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Alkaline leaching of nickel bearing ammonium jarosite precipitate using KOH, NaOH and NH₄OH in the presence of EDTA and Na₂S



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ABSTRACT

Jarosite precipitates produced in base metal refineries contain substantial amounts of base metals. The dissolution of nickel from the jarosite precipitate was investigated in alkaline medium (KOH, NaOH and NH₄OH) at laboratory-scale in the presence of EDTA as a complexing agent and Na₂S as reducing agent. The leaching efficiency of nickel was 82.4%, 84.5% and 88.9% in NaOH, KOH and NH₄OH respectively in the presence of 0.1 M EDTA–Na₂S, pH 9–10, using – 75 μm of ammonium jarosite precipitate at 250 rpm, 45 °C, 5% solids and leaching time of 4 h. Thermodynamic feasibility was explored using Medusa software and the kinetics of the dissolution process was studied using the shrinking core model. The results show that the dissolution process is second order and diffusion controlled. The activation energy was found to be 32.34, 35.31 and 31.52 kJ/mol in KOH, NaOH and NH₄OH mediums respectively in the temperature ranges between 25 and 45 °C. The effects of EDTA–Na₂S concentration, particle size, pH, solid–liquid ratio, stirring speed, temperature and contact time were explored.

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1. Introduction

In the base metal refinery plants, thousands of tonnes of synthetic jarosite precipitates containing 25–35% Fe are produced annually in order to prevent iron from entering the electrowinning process (Dutrizac and Jambor, 2000; Nheta and Makhatha, 2013). However, losses of nickel and other valuable base metals may occur either by entrainment or co-precipitation with jarosite because the precipitate is generally discarded. Such losses could be reduced either at the precipitation stage or by subsequent recovery of contained values by leaching (Nheta and Makhatha, 2013).

At Impala Base Metals Refinery, the converted Ni–Cu matte is treated by a hydrometallurgical process in acidic solution to recover nickel, copper, cobalt and the precious metals. It has been observed that iron is dissolved in huge amounts in the leached liquor and might be eliminated from the solution to avoid its impact during the subsequent processes; therefore it is precipitated as ammonium jarosite. A significant amount of nickel was observed in the jarosite precipitated as a non-optimized iron extraction process (Lamy, 2007).

Unlike the conventional acidic agents used to recover base metals from their ores, alkaline agents such as sodium hydroxide, ammonium hydroxide, and sodium carbonate can selectively bring the desired metal into solution, leaving behind Fe and other metals such as Cd and Mn (Moradkhani et al., 2012). Furthermore, Canterford (1978) and Liu

et al. (2009) in their works noticed that the leaching of a nickel bearing mineral with sulfuric acid at atmospheric pressure and ambient temperature took so long and was extensively acid consuming. They highlighted as well the fact that the acid leaching in the described conditions was not selective and was undertaken along with the dissolution of elements like iron, magnesium and aluminum which will cause difficulties in subsequent unit operations for the separation and recovery of metals. Curlook (2004), Georgiou and Papangelakis (1998) and Whittington and Johnson (2005) while studying the leaching of nickel bearing laterite in acidic medium under pressure, could notice a high amount of nickel recovery at a remarkably fast rate of dissolution in which a simultaneous precipitation of a significant proportions of solubilized iron in the form of Fe₂O₃ with consumption of acid was happening.

This paper presents a process of selectively leaching nickel from ammonium jarosite in alkaline mediums in the presence of EDTA as a complexing agent in synergy with Na₂S as a reducing agent. Thermodynamics and chemistry of nickel and iron in alkaline mediums was involved in the proposed design to investigate the feasibility of the dissolution of nickel from the jarosite precipitate while kinetics was investigated to evaluate the rate and mechanism of nickel dissolution.

1.1. Jarosite

Iron is commonly removed from base metal leach liquor solution by precipitation as jarosite, pseudo jarosite, goethite, hematite and schwertmannite by increasing the pH of the medium (María et al., 2009). Besides the fact that Jarosite-type compounds occur widely in

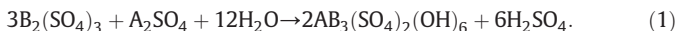
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Table 1
Chemical composition of the ammonium jarosite sample.

