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## REMOVAL AND RECOVERY OF HEAVY METAL FROM MULTI-COMPONENT METAL EFFLUENT BY REDUCTION CRYSTALLIZATION

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### Abstract

Precipitation is the mostly widely used wastewater treatment method because it is the most economical, 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. 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 effluent treatment is now on the removal and re-use of these heavy metals rather than removal and disposal in landfills. Land filling creates a potential environmental hazard, resulting in loss of valuable minerals, contamination of drinking water and pollution of soil and ground water. This study investigated the use of hydrazine as a reducing agent to remove and recover heavy metals from mining and metallurgical effluent by reduction crystallization. In this process chemically reduced aqueous metal ions were plated on to a base substrate with no electrical current required for deposition (electroless plating). 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. This study seeks to efficiently recover and crystallize  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in their elemental form from mining and metallurgical waste water by using hydrazine as a reducing agent and pure/used nickel powder as seeding material. For the initial phase of the project, experiments were conducted on a 20 L batch reactor using synthetic solutions containing a mixture of nickel and copper. The residual concentration of less than 1 mg/L and 1.2 mg/L were obtained in the Ni and Ni-Cu solutions respectively from 100 mg/L initial concentration. Hydrazine removed an optimum of 99.31%  $\text{Ni}^{2+}$  contained in Ni-solution, 98.95%  $\text{Cu}^{2+}$  and 99.26%  $\text{Ni}^{2+}$  in Ni-Cu solution. Breakage and molecular growth were the predominant particulate processes occurring during the crystallization process.

**Key words:** 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 to 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, 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 minerals. Due to the fast depletion of mineral reserves globally, the current focus in effluent treatment is now on the recovery and reuse of these heavy metals rather than removal and disposal. Of the methods currently in use none is capable of recovering metals in a form that is suitable for re-use hence there is a need to develop alternative technologies to address this problem. In this study, reduction crystallization was investigated as a possible method for the removal and recovery of heavy metals.

Reduction crystallization has been widely employed in the electroplating and metallurgical refining industry for metal plating and production of metallic powders respectively [1, 2]. Different reducing agents have been employed namely, hydrogen gas, carbon monoxide, sodium hypophosphite, sodium borohydrides and hydrazine. 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 sulfide sludge.

Limited studies have been done on the use of reduction crystallization for metal removal from 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 copper, iron, cobalt and nickel by reduction crystallization. Secondly, to efficiently recover and crystallize  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$  and  $Fe^{2+}$  in their elemental form, using hydrazine as a reducing agent and pure/used nickel powder as seeding material. The third objective is 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 will be generated.

Later studies will be conducted using effluent from numerous mining and metallurgical industries. The outcomes of this project will be to provide a technique for controlling environmental pollution; provide a sustainable water treatment solution; reduce the impact of mine water on human health, plants, animals, and the environment; and eliminate hazardous metals from the environment. It will also play a major role to numerous mining and metallurgical

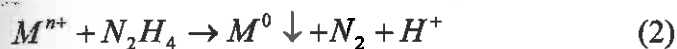
industries discharging effluent streams containing multi-component metals as it will enable them to recover and reuse most of the metals contained in the wastewater.

### 1.1 Hydrazine As A Reducing Agent

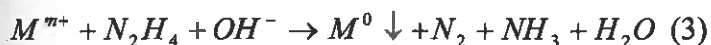
Hydrazine ( $N_2H_4$ ) is a strong reductant widely used in various chemical operations. A series of striking results has been obtained where hydrazine is used as a reducing agent for the production of finely divided metals, of metal-on glass films, and of metallic hydrolysis, and electroless plating [3]. 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 [1]:



Tone and Burgess (1996) [4], discussed that metal ions can also be reduced according to reaction in Eq. (3):



Hydrazine can react with dissolved oxygen (DO) in water according to [5]



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



Precious metals can be easily recovered by using this strong reductant as indicated in Eq. (2). Since metal cations are immediately reduced to metallic state, there is a very limited amount of metal ions left in the solution. Complexation between metal and ammonia due to Eq. (3) and (5) is therefore unlikely to occur. By using air stripping, ammonia is easily removed from the solution. In addition, un-utilized hydrazine can be decomposed by aeration, Eq. 4.

