

Reduction crystallization of heavy metals from acid treated phosphogypsum effluent utilizing hydrazine as a reducing reagent

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Abstract. Phosphogypsum is a by-product generated from phosphoric acid production processes. Due to the negative impact posed to the environment by the material, a chemical treatment process was developed to reduce the hazardous constituents in the material and render the final product useful for other applications. The treatment of phosphogypsum produced an effluent laden with contaminants such as copper, iron, manganese and thallium. This study was conducted to investigate the use of hydrazine as a reducing agent to remove and reduce Cu, Fe, Mn and Tl from effluent, applying a reduction crystallization process. Nickel powder a base substrate was utilised as a seeding material. A feasibility study was carried out to test the efficiency and find the optimum operating conditions for the process. The predominant detected components in the feedstock were 71% Fe, 14% Tl, 5.1% Mn, 4.12% Cu and 2.4% Zn. The results obtained indicate that hydrazine can effectively remove up to 99.8% of metals from the effluent at the optimum pH of 10.5. Growth of the nickel powder particles was evident indicating a reduction and adsorption of contaminants on the surface of the powder. The treated solution was within South African acceptable limits for effluent discharge, which stipulates a concentration of 20 mg/l of copper, iron, manganese and thulium.

1 Introduction

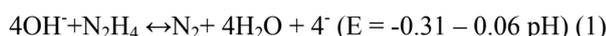
The production process of phosphoric acid from phosphate ore, result in the formation of large quantities of by-product solid waste which is primarily calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), commonly known as phosphogypsum (PG) [1]. PG has relatively high concentrations of toxic heavy metals [2]. Ongoing addition of these fertilizers containing these metals can result in accumulation in soil overtime. High concentration of them in the soil can pose problems to human beings and animals that consume the crops that grew from such soil. Harmful heavy metals that finds their way into the environment may cause harmful effects as they can damage the functions of healthy tissues/organs [3]. High levels of heavy metals in receiving water sources such as oceans, rivers and lakes can result in loss of aquatic life, by excessive development of algal blooms and eutrophication. The dangers that all these incidents have posed are a clear indication that heavy metals must be removed from phosphogypsum [1]. Phosphogypsum, refers to the gypsum formed as a by-product of processing phosphate ore into fertilizer with sulfuric acid. These metals are relatively dense metal that are noted for their potential toxicity. For many years all over the world phosphogypsum has been a problem waste of the fertilizer industry [1]. Heavy metals are probably the biggest concern as they will expose the inhabitants of

dwelling made from the materials. Worldwide, four methods are being used by the phosphate industry to dispose of surplus phosphogypsum, namely: (i) discharging to water bodies; (ii) backfilling in mine pits; (iii) dry stacking; and (iv) wet stacking [1]. Residual deposits of Phosphogypsum are readily available in large quantities in South Africa and currently are landfilled or pumped into the sea, as there are limitations to engineering applications due to the radionuclides content [4].

It is a great concern that when chemical treatment processes frequently provide poor performance with respect to extracting heavy metals from phosphogypsum (PG), that it is disposed in river ponds, landfills, broad open air. Environmental concerns are related with the large stockpiles of PG and their negative impact on surrounding land, water, soil and aquatic lives in the rivers. More than 85% of all PG generated each year is dumped on land or in the sea. Research on impurity removal such as heavy metals on pollutant concentrations linked with PG stacks could allow PG to be used more effectively [1]. Furthermore, PG recycling is not only an engineering or scientific problem, but also an economic and political concern [1]. A proper investigation of the removal of heavy metals from PG will help in reducing the disposal of toxic materials as much as possible [5]. Precipitation is a widely treatment process, to treat wastewater, because it the most economical method, easier to implement and operate on a large scale.

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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 [6]. Hydrazine is a strong reductant widely used in various chemical operations. A series of striking results has been obtained where hydrazine was used as a reducing agent for the production of finely divided metals, metal on glass films, metallic hydrolysis and electro-less plating [7]. An important half reaction involving hydrazine is presented in equation 1, and it can be used effectively in the reduction of numerous metal cations to elemental state [8].



There is not much work reported on the application of reduction crystallization for the removal of heavy metals from the effluent that generated from treating phosphogypsum using citric acid. The main aim of this study was to utilise reduction crystallization as a chemical treatment process to reduce/remove the selected heavy metals in the effluent generated from the treatment of phosphogypsum with citric acid.