Element	Fe	Si	S	Ni	Al	As	Pb	K	Na	Cr	Ca	P	Tl	Co	Cl	Mo	O
Amount (%)	41.3	6.8	5.5	3.5	1.8	1.4	1.1	0.63	0.3	0.2	0.06	0.03	0.03	0.03	0.01	0.01	37.2

nature as red mud, the hydrometallurgical plants apply the jarosite process with the intent to remove iron from the leach liquor in a readily filterable form according to the following reaction (Roeland and Dijkhuis, 2009):



Jarosite is the name given to the compound $AFe_3(SO_4)_2(OH)_6$ and being used as a generic way for iron containing members or a large aluminate mineral family having the general formula $AB_3(SO_4)_2(OH)_6$ where A can be Na^+ , K^+ , Rb^+ , Ag^+ , $Tl^{(I)}$, H_3O^+ , NH_4^+ , $1/2Pb^{(II)}$, or $1/2Hg^{(II)}$ and B Fe^{3+} or Al^{3+} . It has been shown that the substitution of the potassium cation with NH_4^+ , Na^+ or H^+ in jarosite will result in the formation of known ammonium-, sodium- or hydronium-jarosites respectively (Das et al., 1995).

Dutrillac et al. (1984) found out that during the formation of jarosite from a solution containing base metals such as Zn^{2+} , Cu^{2+} , and Ni^{2+} , they are incorporated in the alkali jarosite in the following order $Fe^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$.

It is demonstrated that the jarosite formation has a complex mechanism which is based on the presence of adequate alkali metal, iron and or aluminum in sulfate media and the tendency for aluminum and iron to hydrolyze (Roeland and Dijkhuis, 2009). Nevertheless, detailed studies of jarosite compounds indicate consistent deficiencies in the "alkali" occupancy of the A-site and in the occupancy of the B-site (Dutrillac, 2004a,b). The hydronium ions are assumed to compensate for the deficiencies in the A-site occupancy while the deficiencies in the B-site are charge-compensated by the conversion of some SO_4^{2-} to HSO_4^- . In addition to substitutions in the A-site, it is well established that various species can substitute for Fe, SO_4 , and to a lesser extent for the OH component of the jarosite structure (Dutrillac, 2004a,b).

It is established that most commercial jarosites are based on Na or NH_4 for economic reason, yet the potassium member is the most stable of all the jarosite-type compounds (Dutrillac, 2004a,b).

In 1971 Babcan studied the hydrolysis of a solution containing ferric sulfate and potassium hydroxide and he showed that the stability zone of jarosite is within pH ranges from 1 to 3 and at temperatures between 20 and 200 °C. At low pH no precipitation occurs and at high pH mainly goethite (up to 100 °C) and hematite (above 100 °C) appear.

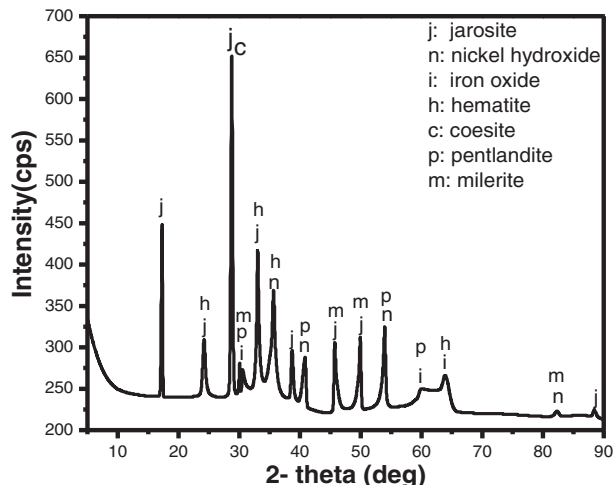


Fig. 1. XRD pattern of the ammonium jarosite sample.

1.2. Alkaline leaching

In comparison to acid, alkaline leaching is suited to ore bodies associated with a large proportion of acid-consuming constituents such as calcium and magnesium. Alkaline leaching can selectively bring the desired metal into the solution leaving behind iron and other undesirable associations from the ore bodies. There are no serious corrosion problems that are encountered with alkaline leaching due to the fact that the alkaline reagents are generally not aggressive. Therefore, alkaline leaching is generally carried out under drastic conditions. A relatively high reagent concentration, elevated temperatures, and pressures are common in alkaline leaching to achieve an acceptable rate of reactions.

Important alkalines that have been most extensively used for leaching are sodium hydroxide, ammonium hydroxide, and sodium carbonate.

