

Removal and recovery of Ni, Cu and Fe from heavy metal effluent by reduction crystallization

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Abstract

Due to the fast depletion of water reserves globally, the toxicity of heavy metals and the negative impact posed to the environment; the current focus in wastewater treatment is now on the removal and re-use of these heavy metals rather than removal and disposal in landfills. This study investigated the use of hydrazine as a reducing agent to remove and recover Ni, Cu and Fe from wastewater by reduction crystallization. Feasibility studies were carried out to test the efficiency and find the optimum operating conditions for this method and generate an understanding of the chemical and particulate process occurring. The experiments were conducted on a 20L batch reactor using synthetic solutions containing a mixture of nickel, copper and iron. The results show that hydrazine can recover and crystallize Ni, Cu and Fe into their elemental form: 99.30% Ni was removed from the Ni-solution, 99.26% Ni and 98.81% Cu were removed from the Ni-Cu solution, over 99.90% Ni and 97.70% Fe were removed from the Ni-Fe solution. Evolution of the PSD revealed that breakage and molecular growth were the predominant particulate processes occurring, a finding which was validated by the scanning electron micrographs of the powder obtained.

Keywords: metal powder, electroless plating, reduction crystallization, chemical reduction, reducing agent.

1 Introduction

Heavy metal contaminated wastewater produced by acid mine drainage and mineral processing occurs at estimated 70% of world's mine sites, which makes it one of the mining industry's most significant environmental and financial



liability. Wastewater treatment is becoming ever more critical due to diminishing water resources, increasing wastewater disposal costs and stricter discharge regulations that have lowered permissible contaminants levels in water streams. The removal and recovery of heavy metals from effluents has been a subject of significant importance due the negative impact these toxic metals have on human health and the environment as a result of water and soil pollution.

A number of treatment methods have been developed for heavy metal removal namely, precipitation, adsorption, ion-exchange and membrane technologies. Of these methods 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, sulphides or hydroxides recover metals in the form of a sludge which is not reusable, requires on-going storage and management thus creating a long-term environmental liability.

Reduction crystallization has been widely employed in the electroplating and metallurgical refining industry for metal plating and production of metallic powders respectively. Limited studies have been done on the use of reduction crystallization for metal removal in effluents and most of these studies focused only on single or bi-metal component systems [1, 2].

Of the available reducing agents, only aqueous reducing agents were considered since these do not require the use of high temperature and pressure as required for gaseous reducing agents. From the aqueous reducing agents hydrazine was selected because its decomposition products are environmentally benign as opposed to sodium borohydride which generates a toxic by-product $B(OH)_3$ and sodium hypophosphite which increases the phosphorus load on the effluent.

The purpose of this work was to use hydrazine as a reducing agent to remove and recover heavy metals from wastewater containing mixed metals of nickel, copper and iron by reduction crystallization. Secondly, to efficiently recover and crystallize Ni, Cu and Fe in their elemental form, using hydrazine as a reducing agent and pure/used nickel powder as seeding material. The third objective was to carry a feasibility study for testing the efficiency and finding the optimum operating conditions for this method. Finally an understanding of chemical and particulate process occurring within the system was generated.

1.1 Reduction crystallization

The use of reducing agents for metal recovery in reduction crystallization is a relatively simple method, which is similar to chemical precipitation except that the different soluble metal cations are recovered by chemical reduction as useful insoluble elemental metal instead of metal hydroxide or sulphide sludge. In the process of reduction crystallization chemically reduced aqueous metals ions are plated on to a base substrate with no electrical current required for deposition, following a process called electroless plating. The process differs from immersion plating in that deposition of the metal is continuous. Components of the electroless bath include an aqueous solution of metal ions, reducing agent(s), complexing agent(s), and bath stabilizer(s) operating at a specific metal ion



concentration, temperature, and pH range. Unlike conventional electroplating, no electrical current is required for deposition. The base substrate being plated must be a conductor or semi-conductor in nature (Henry [3]).

A properly prepared work piece provides a catalyzed surface and, once introduced into the electroless solution, a uniform deposition begins. Minute amounts of the electroless metal (i.e. nickel, copper, etc.) will catalyze the reaction, so the deposition is autocatalytic after the original surfaces are coated (Henry [3]). Electroless deposition then continues, provided that the metal ion and reducing agent are replenished. If air or evolved gas, however, is trapped in downward facing cavity, this will prevent electroless deposition in these areas.

