Kinetic Studies of Nickel Dissolution from Ammonium Jarosite Precipitate in an Alkaline Medium

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Abstract - The dissolution kinetics of nickel from ammonium jarosite precipitate in an alkaline medium was investigated. The effects of various parameters were studied to optimize the dissolution conditions and to determine the kinetics on the leaching process based on the shrinking core model. The results indicated that the increase in the leaching time, temperature, EDTA-Na_2S mixture concentration, decrease in solid–liquid ratio and particle size enhanced the leaching rate of nickel. 80.8% of nickel content and 15.5% of iron was leached from the sample while leaching in the presence of EDTA only and 82.4% of nickel and no iron was leached using EDTA - Na_2S equi-molar mixture. Optimal conditions for recovery of nickel are; particle size of 80 % passing 75 µm, temperature 45°C, 4 hours of leaching, equi-molar concentration of EDTA - Na_2S (0.1M), pH of between 9 and 10 and 5% solids. The experimental data were best fitted by diffusion-controlled model. The activation energy was 70.6 kJ/mol.

Keywords: Kinetics**,** Dissolution, Ammonium jarosite precipitate, Chelation, Reducing reagent.

1. Introduction
1.1   Jarosite

Jarosite-type compounds occur widely in nature and are extensively used in the metallurgical industry to precipitate iron from processing solutions in a readily filterable form. The general formula for jarosite-type compounds is $MFe_3(SO_4)_2(OH)_6$ where M can be Na^+ , K^+, Rb^+, Ag^+, H_3O^+, NH_4^+, $1/2Pb^{2+}$ or $1/2Hg^{2+}$. Many detailed studies of jarosite compounds indicate consistent deficiencies in the ''alkali'' occupancy of the M-site and in the occupancy of the Fe-site and which deficiencies are assumed to be compensated by hydronium ions in the M site. The deficiencies in the Fe-site are charge-compensated by the conversion of some SO_4^{2-} to HSO_4^-. For economic reasons, most commercial jarosites are based on Na or NH_4 while it is recognized that the potassium member is the most stable of all the jarosite-type compounds (Dutrizac, 2004). The behavior of impurities during jarosite precipitation and divalent metals such as Zn^{2+}, Cu^{2+}, and Ni^{2+} were studied by Dutrizac et al.(2004), and have shown that their incorporation in the alkali and ammonium jarosites can be in small amount. The metals are incorporated in the following order: $Fe^{3+}> Cu^{2+}> Zn^{2+} > Co^{2+}> Ni^{2+}$ (Nheta et al., 2013).

Nickel can be produced and recycled from both primary and secondary resources such as spent catalysts, waste batteries and tailings (Gharabaghia et al., 2013). In each leaching reaction, physiochemical processes control dissolution kinetics. These processes are affected by different parameters, such as acid concentration, solid/liquid ratio, stirring speed, particle size, temperature et cetera. The dissolution of nickel from the jarosite involves heterogeneous reactions related to the fluid-solid system (Philip et al., 2004).

As thermodynamic studies have provided required information on the dissolution of nickel from the jarosite precipitate and made it possible to forecast the behavior of the equilibrium with the change of various external conditions, the present work will focus on the behavior of thermodynamic and kinetic parameters. The kinetics of the nickel dissolution is focused in two main steps; the experimental determination of the rate of dissolution and the mathematical model of the determined relationship.

1.2. Kinetic Studies

For a liquid/solid reaction system, the solid reactant is considered to be non-porous and is initially surrounded by a fluid film through which mass transfer occurs between the solid particle and the bulk of the fluid. The reaction rate is generally controlled either by diffusion through the liquid film, diffusion through the ash/product layer, the chemical reaction at the surface of the solid particles or a combination of diffusion and chemical reactions (Philip et al., 2004).