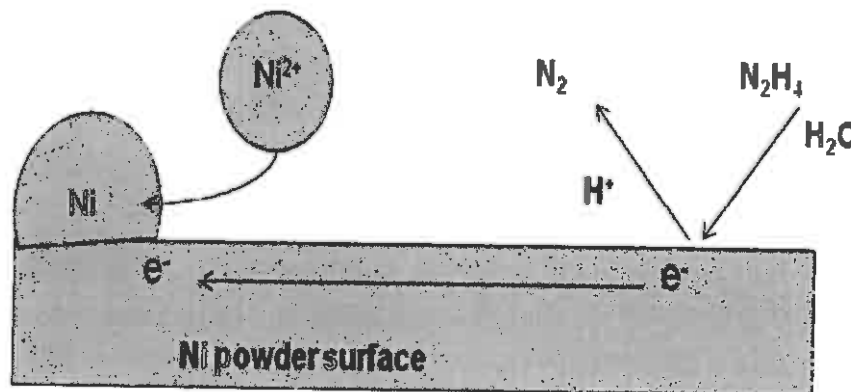
### 1.2 Electroless Plating

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 semiconductor in nature.

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 [6]. Electroless deposition then continues, provided that the metal ion and reducing agent are replenished. If air or evolved gas, however, are trapped in blind hole or downward facing cavity, this will prevent electroless deposition in these areas [6].

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 [6]. A schematic diagram of the reduction crystallization method is shown in Fig. 1.



**Fig.1. Sources of heavy metals**

## **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 [8]. 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 [8]. The following processes occur during crystallization (a) nucleation; (b) aggregation / agglomeration; (c) molecular growth; (d) breakage/ attrition [9].

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 redissolve. 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.).

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 [10].

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.

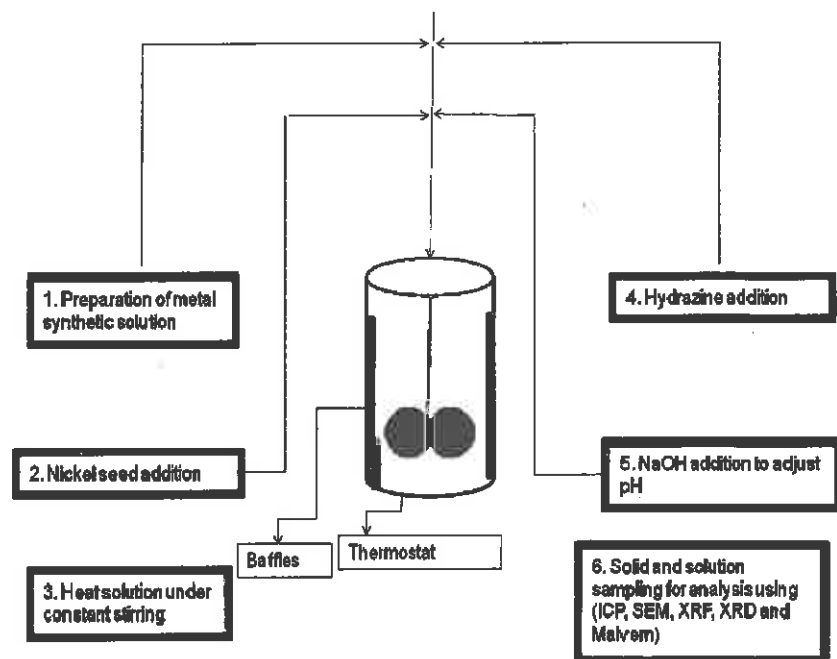
### **3. MATERIALS AND METHODS**

#### **3.1 Synthetic Wastewater**

100 mg/L of synthetic solutions were prepared by weighing 4.48 g of nickel sulfate hexahydrate, 3.929 g cupric sulfate and dissolving the salts into 1000 ml volumetric flask of water.