In electroless plating, metal ions are reduced to metal by the action of chemical reducing agents, which are simply electron donors. The metal ions are electron acceptors, which react with electron donors. The catalyst is the work piece or metallic surface, which accelerates the electroless chemical reaction allowing oxidation of the reducing agent. The metal ion and reducer concentration must be monitored and controlled closely in order to maintain proper ratios, as well as the overall chemical balance of the plating bath. The electroless plating deposition rate is controlled by temperature, pH, and metal ion/reducer concentration (Henry [3]). A schematic diagram of the reduction crystallization method is shown in fig. 1.

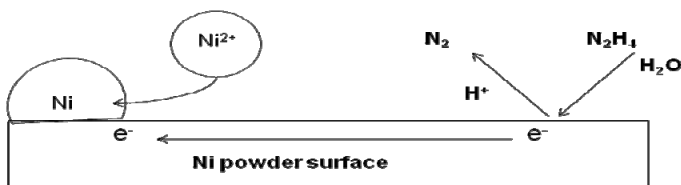
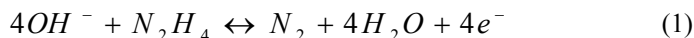


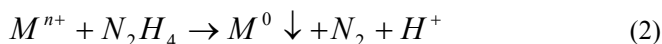
Figure 1: Reduction crystallization method.

1.2 Hydrazine as a reducing agent

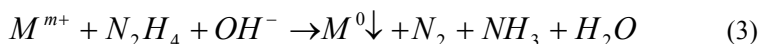
Hydrazine (N_2H_4) is a strong reductant widely used in various chemical operations. A series of striking results has been obtained where hydrazine is used as a reducing agent for the production of finely divided metals, of metal-on glass films, and of metallic hydrolysis, and electroless plating (Simpson [4]). An important half reaction involving hydrazine is:



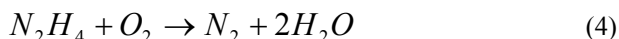
It can effectively be employed in reduction of various metal cations (M^{n+}) to elemental state (M^0) according to the following reaction (Chen and Lim [1]):



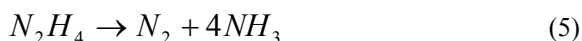
Tobe and Burgess [5] discussed that metal ions can also be reduced according to reaction in eqn. (3):



Hydrazine can react with dissolved oxygen (DO) in water (Audrieth and Ogg [6])



Hydrazine can undergo self oxidation and reduction in both alkaline and acidic solutions. The decomposition of hydrazine proceeds by eqn. (5).



Precious metals can be easily recovered by using this powerful reductant, eqn. (2). Since metal cations are immediately reduced to metallic state, there is very limited amount of metal ions present in the solution. Complexation between metal and ammonia due to eqns. (3) and (5) is therefore unlikely occurs. By using air stripping, ammonia is easily removed from the solution. In addition, unutilized hydrazine can be removed by aeration, eqn. (4).

2 Particulate processes

Crystallization is a particulate process which is widely used in industry for the production of many products including fertilizers, proteins, and pesticides (Christofides *et al.* [7]). In all of these instances, the particle size distribution (PSD) provides the critical link between the product quality indices and the process operating variables; thus, the ability to effectively control the shape of the PSD is essential for regulating the end product quality in these processes (Christofides *et al.* [7]). The following processes occur during crystallization (a) nucleation; (b) aggregation/agglomeration; (c) molecular growth; (d) breakage/attrition.

Nucleation is the step whereby the solute molecules dispersed in the solvent start to gather into clusters that becomes stable under the current operating conditions. These stable clusters constitute the nuclei. However, when the clusters are not stable, they re-dissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such critical size is determined by the operating conditions (temperature, supersaturation, etc.) (Myerson [8]).

Aggregation involves the clustering of separate particles to form larger particles. This initial clustering may be the results of a number of mechanisms and the particles may be held together by several different forces. The aggregation process is characterised by the aggregation rate constant (Ntuli *et al.* [9]).

Molecular or crystal growth is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while supersaturation exists. Supersaturation is the driving force of crystallization; hence the rate of nucleation and growth is driven by the existing supersaturation in the solution. Depending upon the conditions, either



nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained.

In the breakage process the existing particles or crystals breaks into new smaller particles of varying sizes. The smallest particles of crystalline material that have already been formed start breaking from identifiable crystals, and thereby, to be added to the body of solids that are present as individual or discrete particles. Their presence increases as the level of mechanical energy input in the system increases. They can be formed by contact of the crystals with a pump, impeller or due to impact of the slurry on the tube sheets, piping or vessels walls.