The particle is considered to be spherical and as it reacts forms a porous outer layer and an unreacted core. The dissolving part is assumed to be a crystalline phase. The unreacted core shrinks and the dissolved part diffuses through the porous shell towards the solvent. The shrinking core model considers that the leaching process is controlled by one of the mentioned steps. The reaction model between a liquid and a solid may be given as:

$$A \text{ (liquid)} + B \text{ (solid)} \rightarrow \text{Products} \tag{1}$$

In order to determine the kinetic parameters and rate controlling steps in the leaching of nickel in an alkaline medium in the presence of EDTA and Na_2S, the experimental data were analyzed based on the shrinking core model (SCM). The equations of the shrinking core model are based either on diffusion or surface chemical reactions. The slowest step can be expressed as follows (Habashi, 1980):

When the diffusion through liquid film controls

$$1 - \frac{2}{3}R - (1-R)^{2/3} = \frac{2M\mathcal{D}C}{\alpha\delta r_0^2}t = k_d \tag{2}$$

When surface chemical reaction controls

$$1 - (1-R)^{\frac{1}{3}} = \frac{6M\mathcal{D}C}{\alpha\delta r_0^2}t = k_r t \tag{3}$$

Where C = concentration of reagent; δ = density of solid; M = molecular weight of reactant; α = stoichiometry factor; R = fraction reacted; k = kinetic constant; r_0 = initial radius of particle; t = reaction time; D = diffusion coefficient in porous product layer and k_d and k_r = rate constants, which are calculated from Eqs. (2) to (3), respectively.
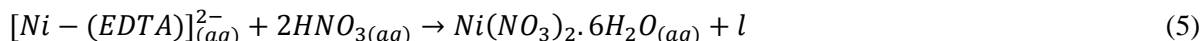
1.3. Chelation

Due to the difficulties encountered during the dissolution of nickel in alkaline medium using KOH at room temperature and atmospheric pressure such as the surface of the Ni particles covered with a thin layer of Ni oxides and hydroxide, Ni_2O_3, NiO and $Ni(OH)_2$ as presented by Ya Xu et al. (2008), the use of chelating agent has been presented as a way to thermodynamically dissolve and maintain nickel as ions by forming the chelate complexes stable in the medium. EDTA has the ability to chelate or complex metal ions in 1:1 metal-to-EDTA ratio. The equilibrium or formation constants for most metals, especially the transition metals, are large; hence the reactions are shifted towards formation of the complex. Many of the reactions are pH dependent (Mahvi et al., 2005).

EDTA forms a complex with nickel depending upon its concentration as presented in the following reaction.

$$[Ni(H_2O)_6]^{2+}_{(aq)} + EDTA^{4-}_{(aq)} \rightarrow [Ni(EDTA)]^{2-}_{(aq)} + 6H_2O_{(l)} \tag{4}$$
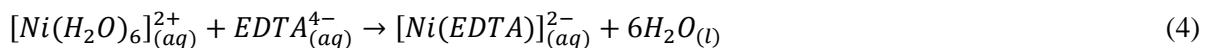
After the chelation, the residue material can be separated from the complex solution by filtration. Filtrate is then subjected to de-chelation process in which metal-chelate is separated by changing the pH of solution depending on the type of complex. Generally, Ni-EDTA complex is not stable in acidic

solutions; therefore acid is used to de-chelate the formed complex during the chelation process according to reaction 5.

$$[Ni - (EDTA)]^{2-}_{(aq)} + 2HNO_{3(aq)} \rightarrow Ni(NO_3)_2.6H_2O_{(aq)} + l \tag{5}$$

Where l represent the aqueous solution containing the ligand EDTA.

After complete settling of precipitated EDTA, it is sent for a filtration process. The EDTA is separated as a spent chelating agent and nickel is extracted as a nickel nitrate solution. The recovered EDTA is further purified and reused. Many studies have been carried out on the recovery of nickel from a spent catalyst using EDTA-di sodium salt as a chelating agent after which sulphuric acid is added to obtain $NiSO_4$ (Goel et al., 2009).

Due the non-selectivity behavior of EDTA on chelating of heavy metals, Na_2S was used as a reducing agent to enhance the selectivity of nickel. .

The aim of this work is to investigate the dissolution kinetics of nickel from the jarosite product generated during the iron removal process from a South African based PGM circuit.

Beside the fact that acid leaching has a widespread use in metallurgical plants due to the fact that it can dissolve most resources of metals and minerals, it has got the disadvantage of being limited to the ore resources which are not associated with large amounts of acid-reactive gangue materials (Gupta et al., 1990). Due to large consumption of acids and dissolution of iron and other impurities during dissolution of nickel from ammonium jarosite, the use of alkalines (KOH, NaOH and NH_4OH) has been suggested. Alkaline leaching has the advantage of being selective by bringing the desired metals (nickel) into the solution leaving behind iron and other undesirable elements in the jarosite precipitate.