Several works have been done previously and show that the oxides, hydroxides, and carbonate intermediates of common metals, for instance aluminum, copper, and zinc are easily solubilized in strong caustic solution to water soluble compounds, such as sodium aluminate, sodium cuprite, and sodium zincate respectively on one side and on the other side the oxidic sources of refractory metals, such as V, Mo, and W, which are predominant forms of their natural resource which can be leached with caustic or soda ash at ambient or elevated pressures to form water-soluble vanadate, molybdate, and tungstate, respectively, provided that these metals are present in their highest oxidation state (Gupta and Mukherjee, 1990).

1.3. Chelation

Previous studies identified four ways in which metals are mobilized in soils: (1) changes in the acidity; (2) changes in solution ionic strength; (3) changes in the REDOX potential; and (4) formation of complexes. In practice, acid washing and chelator soil washing are the two most prevalent removal methods. The most common chelating agent studied in the literature is EDTA. EDTA is the most used chelating agent having a high affinity for heavy metals beside CDTA, DTPA, EDDHA, EGTA, HEDTA, and NTA (Tatiana et al., 2006). Therefore, the acid-base behavior of chelating

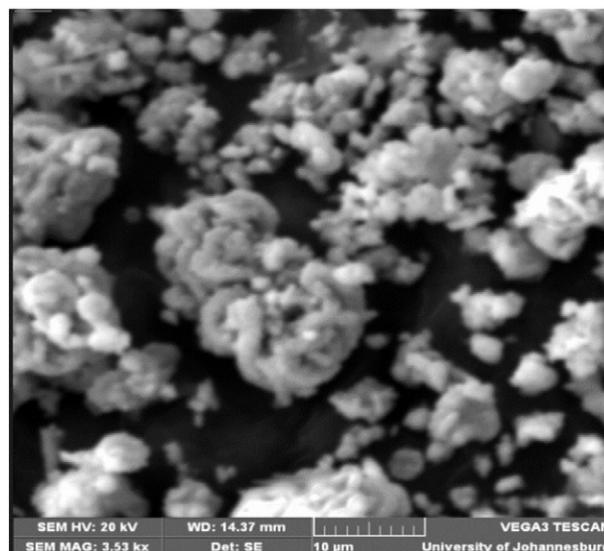


Fig. 2. Morphology of the ammonium jarosite sample.

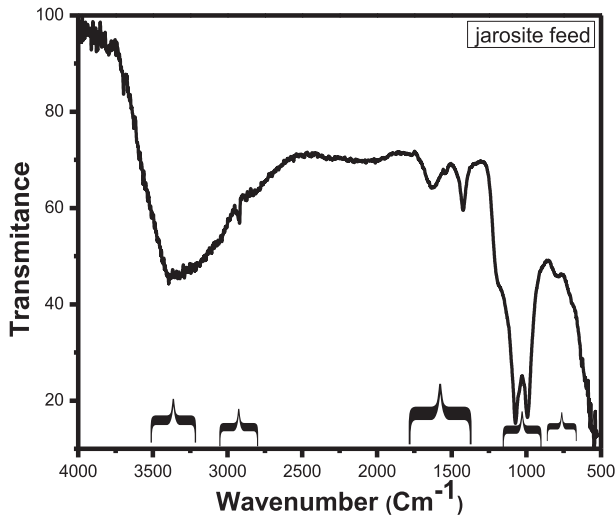
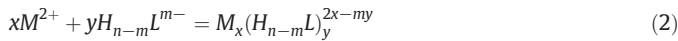


Fig. 3. FTIR spectrum of the ammonium jarosite sample.

agents offers the EDTA multiple coordination sites available for complexation with a metal center. Each conjugate acid/base of the chelating agent may form a strong complex with the metal, resulting in the formation of various complexes $M_x(M_n - mL)_y^{2x-my}$ as follows (Robert, 1999)



with the total complex concentration (ML_{Tot}) given by

$$ML_{Tot} = \sum M_x(H_{n-m}L)_y^{2x-my} \quad (3)$$

Thus, the total metal solubility, M_{Tot} is computed by:

$$M_{Tot} = M_{aq} + ML_{Tot} \quad (4)$$

As a chelating agent, EDTA raises the desorption of sorbed and occluded species and the dissolution of precipitated forms until equilibrium is reached. The chelating agent presents the advantage of solubilizing a large amount of metal compared to more aggressive chemical compounds (Tatiana et al., 2006; Teik-Thye et al., 2005).