### 3.2 Equipment



**Fig.2. Experimental apparatus**

The experimental apparatus is shown in Fig. 3. All the experiments were conducted in a 20 L stirred batch reactor, fitted with 4 baffles, a 4 bladed axial pitch impeller, thermostat and heating element.

### 3.3 Reagents

M hydrazine in tetra-hydrofuran was employed as a reducing agent, 2 M sodium hydroxide as a pH regulator. 100 mg/L nickel and 100 mg/L copper solutions were prepared.

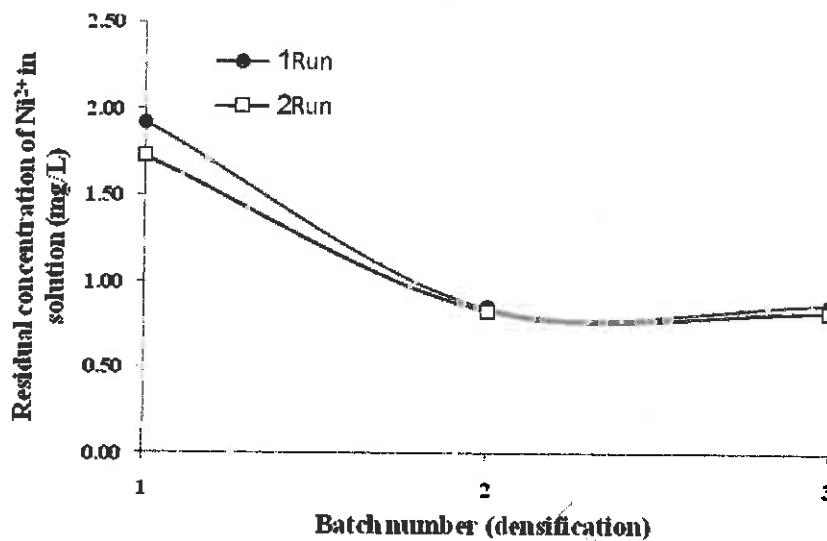
### 3.4 Experimental Method

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, the mixed solution was filtered to obtain the nickel powder and the residual effluent. Residual nickel ion and copper ion concentrations were measured by Inductively Coupled Plasma Optical Emission Spectrometer Spectro Arcos Fsh12 (ICP-OES). The morphology of the powder was obtained using Jeol JSM 5600 Scanning Electron Microscope (SEM). The elemental composition of the powder was obtained using X-ray fluorescence. 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 DISCUSSION

It was discovered that hydrazine can successfully be used as a reducing agent to remove and recover copper and nickel from effluent using reduction crystallization method. Each batch run is termed a densification because the powder becomes denser with each successive batch reduction.



**Fig.3. Residual nickel concentration in solution (Ni-solution)**

Fig. 3 indicates the residual concentration of nickel in solution for three experimental runs using the same nickel powder as seeding material for the three densifications. 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 nickel powder lowered the residual concentration of Ni<sup>2+</sup> from 3 mg/l to less than 1 mg/l.