3 Materials and methods

3.1 Experimental

100 mg/l of copper and nickel synthetic solutions were prepared by weighing 4.48 g of nickel sulphate hexahydrate and 3.93 g cupric sulphate. 97.77 mg/l iron was prepared by weighing 4.98 g ferrous sulphate and dissolving all the salts into 1000 ml of water in a volumetric flask.

1 M hydrazine in tetra-hydrofuran was employed as a reducing agent, 2 M sodium hydroxide as a pH regulator. 10 L of 100 mg/L prepared synthetic solution was fed into a 20 L stirred batch reactor. 30 g of pure nickel powder was added into a reactor as a seeding material. The solution was then heated to 45°C and at this temperature 0.3 ml of 1 M hydrazine was added into the reactor, under constant stirring. Reduction crystallization proceeded under pH 10.7-11, whereby 1 M sodium hydroxide solution was added at 60°C. Three minutes was employed for the reaction to complete. After the reaction was complete, the agitator was switched off and the solution was allowed to cool. Thereafter the reduced solution was discharged leaving behind the seed material. A fresh metal solution was then added and the process was repeated. The seed particles were discharged after the third batch reduction. The batch experiments were repeated three times using the same nickel powder seed, thereafter the mixed solution was filtered to obtain the nickel powder and the residual effluent.

Residual nickel, copper and iron concentrations were measured by Inductively Coupled Plasma-Optical Emission Spectrometer (Spectro Arcos Fsh12). The Ni powder morphology analyses were performed using Scanning Electron Microscopy (Jeol JMS 5600). Laser diffraction Malvern (Mastersizer 2000) was used to measure the PSD of the powder samples in order to study and understand the particulate process occurring during reduction crystallization.

4 Results and discussions

It was found that hydrazine can successfully be used as a reducing agent to remove and recover nickel, copper and iron from wastewater using reduction crystallization. For the experiments using Ni-Cu and Ni-Fe solutions, the experimental conditions used were similar to those used for the Ni-solution as



the main focus was not on the selective removal of the metals. Therefore, the operating conditions were pH of 10.7-11 and 60°C for all the experiments. Each batch run is termed a densification because the powder becomes denser with each successive batch reduction.

4.1 Residual concentration and removal efficiency

4.1.1 Nickel solution

Fig. 2 indicates the residual concentration of nickel in solution for three experimental runs using the same nickel powder as seeding material for the three densifications and the %removal of nickel from Ni-solution for the three experimental runs. The initial concentration was 100 mg/l and the residual concentration of nickel in the effluent decreased with increase in the number of densifications. Reusing the nickel powder seeding material for the subsequent densifications lowered the residual concentration of Ni^{2+} from 2 mg/l to less than 1 mg/l, fig. 2(a). The removal rate increased from 99.00% in the first densification to 99.30% in the second densification and remained nearly constant thereafter, fig. 2(b). The sudden increase from 1st to 2nd densification can be attributed to the change in surface area of the nickel powder, due to either molecular growth or nucleation occurring during the crystallization process.

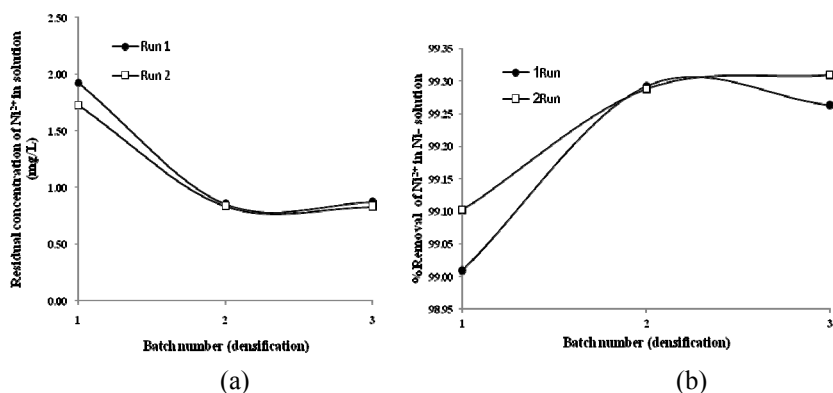


Figure 2: (a) Residual nickel concentration in solution (Ni-solution).
(b) %Removal of nickel in solution (Ni-solution).

