influence of initial pH on preparation of Ni loading coal

The initial pH of the loading solutions is considered one of the most important parameters affecting an ion exchange process. The influence of pH on nickel loading is discussed. A dose of LY coal was immersed in the  $\text{NiSO}_4$  solution or original spent ENP solution for ion-exchange, to which a 29% ammonia solution was added to adjust the initial solution pH. Fig. 3 shows the Ni loading as a function of the initial solution pH values.

Download English Version:

<https://daneshyari.com/en/article/640523>

Download Persian Version:

<https://daneshyari.com/article/640523>

[Daneshyari.com](https://daneshyari.com)