World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:6, No:8, 2012

# The removal of Ni, Cu & Fe from a Mixed Metal System using Sodium Hypophosphite as a Reducing Agent

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***Abstract*—**The main objective of this study was to remove and recover Ni, Cu and Fe from a mixed metal system using sodium hypophosphite as a reducing agent and nickel powder as seeding material. The metal systems studied consisted of Ni-Cu, Ni-Fe and Ni-Cu-Fe solutions. A 5 L batch reactor was used to conduct experiments where 100 mg/l of each respective metal was used. It was found that the metals were reduced to their elemental form with removal efficiencies of over 80%. The removal efficiency decreased in the order Fe>Ni>Cu. The metal powder obtained contained between 97-99% Ni and was almost spherical and porous. Size enlargement by aggregation was the dominant particulate process.

***Keywords*—**crystallization, electroless plating, heavy metal removal, wastewater treatment

Open Science Index, Materials and Metallurgical Engineering Vol:6, No:8, 2012 publications.waset.org/5356.pdf

## I. INTRODUCTION

WASTEWATER from industrial activities is known to contain metals such as silver, copper, nickel, iron and mercury. The disposal of this wastewater to the environment has been prohibited by environmental legislation in most parts of the world, as a result of the negative impact of polluted wastewater on the environment [1]. In many parts of the world, health problems and diseases are caused by discharging polluted waste water. Increased industrialization has increased the volume of polluted wastewater discharged to the environment leading to an increase in the incidents of water pollution and destruction of aquatic life. The pollution of water has a serious impact on all living creatures, and can negatively affect the use of water for drinking, household needs, recreation, fishing, transportation, and commerce.

In human beings, poisoning by these metals can cause dysfunction of kidney, reproduction system, liver, brain and central nervous system [2]. Thus, the discharge of such wastewater to the environment needs to be controlled and monitored. Wastewater treatment facilities have been used as a means of removing pollutants from wastewater in order to limit pollution to the environment, and different technologies have been developed and implemented over the years. These technologies; such as membranes techniques, ion exchange, precipitation and adsorption, have made it possible to remove dissolved matter and toxic substances from wastewater. Precipitation is the mostly widely used because it is the most economical method and easier to implement and operate on a large scale. However, traditional precipitation methods using lime, sulfides or hydroxides recover metals in the form of a sludge which is not reusable and has to be disposed in landfills creating a potential environmental hazard and resulting in loss of valuable mineral.

A modified precipitation process, reduction crystallization allows heavy metal to be removed and recovered in their elemental state as metallic powders by using a reducing agent [3]. Reducing agents such as sodium hypophosphite, hydrazine and formaldehyde have been used in a wide variety of chemical reactions from organic compounds synthesis to metal production [4]. In order to reduce metal ions into the metallic state, the solution electrochemical potential must be sufficiently low to allow the metal to accept electrons from the reducing agent [5].

Previous studies using nickel powder as seeding material have demonstrated that hydrazine is an effective reducing agent for Ni, Cu, Co and Fe with removal efficiencies of over 97% [6]. Based on these findings the feasibility of using the same technique with a different reducing agent, sodium hypophosphite, was explored.

Hirasawa and Horikawa (2000) investigated the removal and recovery of nickel ions from waste water from electroless plating by reduction crystallization, using sodium hypophosphite ion as a reducing agent [7]. They found that over 99% of Ni was removed and recovered; however, the surface of the resulting nickel seeds were covered with phosphorus resulting in a 10% decrease in the amount of nickel recovered in the subsequent batch reduction.

Equation 1, shows the principal half reaction occurring when the hypophosphite ion is used as a reducing agent.

$$H_2PO_2^- + 3OH^- \rightarrow HPO_3^{2-} + 2H_2O + 2e \qquad (1)$$

## II. MATERIALS AND METHODS

### A. Materials

A basic hypophosphite reduced sulphate bath was chosen as the plating bath, where nickel sulphate, copper sulphate and iron sulphate were used as the source of metal while sodium hypophosphite served as the reducing agent. Nickel powder supplied by Impala Platinum Refineries was used as seeding material. Ammonium hydroxide (1 M) was used to adjust the pH. The experiments were conducted using a 5 L stainless steel batch reactor fitted with a 4 pitched blade axial impeller (diameter 50 mm), heating element and a thermostat for temperature control. The reagents were weighed on an analytical balance (model Radweg PS 6000/c/l). A pH meter (model Mettler Toledo, InLab 74X Series) was used to measure the pH and also the temperature during the reduction process. Inductively coupled plasma optical emission spectroscopy (ICP-OES; model Spectro Arcos FSH12) was used to measure the concentrations of Ni, Cu and Fe in solution after reduction. X-Ray fluorescence (XRF; model Magix Pro Phillips) was used to determine the elemental composition of the powder product. The particle size distribution (PSD) of the powder was measured using the laser diffraction technique (Malvern Particle Analyser; model Mastersizer 2000). The powder morphology was captured using a Scanning Electron Microscopy (SEM, model Jeol JSM 5600).