This project is focused on the optimization of the recovery of nickel from ammonium jarosite in the presence of EDTA and Na_2S in alkaline medium.

2. Material and methodology
2.1. Material
Leaching experiments were carried out on the ammonium jarosite product generated during the iron removal process from a South African based PGM producing circuit. Potassium hydroxide, EDTA and Na_2S were used as alkaline medium, complexion agent and reducing agent respectively.

2.2. Method
The samples were ground and sieved using ASTM standard sieves. The solids were characterized using XRF, and XRD. The solutions were analyzed using atomic absorption spectrophotometer (AAS) for nickel and iron. The Inductive Coupled Plasma (ICP) was used for the full analysis of the solutions.

The dissolution process was carried out in a 100 ml glass beaker and the slurry was agitated by a glass bladed overhead stirrer. The reaction temperature was maintained constant during the dissolution process in a water bath while the pH was continually controlled in the range between 9 and 10. The leaching experiments were performed using 80% passing 75 µm grain sizes, except those related to the effects of particles size on the reaction kinetics. The effect of EDTA concentration, particle size, solid–liquid ratio, stirring speed and temperature on the dissolution kinetics were investigated in the presence and absence of Na_2S.

3. Results and Discussion
3.1. Sample Characterization

The chemical composition of the ammonium jarosite is shown in Table 1.

Table 1. Chemical composition of the ammonium jarosite sample.

Element	Fe	Si	S	Ni	Al	As	Pb	K	Na	Cr	Ca	P	Ti	Co	Cl	Mo
Amount (%)	65.9	10.9	7.7	5.6	2.9	2.3	1.8	1	0.4	0.3	0.1	0.05	0.04	0.05	0.02	0.01

Table 1 show that the jarosite precipitate contains 65.9 % of Fe with 5.6 % of Ni while the XRD on figure 1 shows the presence of 3 main phases which are jarosite, nickel hydroxide and iron oxide.
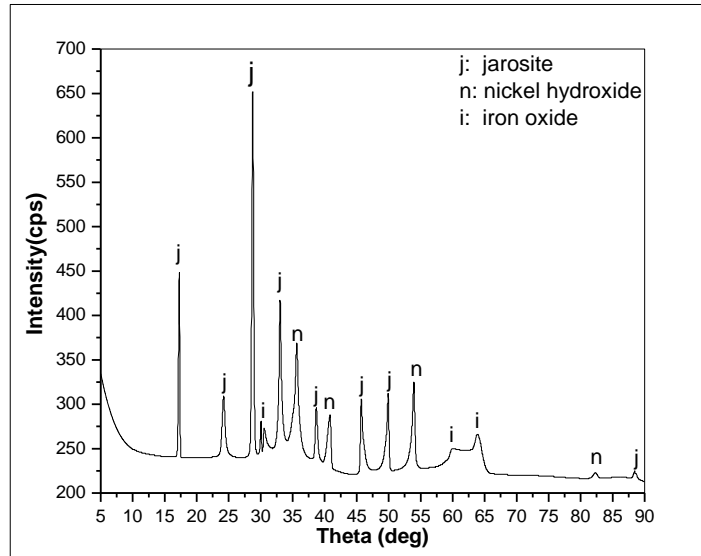

Fig. 1. XRD pattern of the ammonium jarosite.

4. Leaching Process
4.1. Dissolution Process with EDTA
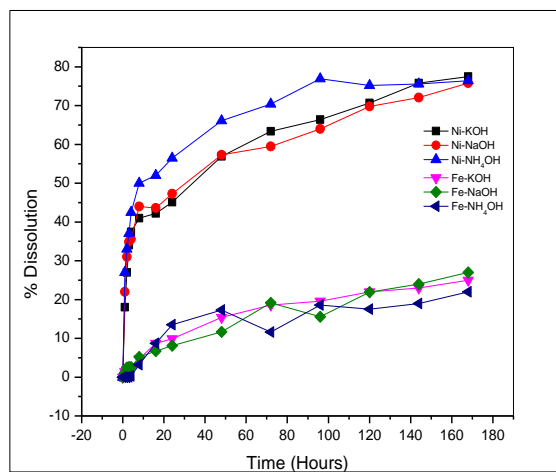
Fig 2. % Dissolution of nickel and iron in different alkaline mediums in presence of the complexant agent (EDTA: 0.1 molar) while varying time at pH 9-10 and room temperature.