4.1.2 Nickel-copper solution

Copper residual concentration was higher than nickel residual concentration in Ni-Cu solution for all the experimental runs, fig. 3(a). The highest Cu and Ni concentrations were 1.190 mg/L and 0.990 mg/L respectively from a 100 mg/L initial concentration of both Ni and Cu. The percentage of Ni removed was 99.26% and was higher than the percentage of Cu removed which was 98.81%, fig. 3(b). The %removal of Ni^{2+} and Cu^{2+} was the highest in the 2nd densification and decreased sharply with the increasing number of densifications. The decrease in the removal rate can be attributed to the change in particle surface

area as a result of particle aggregation. Removal of nickel from the effluent was favoured over that of copper.

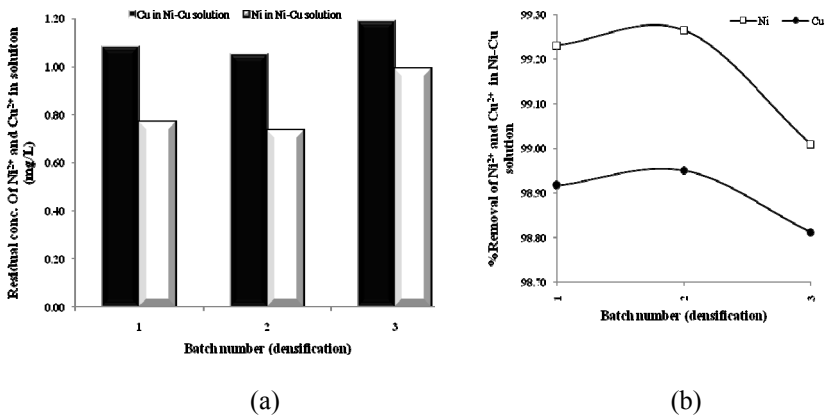


Figure 3: (a) %Residual nickel and copper concentration in solution (Ni-Cu solution). (b) %Removal of nickel and copper in solution (Ni-Cu solution).

4.1.3 Nickel-iron solution

The residual concentration for both Ni and Fe decreased with the increase in number of densifications. The highest residual concentration was 0.037 mg/L and 0.032 mg/L for nickel and iron respectively in Ni-Fe solution, from an initial concentration of 100 mg/L Ni and 97.73 mg/L Fe, fig. 4(a). 97.70% of Fe was removed and almost 100% Ni was removed from the solution in all the densifications, fig. 4(b).

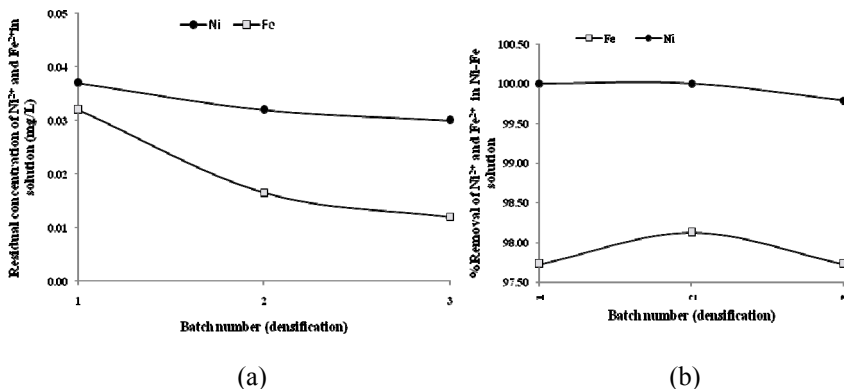


Figure 4: (a) %Residual nickel and iron concentration in solution (Ni-Fe solution). (b) %Removal of nickel and iron in solution (Ni-Fe solution).



4.2 Evolution of PSD

Fig. 5 shows the evolution of the particle size distribution (PSD) of the powder obtained from the Ni-solution, Ni-Cu solution and Ni-Fe solution respectively, fig.5. From the evolution of the volume distribution it can be concluded that the size enlargement is not significant as the modal size remains unchanged. The PSD data was transformed into its moments using eqns. (6) and (7).

$$n(L)dL = \sum_i \frac{vol \%_i \times conc (vol \%)}{100} \cdot \frac{1}{k_v L^3} \tag{6}$$

$$m_j = \int_0^\infty L^j n(L)dL \tag{7}$$

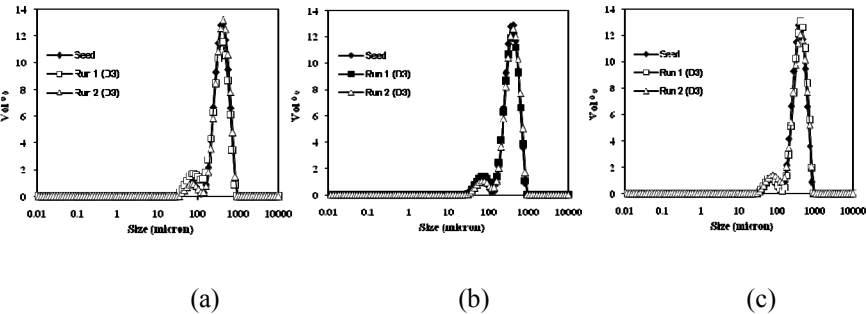


Figure 5: Evolution of the PSD in vol%. (a) Ni (b) Ni-Cu (c) Ni-Fe.