1.4. Reduction

Usually dissolved heavy metals can be discarded out of the solution through various precipitation reactions as shown below:

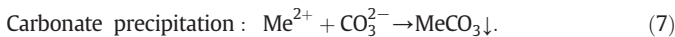
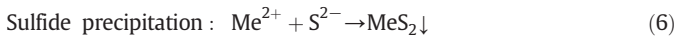
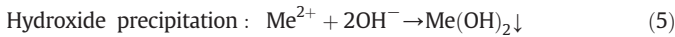


Table 2
Vibrational type in the jarosite precipitate.

Vibration	Wavenumber range (cm ⁻¹)	Nature
O–H stretch	3550–3400	M
O–H bend	1684–1621	W
S–O stretch	1140–1080	VS
S–O Bend	680–610	M
M–O	<400	
M–N end group	1440–1390	VS
M–N bridging group	1485–1470	
M–NH ⁴⁺	3335–3030	VS
	1485–1390	S

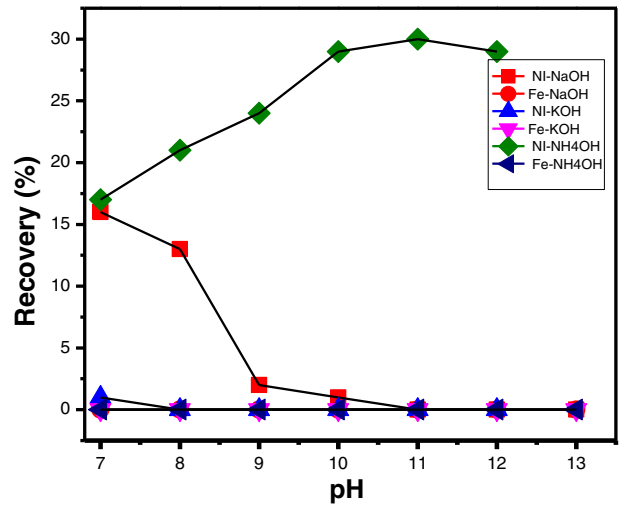


Fig. 4. % Recovery of nickel and iron in 1 M of NaOH, KOH and NH₄OH, pH 7–14, T = 25 °C, S/L = 5%, t = 1 h and 250 rpm.

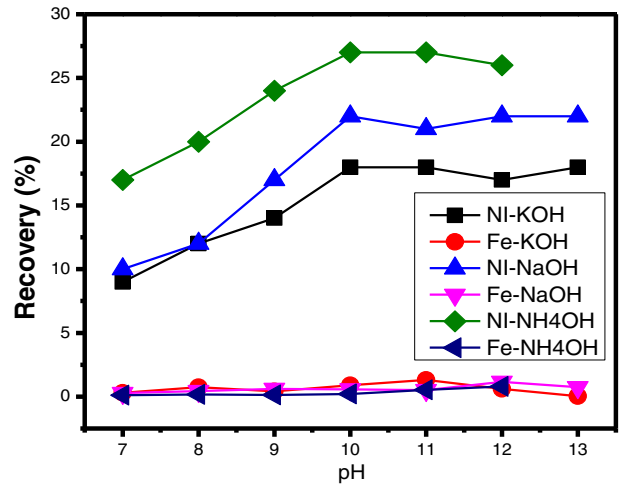


Fig. 5. % Recovery of nickel and iron in 1 M of NaOH, KOH and NH₄OH solution in the presence of the complexant agent (EDTA: 0.1 M), pH 7–14, T = 25 °C, S/L = 5%, t = 1 h and 250 rpm.