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### B. *Experimental Procedure*

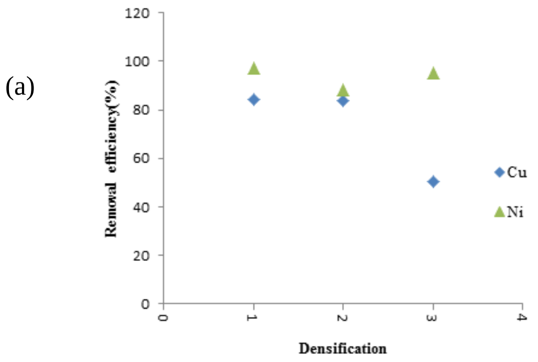
5 L solutions of mixed metal solutions of Ni-Cu, Ni-Fe and Ni-Cu-Fe containing 100 mg/L of each respective metal were prepared. Only one solution was used in each experimental run and each experimental run was replicated. 30 g of nickel powder (seed) and 5 L of the metal solution were then added to the batch reactor. Thereafter, agitation (agitator output speed 450 rpm) and heating was commenced. 2.94 g of sodium hypophosphite was then added for experiments where Ni-Cu and Ni-Fe solutions were used, and 4.41 g was added for the Ni-Cu-Fe based on the stoichiometric ratios of each reduction reaction. Heating and agitation continued until the temperature reached 60°C. The reduction reaction was initiated by adding 1 M ammonium hydroxide to adjust and control the pH of the solution to between 8 and 8.5. Temperature was maintained at 65-70°C during the course of the reduction reaction. The addition of $NH_3$ initiated the reduction reaction (1), since hypophosphite reduction is pH dependent. The reaction was allowed to occur for 3 min, thereafter, the agitator and heating element were switched off and the nickel powder was allowed to settle. A reaction time of 3 min was selected since it was observed that the pH became stable after 3 min, indicating that the reaction had almost gone to completion. After the reaction time of 3 min, agitation and heating was stopped and the nickel powder was allowed to settle. A 5 ml sample of the reduced solution was sampled and analysed for the residual metal concentration using ICP-OES. The reduced solution was then discharged and the nickel seed left in the reactor to act as seeding material for the next batch reduction (termed a densification). A fresh metal solution was then introduced into the batch reactor with the seed from the previous densification. A similar procedure was followed as for the first densification. A total of three densifications were conducted in each experimental run. After the third densification, the reduced solution and the nickel powder were discharged from the reactor. The powder was then separated from the liquor by filtration using a vacuum pump and dried overnight in an oven at 90°C. The PSD, elemental composition and morphology of the powder samples were then analysed using laser diffraction, XRF and SEM respectively.

A similar experimental procedure was followed for the other metal solutions.

## III. RESULTS AND DISCUSSION

### A. *Removal Efficiency*

The average removal efficiency of each metal per batch reduction (densification) for the different mixed metal systems after reduction is shown in Fig 1.