2 Experimental

The effluent used in this study was from the treatment process of waste phosphogypsum, whereby citric acid was used as a leaching reagent. Nickel powder was used as the seeding material. 1 M of Sodium hydroxide (NaOH) was used to regulate pH. 2 M of Hydrazine (N₂H₄) was used as a reducing agent. The experiments were conducted in a 1L batch reactor. A pH meter was used to monitor pH. Thermometer was used to measure the temperature when the experiments were conducted. The solution samples were analysed by inductively coupled plasma (ICP). The elemental composition of the solid samples was analysed by X-ray Fluorescence (Rigaku XRF ZSX Primus) and the mineralogy of the seeding material was studied by X-ray diffraction (XRD).

3 Results and discussion

3.1 Analysis of effluent before treatment

Table 1 shows the concentration of the effluent generated from the phosphogypsum treatment process before the reduction crystallisation process. The highest contaminants concentrations, as presented in Table 1, were associated with Iron (Fe), Copper (Cu), Manganese (Mn), Thallium (TI) and Zinc (Zn). The effluent was laden with 71% iron, followed by 15% thallium and 4% copper.

Hydrazine can serve as a reducing agent in both acidic and alkaline solutions, in the experiment conducted, the pH of the solution was varied from acidic (pH 5) to alkali pH 10 and 10.5. This was conducted to investigate the

heavy metals that can be removed at different pH conditions. The volume of hydrazine was also varied from 0.05 mL, 0.1 mL and 0.2 mL. Removal efficiency of metals at different pH conditions, at a constant hydrazine (N₂H₄) volume of 0.05.

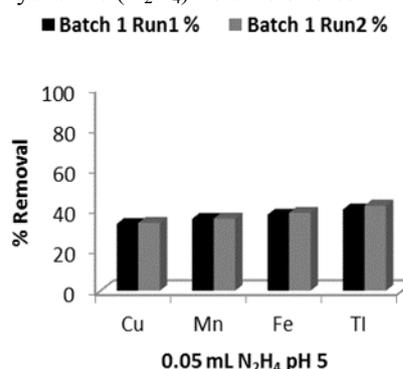


Fig. 1. % removal of metals at pH 5 and constant volume of 0.05 mL hydrazine.

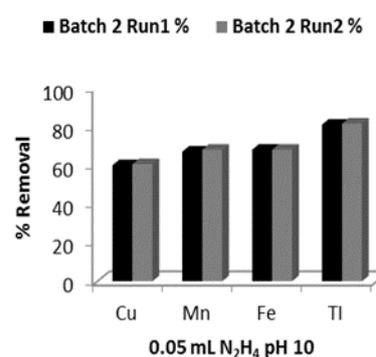


Fig. 2. % removal of metals at pH 10 and constant volume of 0.05 mL hydrazine.

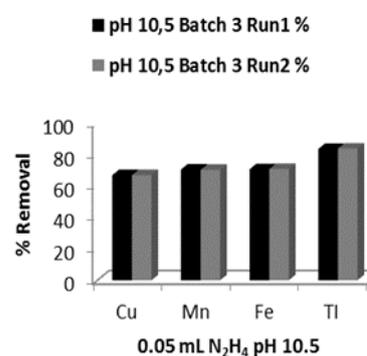


Fig. 3. % removal of metals at pH 10.5 and constant volume of 0.05 mL hydrazine.

The process pH was varied from 5 (acidic) to 10 and 10.5 (basic) from run 1 to 3 respectively, while temperature and hydrazine concentration were kept at 60 °C and 0.05 mL respectively. Each sample was analysed for % removal of Copper, Iron, Manganese and Thallium after reduction has taken place as presented in Figures 1-3. The average highest percentage of up to 72.6% was obtained at the pH of 10.5. Batch 3 shows a major improvement in % removal of metals and it was chosen as the optimum pH. Further tests were conducted using the optimum pH of 10.5 and varying the volume of

hydrazine from 0.05 mL to 0.1 mL and 0.2 mL. Each experiment was repeated three times (3 batches).

Table 1. Effluent analysis before reduction crystallization.

Component	Cu	Fe	Mn	TI	As	Cr	Ni	Zn	Pb	Se	Cd
Elemental concentration (mg/L)	158	2740	196	561	38	29	18	91	10	19	0.4
Elemental concentration (%)	4.12	70.97	5.07	14.54	0.98	0.75	0.47	2.37	0.25	0.49	0.01

3.2 Removal efficiency of metals at different hydrazine volume and constant pH and temperature

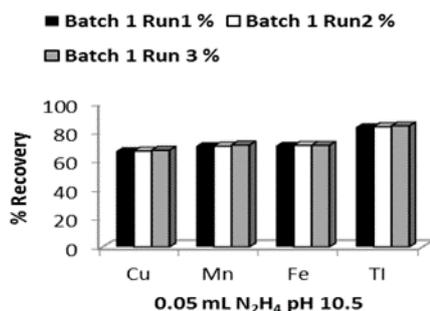


Fig. 4. % removal of metals with 0.05 mL volume of Hydrazine at a constant pH of 10.5.