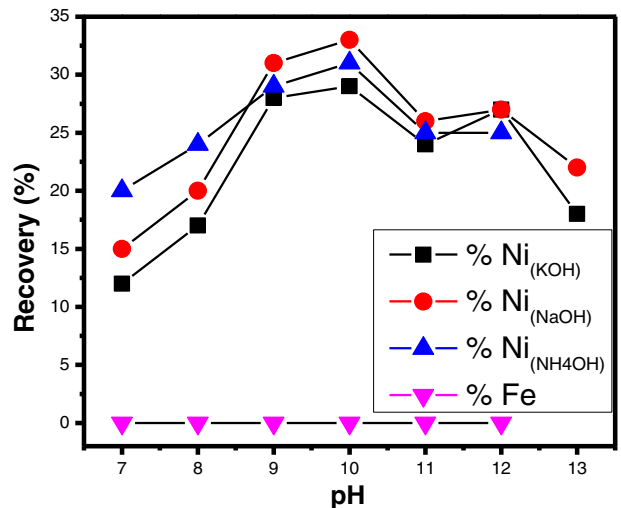


Fig. 6. % Recovery of nickel and iron in 1 M of NaOH, KOH and NH₄OH solution in the presence of the EDTA–Na₂S mixture 0.1 M, pH 7–14, T = 25 °C, S/L = 5%, t = 1 h and 250 rpm.

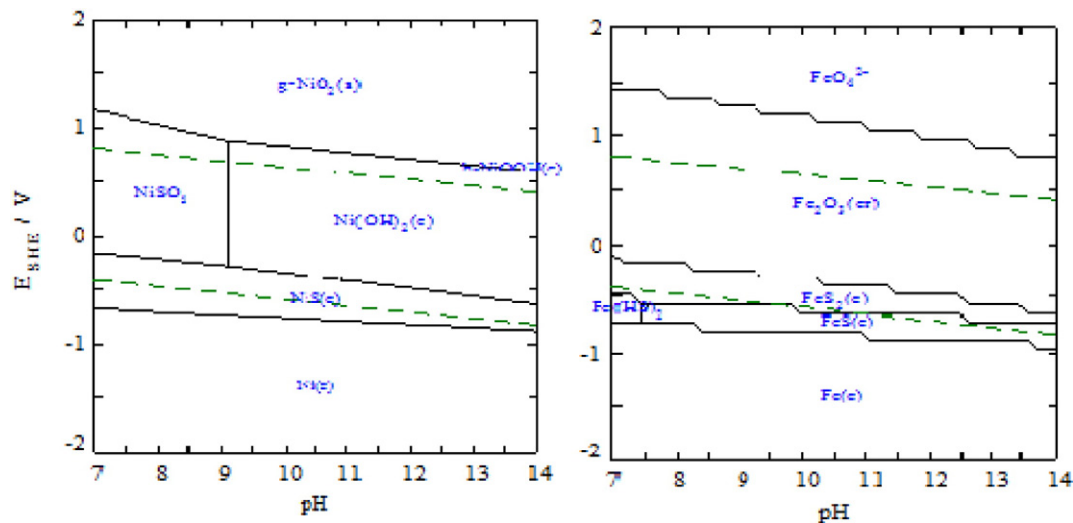


Fig. 7. Eh–pH diagram for the (a) Ni–Na₂S–H₂O and (b) Fe–Na₂S–H₂O system at 25 °C; 1.00 M and 1 atm (M = molality).

Compared to hydroxide precipitation, sulfide precipitates have successful usage in conventional hydrometallurgical treatment of ore and effluents. The low solubility of metal sulfide and their selectivity of metal removal present an exceptional advantage. Sulfide precipitation can be effected using either solid (FeS, CaS), aqueous (Na₂S, NaHS, NH₄S) or gaseous sulfide sources (H₂S) (Alison, 2010). Migdisov et al. (2002) studied the estimates of the second dissociation constant of H₂S from the surface sulfidation of crystalline sulfur and demonstrated that the concentration of sulfur species is strongly a function of pH.

Based on the working conditions of sulfide formation on the pH dependence, Karbanee et al. (2008) studied the control of nickel sulfide precipitation and found that using gaseous hydrogen sulfide could not precipitate Ni²⁺ at ambient condition.

The reactivity of metal sulfide formation from an aqueous solution containing metals shows that in accordance with the kinetics of the water, PbS, CdS and ZnS precipitate faster than FeS, but CoS and NiS are slower. In the presence of a complexing agent, the nucleation rate of nickel sulfide formation is reduced (Alison, 2010).