Fig 2 shows the dissolution of nickel and iron in different alkaline mediums (KOH, NaOH, and NH_4OH). It can be seen that nickel dissolve in the order $NH_4OH>KOH>NaOH$. Maximum nickel (76.9%) dissolved in NH_4OH after 96 hours. However as nickel dissolve iron also dissolved with a maximum dissolution of 27% in NaOH which is not desirable. Hence there was need to leach the jarosite precipitate in the presence of EDTA and a reducing agent.

4.2. Dissolution Process with EDTA-Na$_2$S

4.2.1. Effect of Concentration

Fig. 3 illustrates the dissolution of nickel and iron from jarosite precipitates in the presence of EDTA-Na_2S. It can be seen that the dissolution of nickel increases as the concentration of EDTA-Na_2S is increased from 0.01 to 0.1M. With 0.1 M of EDTA-Na_2S the dissolution of nickel was 37.4% compared with 25% which was achieved with 0.05M. An increase in EDTA – Na_2S concentration beyond 0.1M did not result in any further change in dissolution. For the experimental conditions tested, a maximum extraction of 40% was achieved with 0.1M EDTA- Na_2S. No iron was detected in the solution.
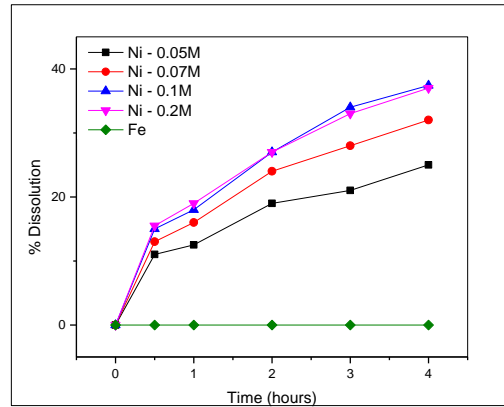
Fig. 3. Effects of EDTA- Na_2S concentration on nickel extraction from jarosite (25°C; 250 rpm, S/L = 5%, particle size:-75 µm).

4.2.2. Effect of Particle Size

Fig.4 shows that the nickel dissolution is also dependent on particle size. The smaller the particle size the greater the dissolution of nickel. The increase in dissolution with reduction in particle size is due to the increased surface area of the particles exposed to the leaching solution. The finer the particle size was the greater geometric surface area and degree of contact surface between the EDTA- Na_2S solution and the particles. Results show that an average of 40% of nickel was extracted from the -38 + 25 µm size fraction which is an increase of 15% compare to the dissolution at +106 µm.
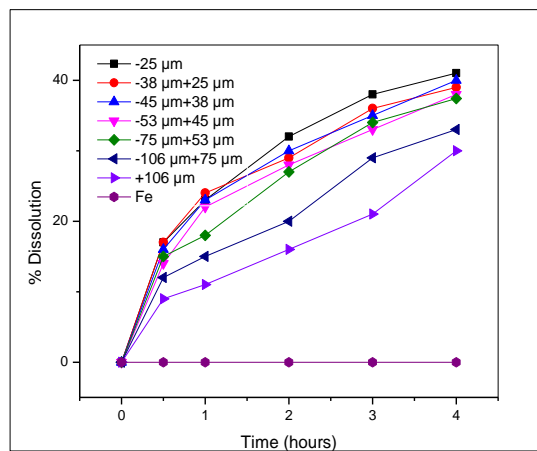

Fig. 4. Effect of particle sizes on the nickel leaching 0.1M EDTA- Na_2S, 25°C; 250 rpm, S/L = 5%).

5. Effect of Solid/liquid Ratio

The effect of solid/liquid ratio on the dissolution rate is shown in Fig. 5. For the ranges tested nickel dissolution increases with increase in the amount of solids in solution from 2% to 5% and then decreased as the % solids further increased to 20%. After 4 hours dissolution was 37 % for solid to liquid ratio of 5% compared to 28 % for solid to liquid ratio of 2%. Beyond 5% solid to liquid ratio there was a