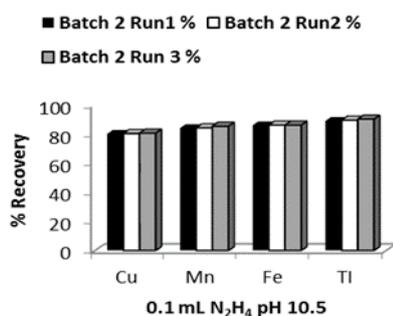


Fig. 5. % removal of metals with 0.1 mL volume of Hydrazine at a constant pH of 10.5.

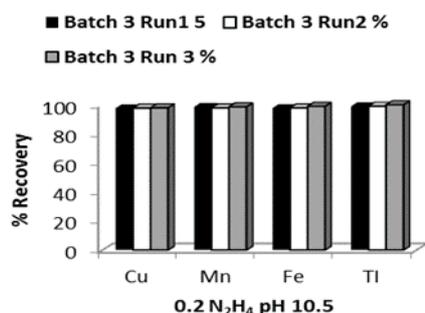


Fig. 6. % removal of metals with 0.2 mL volume of Hydrazine at a constant pH of 10.5.

The highest % removal of metals in the effluent is presented by batch 3, when 0.2 mL N₂H₄ was used, at an alkaline pH conditions of 10.5. From the results presented

in Figure 5 and 6, it is evident that in the alkaline medium, reductive crystallization can effectively remove heavy metals from effluent up to 99.9% TI, 99.8% Mn, 99.8% Fe and 97.9%. The % removal of all the metals in solution showed an increase in metal reduction from the first run (less dense nickel powder) to the third run (more dense nickel Powder). In 2012, Phetla conducted a study on the reduction crystallization of copper, nickel and iron using hydrazine as a reducing agent. The results reported showed that applying hydrazine as a reducing agent, in the presence of nickel powder as seeding material, effectively reduced the concentrations to their elemental states. The removal efficiencies of over 97% were reported for all the metals investigated. In this study, the treated solution was able to meet the general limit for effluent discharge, which stipulates a standard of 20 mg/l of all the metals, copper, iron, manganese and thallium (Johannesburg acceptance standards for industrial effluents).

3.3 Particle size distribution (PSD) of the seeding material

The evolution of the PSD was studied using the conditions that yielded highest removal %, thus the pH of 10.5 and hydrazine volume of 0.2 mL. The results are presented in Figures 7-10.

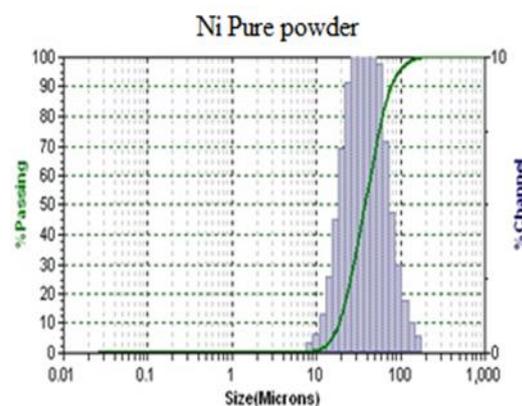


Fig. 7. Evolution of PSD for pure nickel powder.

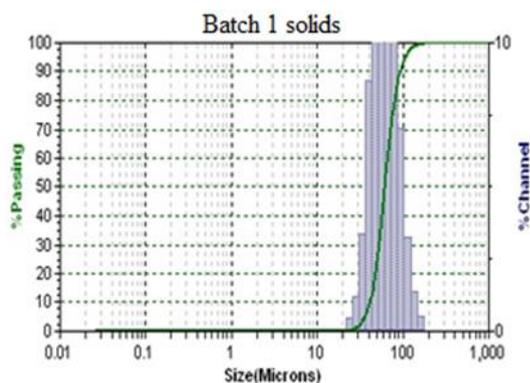


Fig. 8. Evolution of PSD for 1st densification (batch 1).