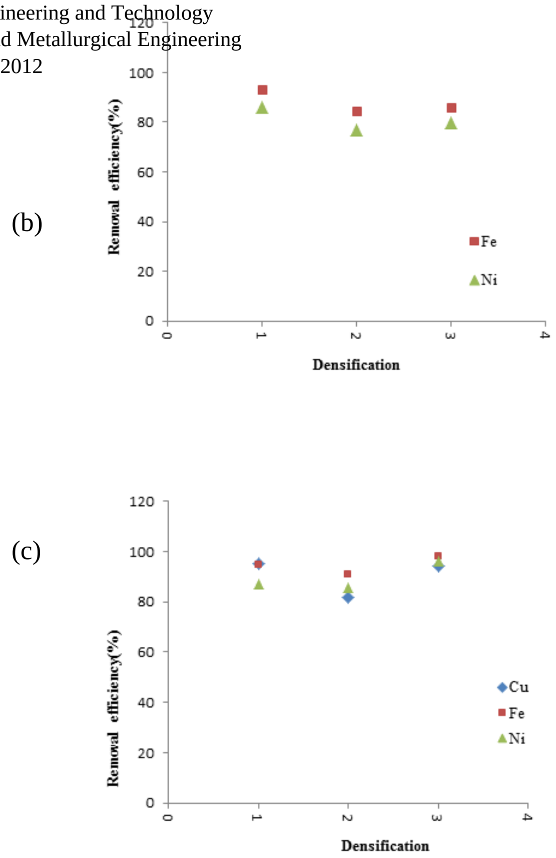


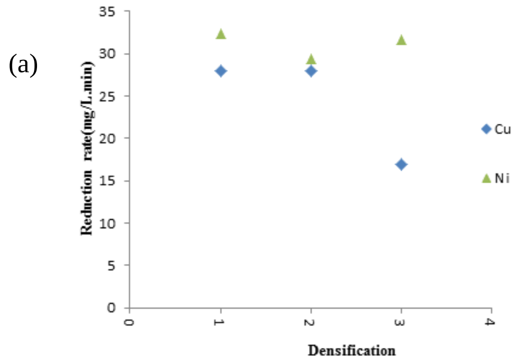
Fig. 1 Average removal efficiency of Ni, Cu and Fe (a) Ni-Cu solution (b) Ni-Fe solution and (c) Ni-Cu-Fe solution.

Similar trends were observed in the removal efficiency of all three metals. All three metals had the lowest removal efficiency in the 2nd densification as compared to the 1st and 3rd densification. The removal efficiency was highest in the first densification. The removal efficiency decreased in the following order Fe>Ni>Cu.

The removal efficiency of the metals studied was lower than that obtained using hydrazine as a reducing agent where removal efficiencies were above 99% [6]. This shows that sodium hypophosphite is not as effective as hydrazine in reducing the metals from solution.

### B. *Reduction Rate*

The reduction rate of each metal per batch reduction (densification) for the different mixed metal systems studied is shown in Fig 2.



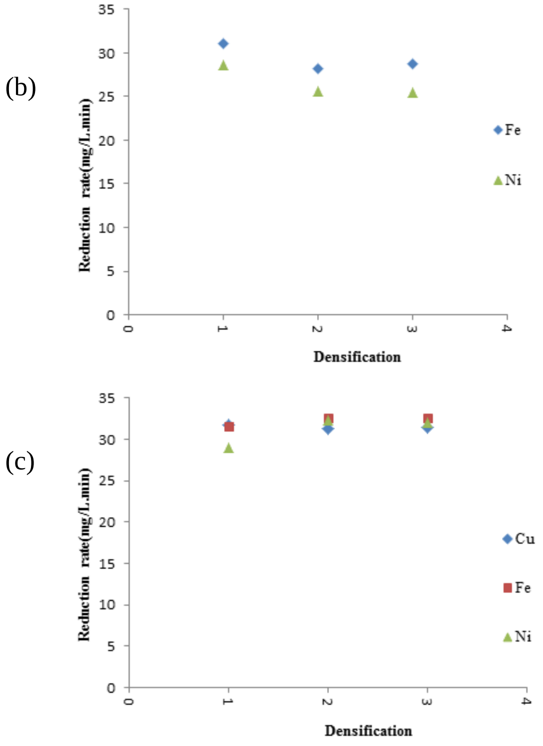


Fig. 2 Average reduction rate of Ni, Cu and Fe (a) Ni-Cu solution (b) Ni-Fe solution and (c) Ni-Cu-Fe solution

The reduction rate of Ni was higher in the presence of Cu (Ni-Cu solution) than in presence of Fe (Ni-Fe solution). The presence of Fe was found to increase the reduction rate of Cu and the reduction rate of all the three metals for the Ni-Cu-Fe system were not significantly different, with the exception of Ni in the 1st densification (Fig. 2c). Based on the reduction potential of Ni (-0.23) and Cu (0.34), the reduction of Cu is thermodynamically more favourable to that of Ni. However, from the results obtained Ni was preferential removed when compared to Cu. Since Ni seed was used as seeding material it is proposed this favours the preferential deposition of Ni over Cu. The reduction of Fe was preferential favourable compared to that of both Ni and Cu.

## C. *Elemental Composition of Powder*

The elemental composition of the powder obtained after three densifications was determined using XRF and is shown in Table 1.

TABLE I
ELEMENTAL COMPOSITION OF POWDER

| Element | Composition % | | | |
|---|---|---|---|---|
| | Seed | Ni-Cu | Ni-Fe | Ni-Cu-Fe |
| O | 0.49 | 0.88 | 0.49 | 0.56 |
| Al | 0.05 | 0.25 | 0.04 | 0.07 |
| Si | 0.25 | 0.41 | 0.21 | 0.17 |
| S | 0.04 | 0.06 | 0.04 | 0.05 |
| Fe | 0.07 | 0.15 | 0.22 | 0.36 |
| Co | 0.11 | 0.10 | 0.00 | 0.09 |
| Ni | 98.87 | 98.00 | 99.00 | 97.00 |
| Mg | 0.12 | 0.03 | 0.05 | 0.03 |
| Cu | 0.00 | 0.54 | 0.08 | 1.60 |
| P | 0.00 | 0.02 | 0.01 | 0.05 |

The nickel content (97-99%) was higher than that for iron and copper in all three samples, since Ni powder was used as seeding material. The P content in the powder was due to the oxidation of the hypophosphite ion used as a reducing agent and was higher in the powder produced from the Ni-Cu-Fe solution since stoichiometric amounts of the hypophosphite were added to each metal solution. The amount of Cu in the powder was also higher in the powder produced from the Ni-Cu-Fe solution as compared to the powder from the Ni-Cu solution. This can be attributed to the higher reduction rate of Cu in the presence of Fe.