decreases in dissolution with further increase in percent solids from 10 to 20. It is possible to improve leaching rate with decreasing pulp solid percent, but it has a limitation because of process economy ((Bingfl et al., 2005). Considering the process performance the results indicate S/L = 5% as the optimum solid percent.
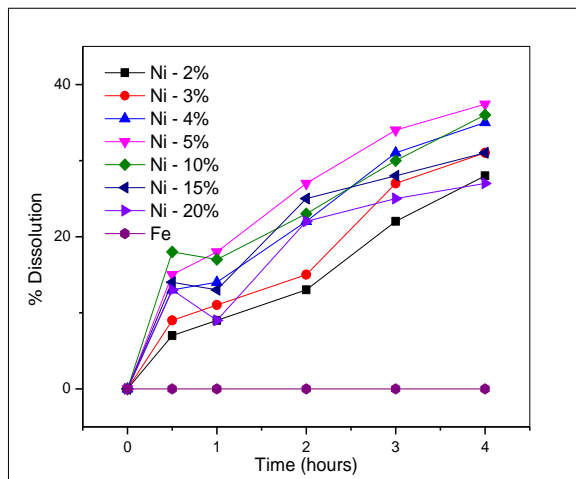

Fig. 5. Effect of solid to liquid ratio (S/L) on leaching recovery 0.1M EDTA, 25°C; 250 rpm, particle size:-75 µm).

6. Effect of Stirring Speed

The effect of stirring speed on the dissolution of nickel is shown in Fig 6. The rate of nickel dissolution increases with an increase in stirring speed. Dissolution increased from 25% to 37.4% as the stirring speed was increased from 100 to 250 rpm. Any further increase in speed of stirring beyond 250 rpm did not have an effect. This indicates that at 250 rpm stirring speed, there is an adequate suspension of the solid particles in the solution; hence, rate of 250 rpm was used in all experiments.
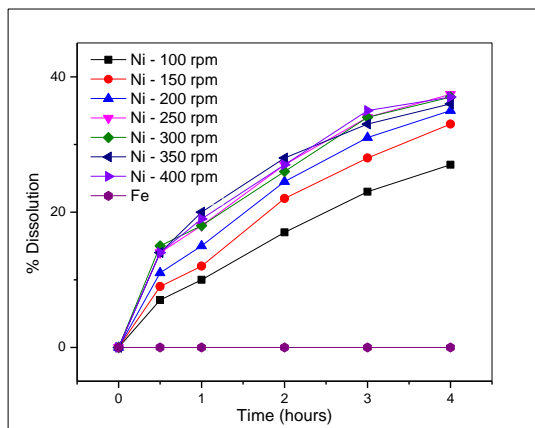

Fig. 6. Effect of stirring speed on the nickel leaching 0.1 M, 25°C, S/L = 5%).

7. Effect of Temperature on the Nickel Leaching

Temperature plays an important role in the dissolution of nickel from the jarosite. Jarosite was leached at different temperatures (25–60°C) in the presence and absence of a reducing agent and the results are shown in Fig. 7. The nickel recovery increased from 40% at 25°C to 82.2 % at 45°C after leaching for 4 hours. This increase is due to the increase in reaction velocity constant K with the

development of reaction temperature. The leaching at 60°C could provide better recovery of nickel if the process was critically controlled as the experiment was happening under atmospheric pressure. When leaching temperature increased to 60°C at 4 hours dissolution time, leaching recovery of nickel dropped to 64%. The decrease can be due to the co-precipitation of nickel into the bulk of the pyrite formation.

As temperature increases, the time required to attain the maximum nickel extraction decreases. At higher temperature nickel dissolution increased at a certain leaching time, but by increasing the leaching time further to 8 hours, the temperature does not have any positive effect.

It can be seen that no iron was dissolved into the solution at all temperatures in the presence of EDTA- Na_2S mixture.
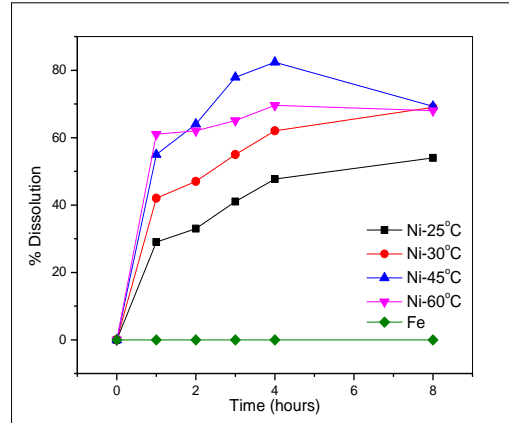