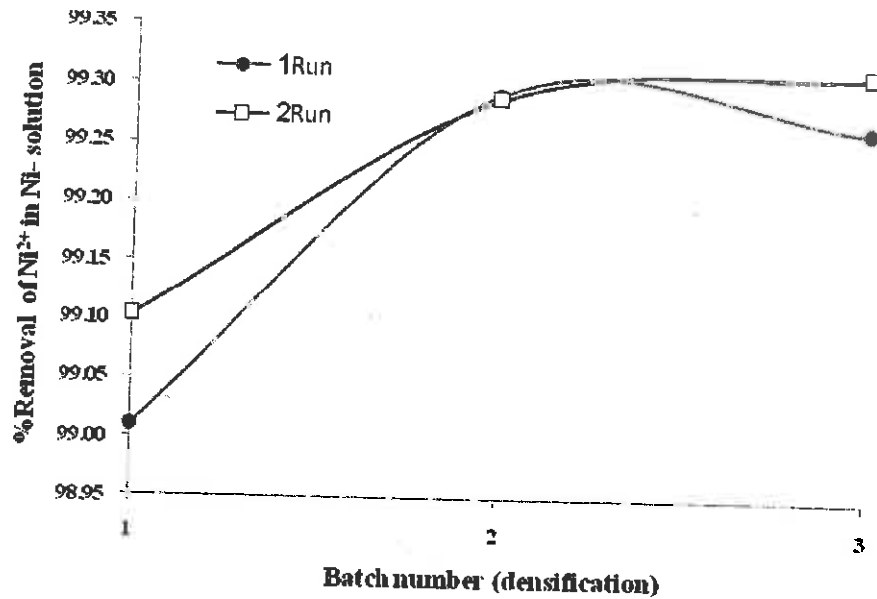


Fig.4. % Removal of nickel in Ni-solution

The % removal of nickel from Ni-solution for the three experimental runs is shown in fig.4. The removal rate increased dramatically from 99.0 % in the first densification to 99.30 % in the second densification and remained constant thereafter. The sudden increase from 1<sup>st</sup> to 2<sup>nd</sup> densification can be attributed to the change in surface area of the nickel powder, due to the particulate process occurring during the crystallization process.

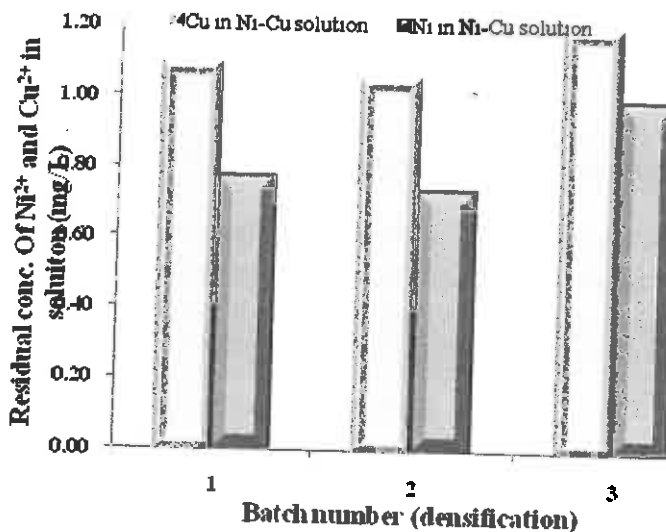


Fig.5. Residual copper and nickel concentration in solution (Ni-Cu solution)

Copper residual concentration was higher than nickel residual concentration in Ni-Cu solution for all the experimental runs, as illustrated in Fig. 5. The highest copper concentration was 1.19 mg/L and 0.99 mg/L for nickel from a 100 mg/L initial concentration of Ni and Cu.

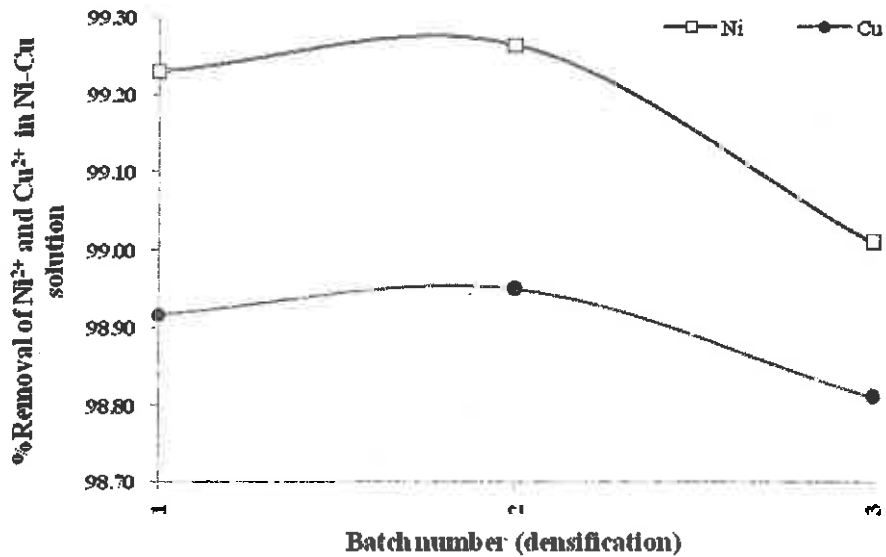


Fig.6. %Removal of copper and nickel in solution (Ni-Cu solution)