The volume based histogram *vol%* versus L_i where i indicates the size sub-range and the particle concentration (*vol%*) were generated by laser diffraction Malvern Mastersizer and the volume shape factor k_v equal to $\pi/6$ was used. The first four moments (0^{th} , 1^{st} , 2^{nd} and 3^{rd}) are of special interest and are related to the total number, length, area and volume of solid per unit volume of suspension respectively [10]. The 0^{th} , 2^{nd} and 3^{rd} moments for seed particles and the powder from the third densification is shown in table 1.

Table 1: Moments of the PSD of the powder.

Moments	$0^{th}(\# \cdot m^{-3} \times 10^{11})$	$2^{nd}(m^2 \cdot m^{-3} \times 10^3)$	$3^{rd}(m^3 \cdot m^{-3} \times 10^{-6})$
Seed	7.79	5.91	6.44
D3 Powder (Ni)	11.19	8.18	6.65
D3 Powder (Ni-Cu)	12.93	9.90	6.86
D3 Powder (Ni-Fe)	14.40	12.00	6.86

There was an increase in the 0^{th} , 2^{nd} and 3^{rd} moments in all the experimental runs, as shown in table 1, corresponding to an increase in the number, surface area and volume of particles respectively. Increase in particle number can be

attributed to either nucleation/breakage or both while increase in the surface area can be due to molecular growth/nucleation/breakage or a combination of the three. The 3rd moment was higher for the Ni-Cu and Ni-Fe solution due to higher metal concentration available for reduction. The increase in the particle volume can be attributed to growth/nucleation. The 0th and 2nd moment obtained from the Ni-Fe solution was higher than that obtained from the Ni and Ni-Cu solution, indicating that Fe catalysed the reduction of Ni to a greater extent than Cu. Previous studies on Ni reduction have shown that Fe acts as a growth promoter and nucleating agent which might explain the high values obtained for the 0th and 2nd moments (Ntuli and Lewis [11]).

4.3 SEM micrograph of nickel powder

From the SEM micrograph it seems breakage by attrition and molecular growth were more predominant than nucleation, fig. 6. This finding seems to agree with the evolution of the PSD where there was no significant change in the volume distribution, fig. 5. Nucleation and breakage by fragmentation normally results in significant changes in the volume distribution.

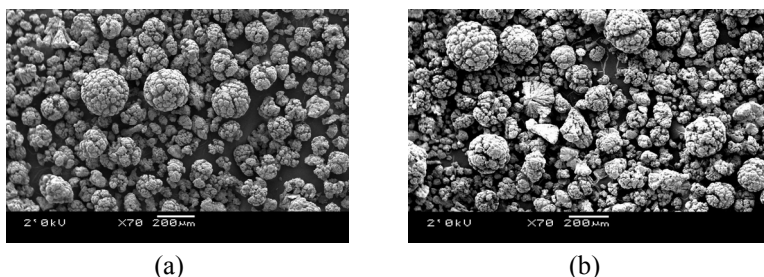


Figure 6: Scanning electron micrograph of D3 powder (a) Ni-Cu. (b) Ni-Fe.

5 Conclusions

The results obtained indicate that hydrazine is an effective agent to crystallize Ni, Cu and Fe into their elemental states with nickel powder as a seeding material. %Ni removal was higher than %Cu removal in the Ni-Cu solution and the presence of copper slightly reduced %Ni removal. Over 99.9% Ni was removed in Ni-Fe solution, making the %removal of Ni higher in the Ni-Fe solution as compared to the Ni and Ni-Cu solution. This was attributed to the greater catalytic effect of Fe as compared to Cu. Reusing the nickel powder seeding material for subsequent batch reductions resulted in lower residual metal concentrations. Based on the evolution of volume distribution and 0th, 2nd and 3rd moments, breakage by attrition and molecular growth were identified as the predominant mechanisms occurring during the reduction crystallization process. The finding was confirmed by the scanning electron micrographs of the powder obtained.

Acknowledgement

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