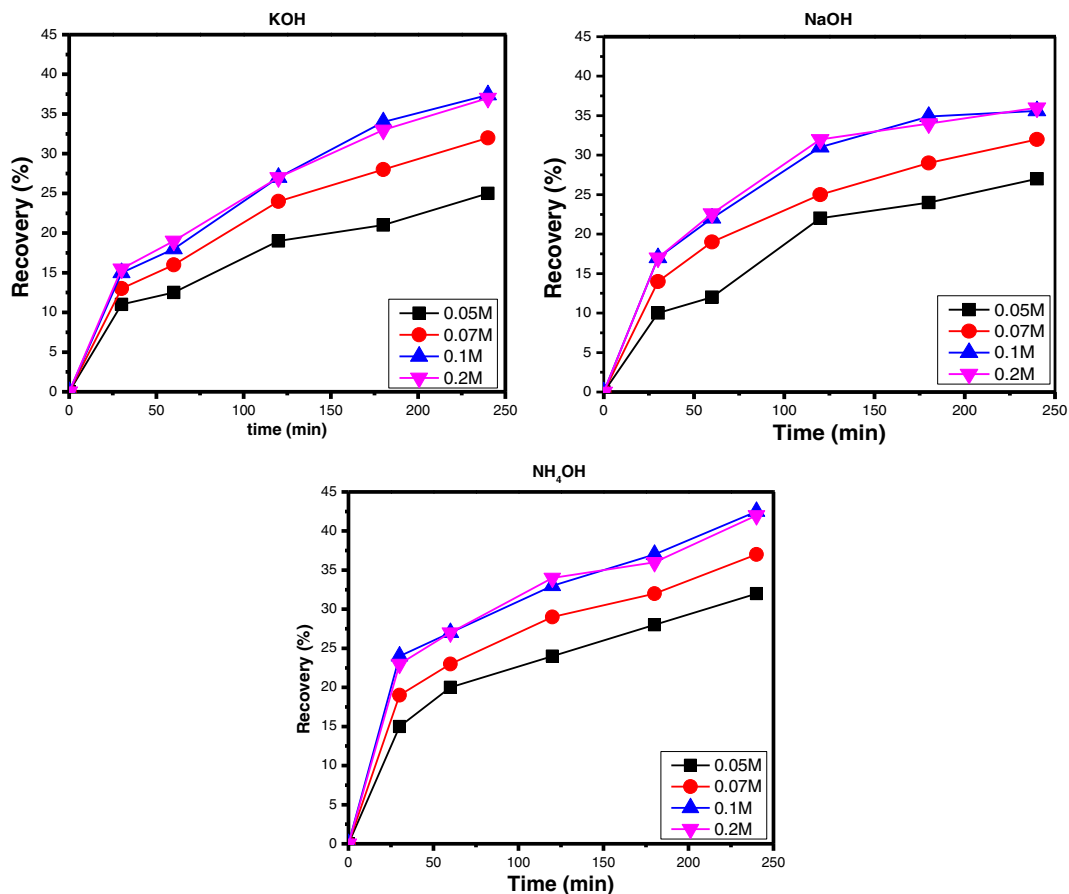


Fig. 8. Effects of EDTA–Na₂S concentration on nickel extraction from jarosite (25 °C; 250 rpm, S/L = 5%, particle size: –75 μm, 4 h).

2. Experimental

2.1. Material

The ammonium jarosite precipitate used in the present study was generated from Impala Base Metal Refinery (BMR). The elemental analysis of the ammonium jarosite was performed using “RigakuZSX Primus II” X-ray fluorescence (XRF) and the results are presented in Table 1. It can be seen that the jarosite precipitate contains a 3.5% mass of nickel at a concurrence of 41.3% of iron. The mineralogical analyses was done using “Rigaku Ultimal V” X-ray diffractometer (XRD) and the pattern is shown in Fig. 1. Major phases present in the sample are jarosite, nickel hydroxide and iron oxide. Minor phases like hematite (Fe_2O_3), coesite (SiO_2), pentlandite ($(\text{Ni}_{4.18}\text{Fe}_{4.82})\text{S}_8$) and millerite (NiS) are also present.

The morphology of the jarosite shown in Fig. 2 was achieved using “TESCAN” scanning electron microscopy (SEM) and it reveals that the sample is a product of precipitation while its pattern in Fig. 3 performed using a Thermo Fisher “Nicolet Is™10 iTR” FTIR spectrometer with Smart iTX sampling accessory indicates the presence of MO, OH, S–M, M– NH_4^+ and Si–O groups in the sample. The type of vibration of different functional groups are summarized in Table 2.

Potassium, sodium and ammonium hydroxides were used for alkaline leaching. EDTA and Na_2S were used as complexing and reducing agents respectively. All reagents were of high purity.