Fig.6 indicates the removal of copper and nickel in Ni-Cu solution. The % of nickel removed was 99.26 % higher than the % of copper removed which was 98.81%. The % removal of Ni<sup>2+</sup> and Cu<sup>2+</sup> was the highest in the 2<sup>nd</sup> densification and decreased sharply with the increasing number of densifications. The decrease in the removal rate can be attributed to the change on seeding material surface area. Removal of nickel from the effluent was favored over that of copper.

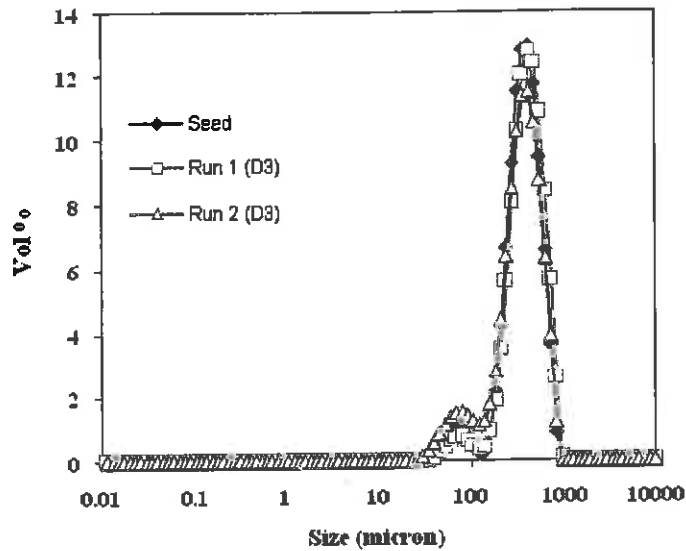


Fig.7. Evolution of the PSD of powder in Ni-solution

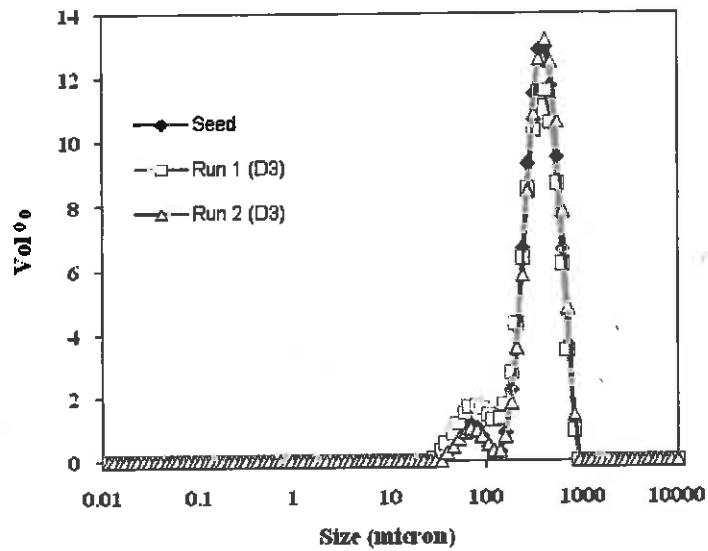


Fig.8. Evolution of the PSD of powder in Ni-Cu solution

Fig.7 and fig.8 shows the evolution of the particle size distribution (PSD) of the powder obtained from the Ni-solution and Ni-Cu solution respectively. From the evolution of the volume distribution it can be concluded that the size enlargement is not significant size as the modal size remains unchanged. The PSD data was transformed into its moments using equation 6 and 7.