Fig. 7. Effect of temperature on the nickel and iron leaching 0.1 M EDTA- Na_2S, 250 rpm, S/L = 5%

8. Kinetic Analysis

In order to determine the main controlling step and the effects of temperature on the leaching kinetics, the experimental data in Fig. 7 were analyzed based on Equations. (1) and (2), and the dissolution trend are shown in Fig. 8 and 9 respectively. By comparing the R^2 values of plots from Fig 8 and 9, Fig. 9 shows a good correlation between the experimental data and Eq. (1). This indicates that the leaching kinetics can be described by the SCM with an ash layer diffusion control and that the dissolution is temperature dependent (Habashi, 1999).

Fig. 10 shows the Arrhenius plot is a straight line constructed with the $ln\ k$ versus $\frac{1}{T}$ for the k values determined from Eq. (1) and its slope is $(\frac{-E_a}{R})$. The activation energy of Ea =70.7 kJ/mol was calculated using the Arrhenius equation.

The rate constants k_d for the various EDTA concentrations were obtained from the slope of straight lines and presented in Fig. 11. Fig. 11 shows the plot of Log k_d versus ln [EDTA] from which the reaction order with respect to the EDTA concentration was determined as 1.36.

The results for the effect of liquid to solid ratio on leaching kinetics were applied to the diffusion kinetics models and kd values for each S/L were determined. ln k_d versus ln (S/L) was plotted in Fig. 12 and the reaction order with respect to S/L was obtained as 0.28 with a correlation coefficient of 0.9957.

From the variation in kinetics model with time at various particle sizes kd values were obtained. From the kd and particle size values, a plot of ln kd versus ln (r_0) was plotted in Fig. 12, the order of reaction with respect to particle size was found to be −0.69.

As shown in Figs. 7–12, the main resistance to the process is the diffusion through the product layer, so a combination of the shrinking core rate expression and the effects of temperature, acid concentration, S/L and particle size on the rate constant gives the following expression for the leaching kinetics of nickel in EDTA-Na_2S combined:

$$1 - \frac{2}{3}R - (1 - R)^{\frac{2}{3}} = k_d t = k_0 (EDTA)^{1.36} (S/L)^{0.28} (r_0)^{-0.69} exp\left(\frac{70,7}{RT}\right) t \tag{6}$$
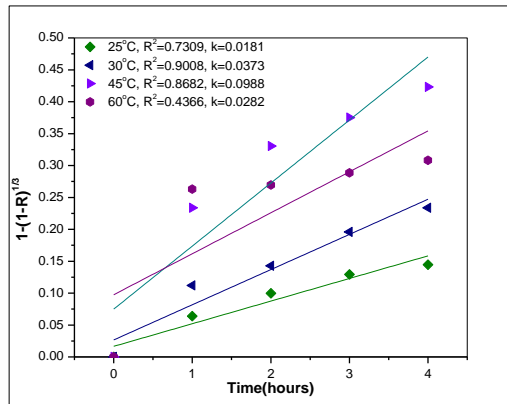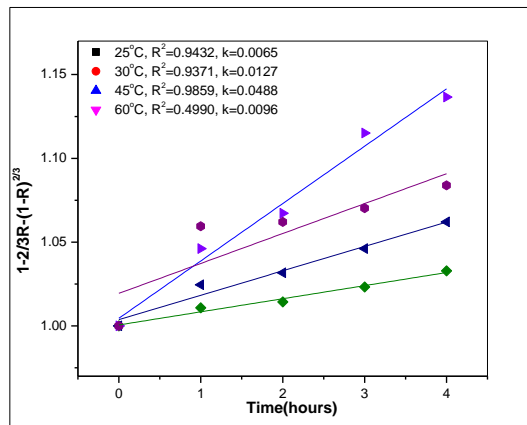
Fig. 8. Plot of equation (2) with time at various temperatures (A) reaction without Na_2S, (B) reaction with Na_2S, (0.1M EDTA concentration, S/L: 5%, 250 rpm, particle size: −75 μm).