2.2. Leaching experiments

An ammonium jarosite sample was pulverized and sieved using ASTM standard sieves. XRF, XRD and FTIR were used to analyze the solid sample before any treatment, while inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectroscopy (AAS) were used to measure the amount of nickel and iron during the dissolution processes. The leaching process was performed using a 100 ml open beaker while the agitation of the slurry was maintained by means of 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. 80% particles passing $75\ \mu\text{m}$ were used to perform the leaching experiments.

The dissolution of nickel in an alkaline medium was studied in 3 steps:

- Leaching in different alkaline mediums (KOH, NaOH and NH_4OH)
- Leaching in the presence of different alkaline mediums with EDTA as a complexing agent
- Leaching in the presence of different alkaline mediums with a mixture EDTA– Na_2S as a complexing and reducing agent respectively.

The effect of variables such EDTA– Na_2S concentration, particle size, pH, solid–liquid ratio, stirring speed and temperature were investigated.

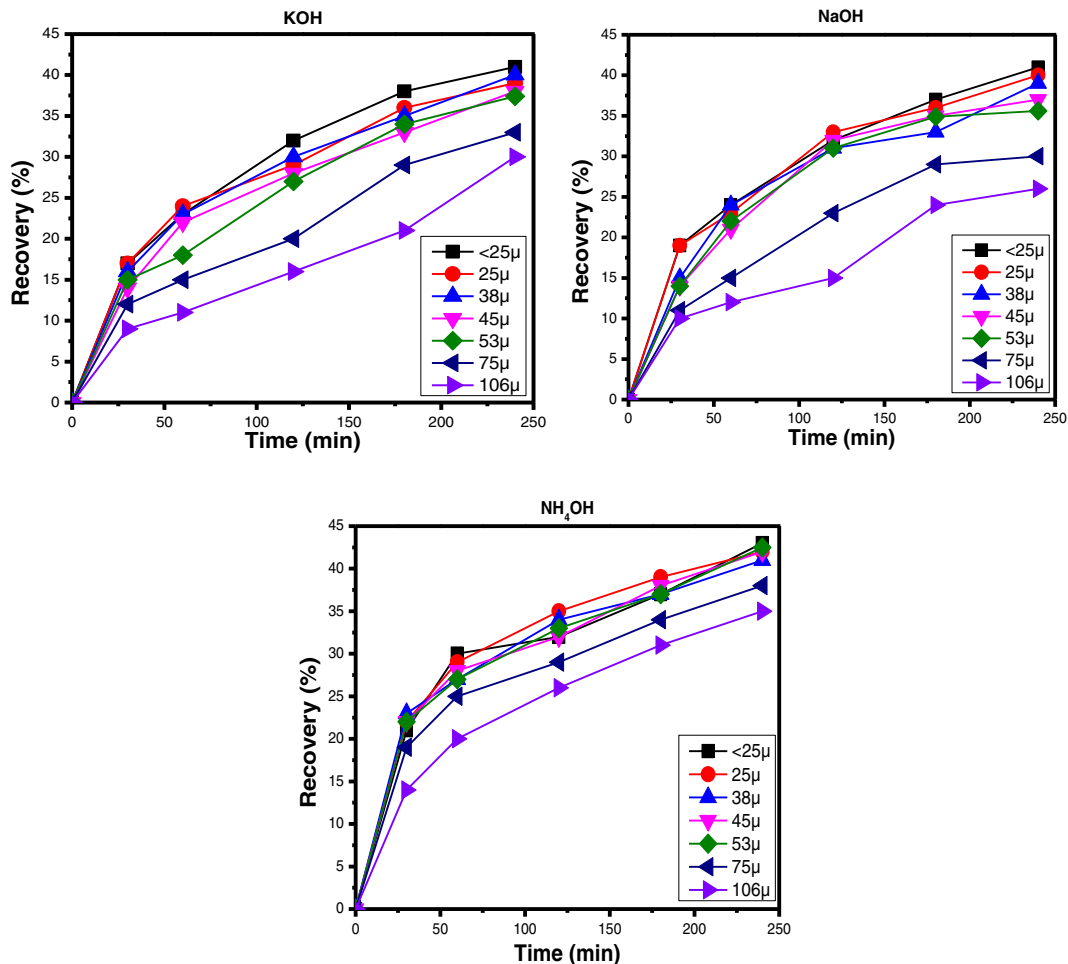


Fig. 9. Effect of particle sizes on the nickel leaching (0.1 M EDTA– Na_2S , 25 °C; 250 rpm, S/L = 5%, 4 h).