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

$$m_j = \int L^j n(L) dL \quad (7)$$

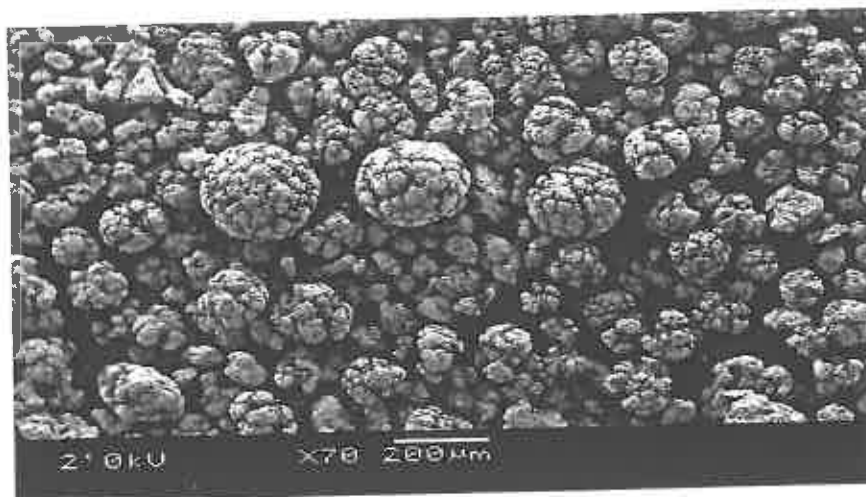
The volume based histogram ( $\text{vol}\%_i$  versus  $L_i$  where  $i$  indicates the size sub-range and the particle concentration ( $\text{conc}(\text{vol}\%)$ ) were generated by laser diffraction (Malvern Mastersizer 2000) and the volume shape factor ( $k_v$ ) equal to  $\pi/6$  was used. The first four moments ( $0^{\text{th}}$ ,  $1^{\text{st}}$ ,  $2^{\text{nd}}$  and  $3^{\text{rd}}$ ) are of special interest and are related to the total number, length, area and volume of solid per unit volume of suspension respectively [11]. The  $0^{\text{th}}$  and  $2^{\text{nd}}$  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**

Moment	$0^{\text{th}}$ ( $\# \cdot \text{m}^{-3} \times 10^{11}$ )	$2^{\text{nd}}$ ( $\text{m}^2 \cdot \text{m}^{-3} \times 10^3$ )
Seed	7.79	5.91
D3 Powder (Ni)	11.19	8.18
D3 Powder (Ni-Cu)	12.93	9.90

There was an increase in the  $0^{\text{th}}$  and  $2^{\text{nd}}$  moments (Table 1) for both experimental runs corresponding to an increase in the number of particles and surface area 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 or a combination of the two. The  $0^{\text{th}}$  and  $2^{\text{nd}}$  moment of the powder obtained from the Ni-Cu solution was higher than that of the powder obtained from the Ni-solution since the total metal concentration was higher in the Ni-Cu solution.

From the SEM micrograph (Fig. 9) it seems breakage by attrition and molecular growth were more predominant than nucleation. This finding seems to agree with the evolution of the PSD (Fig. 7 and 8) where there was no significant change in the volume distribution. Nucleation and breakage by fragmentation normally results in significant changes in the volume distribution.



**Fig.9. Scanning electron micrograph of D3 powder (Ni-Cu)**

## **5. CONCLUSIONS**

Hydrazine effectively crystallized  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  into their elemental states with nickel powder as a seeding material. The operating conditions for this method were  $\text{pH} \geq 11$  and temperature of  $60^\circ\text{C}$ . %Nickel removal was higher than %copper removal in the Ni-Cu solution and the presence of copper slightly reduced %nickel removal. Based on the evolution of volume distribution and  $0^{\text{th}}$  and  $2^{\text{nd}}$  moments, breakage by attrition and molecular growth were identified as the predominant mechanisms occurring during the reduction crystallization process.

## **6. ACKNOWLEDGMENT**

The authors are indebted to the University of Johannesburg and Council for Scientific and Industrial Research (CSIR) Scholarship for funding this research.

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