Fig. 9. Plot of equation (1) with time at various temperatures (A) reaction without Na_2S, (B) reaction with Na_2S, (0.1M EDTA concentration, S/L: 5%, 250 rpm, particle size: −75 μm).
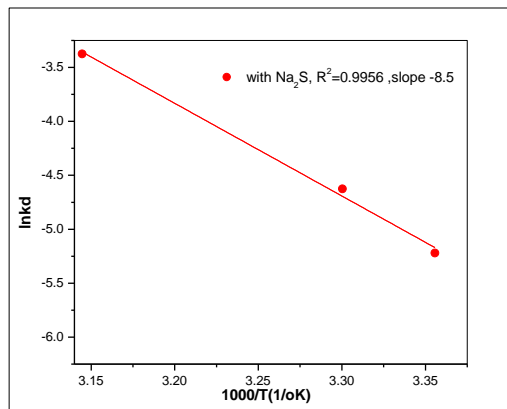

Fig. 10– Arrhenius plot for the dissolution process (0.1M EDTA concentration, 5% S/L, 250 rpm, and particle size: −75μm).
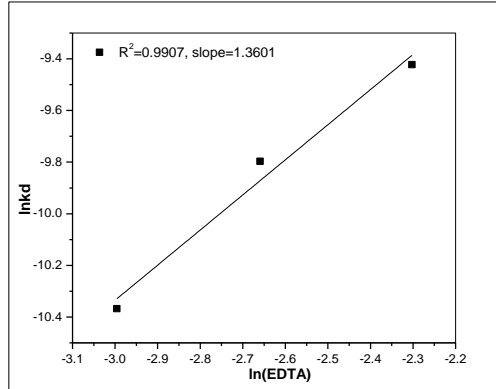
$Ea = 8.5*8.314= 70.669$ kJ/mol

Fig. 11. The variation in equation (2) with time at different EDTA concentration; (S/L: 5%, 250 rpm, particle size: −75 µm.
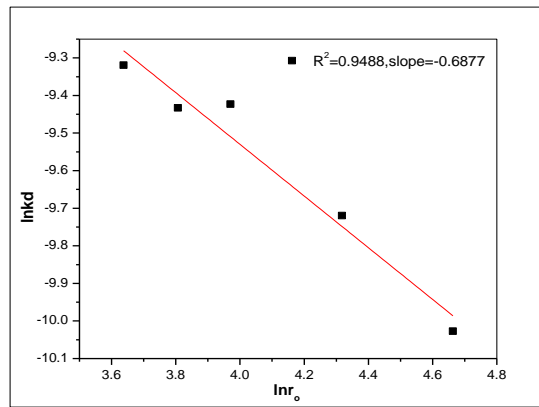

Fig. 12. reaction order with respect to particle size (0.1M EDTA concentration, 250 rpm, 25°C).
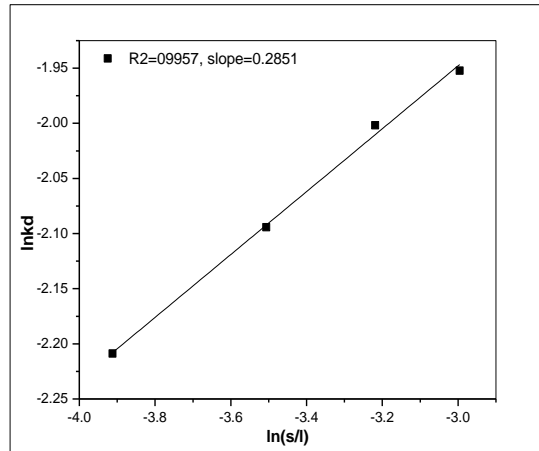

Fig. 13. Determination of reaction order with respect to (S/L), (0.1M EDTA concentration, 250 rpm, 25 $^{\circ}$C).

9.   Conclusion

The dissolution of nickel increases with increase in temperature, leaching time, particle size and EDTA concentration. However, leaching in the presence of EDTA increases the dissolution of iron into solution which is not desirable. Leaching in the presence of EDTA and a reducing agent (Na_2S) gives the same amount of nickel dissolved with no iron. Hence an EDTA- Na_2S mixture is recommended for the leaching of nickel from ammonium jarosite. The decrease in the particle size and solid to liquid ratio increased nickel dissolution. The extraction rate increased with increasing stirring speed and it was the

highest at 250 rpm. The maximum leaching degree was 83% at 45 ^{o}C after 240 min. Dissolution of nickel from jarosite precipitate obeys the shrinking core model. The activation energy was 70.7 kJ/mol and it supported that the process was diffusion controlled.

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