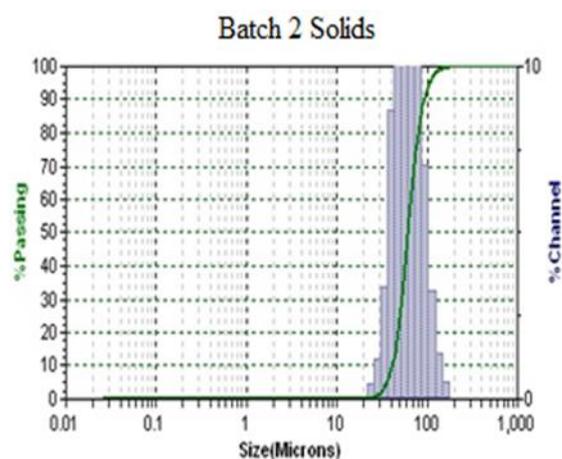


Fig. 9. Evolution of PSD for 2nd densification (batch 2).

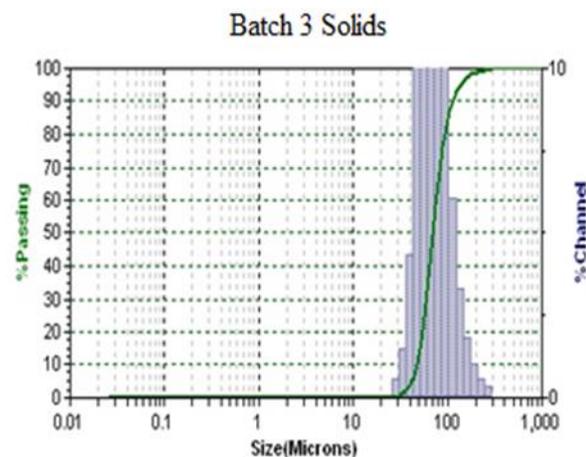


Fig. 10. Evolution of PSD for pure 3rd densification (batch 3).

The particle size distributions (PSD) in Figure 7-10 are described in terms of D values. The D10, D50 and D90 were used to represent the midpoint and range of the particle size of the samples from the 3 batches conducted. Particle size distributions creates an S-curve of cumulative mass retained against sieve mesh size, and intercepts for 10%, 50% and 90% mass are calculated. The D10 diameter is the diameter at which 10% of a sample's mass is comprised of smaller particles, and the D50 is the diameter at which 50% of a sample's mass is comprised of smaller particles. The D50 is also known as the "mass median diameter" as it divides the sample

equally by mass. As the graph shows, the D10, D50 and D90 are given by the X axis (diameter) value 10%, 50% and 90% on the Y axis. There is a significant modal size shift from pure nickel seed to batch 1 to batch 3. A bimodal size shift to the right is observed with all the batches, showing a change in the proportion of the larger sized particles of the PSD, thus enlargement of particles.

3.4. X-ray diffraction (XRD) analysis

XRD analysis was conducted on the dried solids before and after treatment as shown by Figure 11. The main minerals deducted on the solids were that of, manganese, iron, copper and also thallium, which were the same elements that were reduced from the effluent.

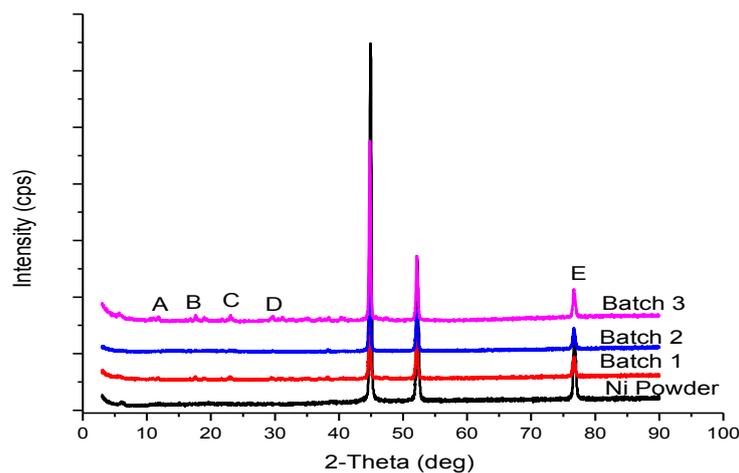


Fig. 11. XRD Analysis of seeding material before and after treatment.