## D. *Evolution of the PSD (Particle Size Distribution)*

The evolution of the PSD in terms of the number distribution for the mixed metal systems is shown in Fig. 3.

There was a shift in the modal size to the right and a decrease in the area under the curve (equivalent to total number of particles). This is evidence of size enlargement by aggregation. The PSD of the powder after three batch reductions also exhibited a developing bi-modal distribution, which is also further evidence for aggregation.

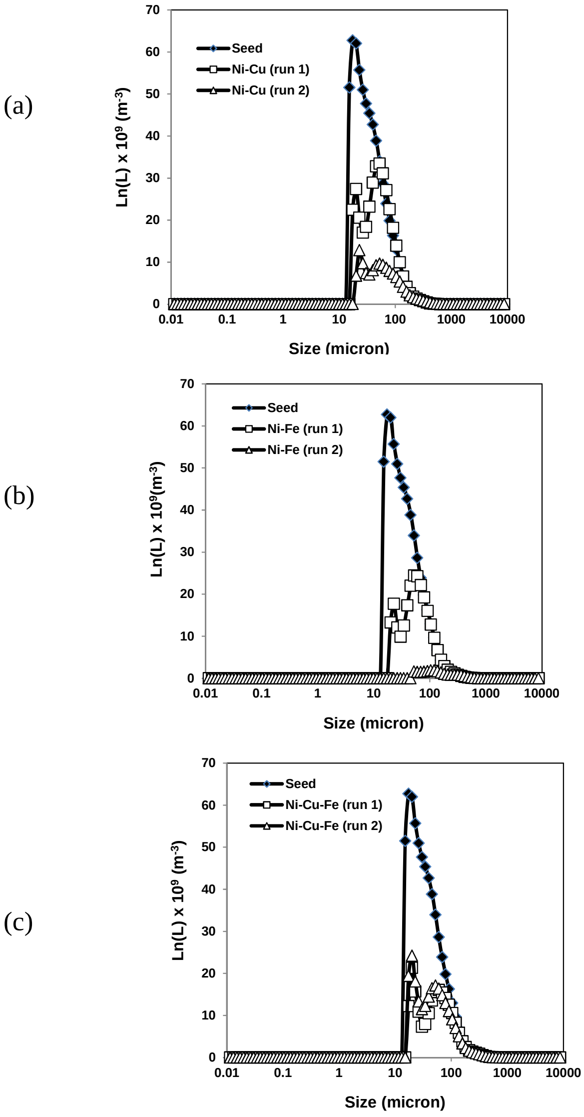


Fig. 3 Evolution of the PSD (a) Ni-Cu (b) Ni-Fe (c) Ni-Cu-Fe

### *E. Morphology of the powder particles*

The scanning electron micrographs of the powder produced after three densifications is shown in Fig. 4. In all cases the particles were almost spherical and porous.

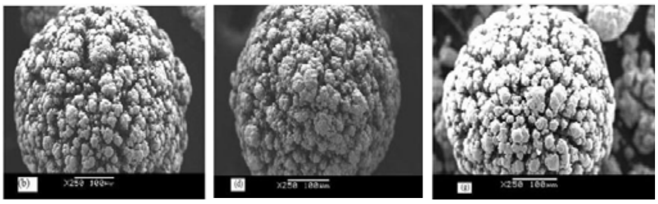


Fig. 4 SEM micrographs of powder produced from (b) Ni-Cu (d) Ni-Fe (g) Ni-Cu-Fe

## IV. CONCLUSION

Sodium hypophosphite was found to be an effective reducing agent for the recovery of Ni, Cu and Fe. The current study showed that more than 80% of the metals were removed from a mixed metal system by reduction crystallization. The removal efficiency was found to decrease in the following order Fe>Ni>Cu. However, the removal efficiency was found to be less than that of hydrazine, where over 99% of the metals studied were recovered. It is recommended that additives be used to increase the reduction rate, in order to ensure maximum removal of the metals from the effluent.

## ACKNOWLEDGMENT

The authors will like to thank the University of Johannesburg Research Committee (URC) for their financial assistance and Impala Platinum Refineries for providing the materials used in the project.

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