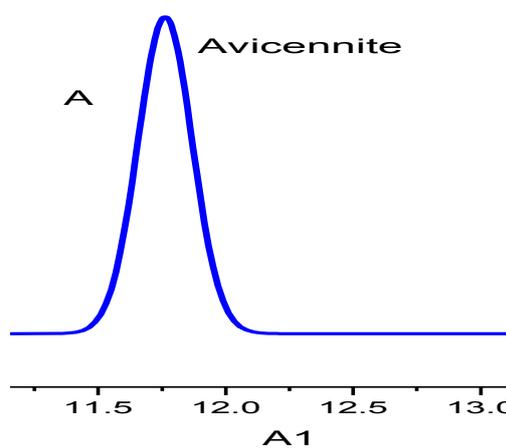


Fig. 11. (a) XRD Analysis of seeding material before and after treatment.

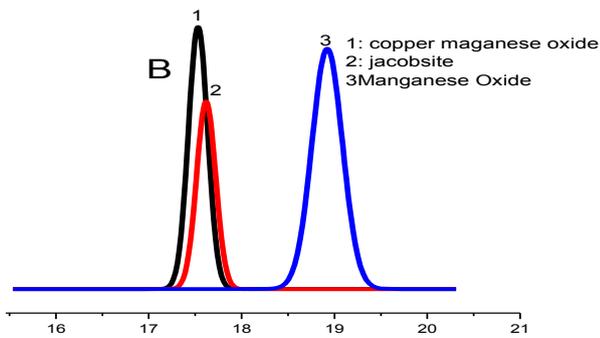


Fig. 11. (b) XRD Analysis of seeding material before and after treatment.

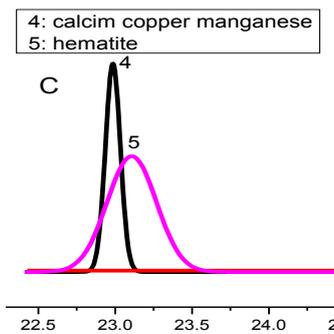


Fig. 11. (c) XRD Analysis of seeding material before and after treatment.

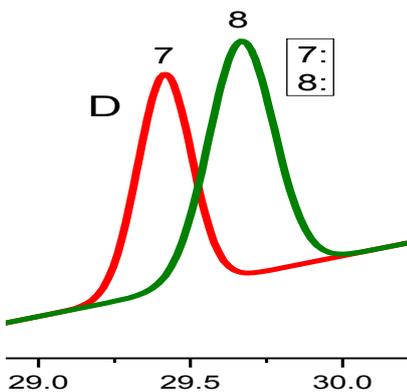


Fig. 11. (d) XRD Analysis of seeding material before and after treatment.

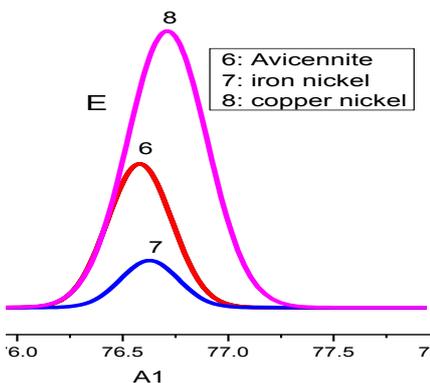


Fig. 11. (e) XRD Analysis of seeding material before and after treatment.

The peak intensity of nickel in the pure nickel powder is higher than that of batch 1, 2 and 3, because of the purity of the powder, which was free of contaminants. The peaks labelled A to E are; A: Avicennite (Thallium oxide), B: Copper manganese oxide, Jacobsite (manganese iron oxide), and manganese oxide, C: calcium copper manganese, hematite, D: iron nickel, copper nickel, E: Avicennite, iron nickel, copper nickel. Presence of metals on the surface of nickel powder indicates that reduction crystallization had taken place and the powder is no longer pure. Batch 3 shows higher peaks as compared to batch 1, and 2 of pure nickel, because a large number of metals were removed from batch 3 when 0.02ml of hydrazine was used at a pH of 10.5, for about 99.8% of metals were removed under these conditions.

3 Conclusion

In accordance to the literature review and the results obtained, it can be concluded that reductive crystallization process using hydrazine as a reducing agent, can effectively remove heavy metals from effluents up to 99.9% TI, 99.8% Mn, 99.8% Fe and 97.9% Cu. The treated solution was able to meet the general limit for effluent discharge, which stipulates a standard of 20 mg/l of all the metals, copper, iron, manganese and thulium (Johannesburg acceptance standards for industrial effluents). Hydrazine as a reducing agent can be utilized for controlling environmental pollution and eliminating hazardous metals from the environment.

Acknowledgments

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