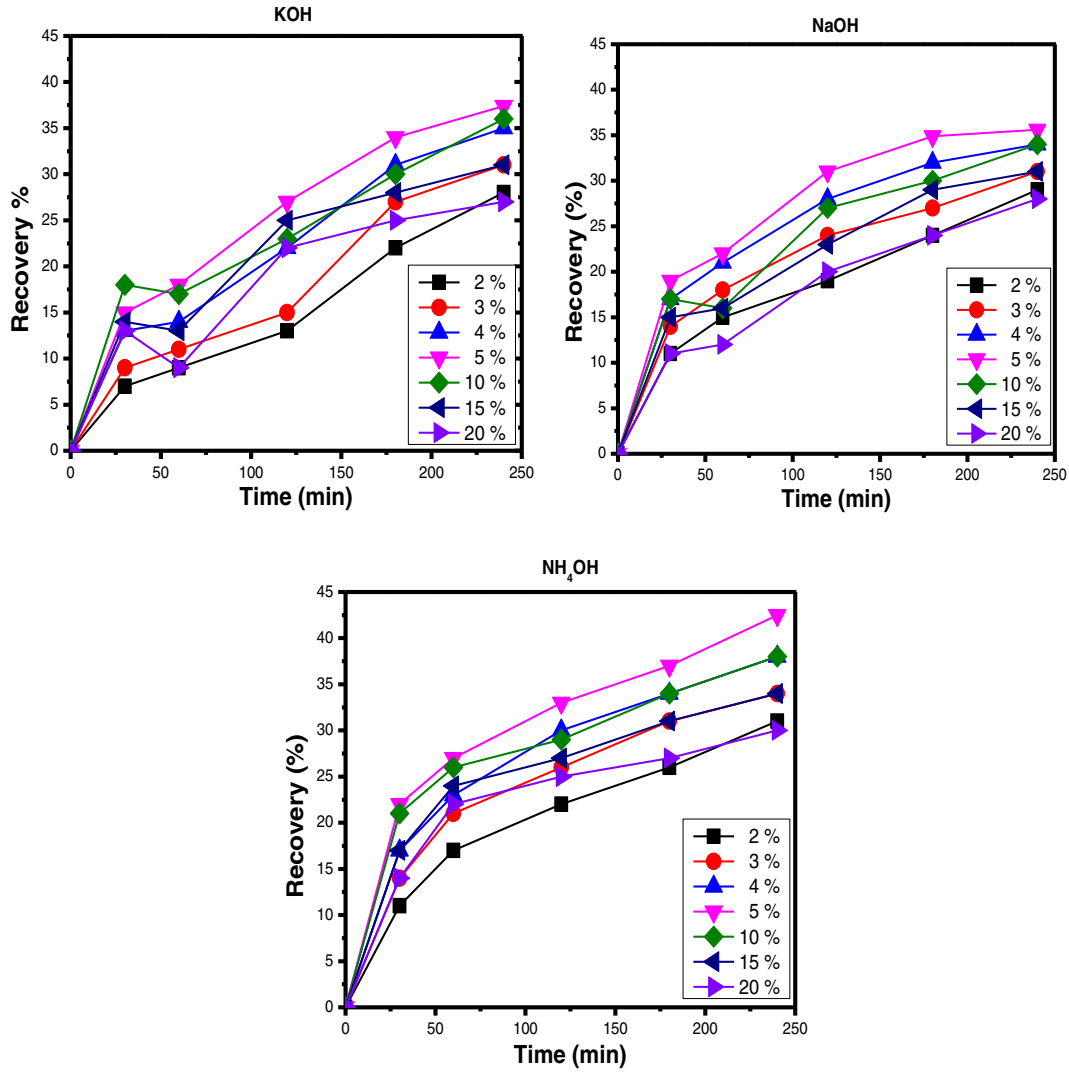


Fig. 10. Effect of solid to liquid ratio (S/L) on leaching recovery of nickel (0.1 M EDTA, 25 °C; 250 rpm, particle size: $-75 \mu\text{m}$, 4 h).

The recovery efficiency was calculated according to the formula (8).

$$\% \text{ Recovery} = \frac{C_{ml} * V_{sol}}{M_{sd} * G_M} * 100 \quad (8)$$

where,

C_{ml}	Concentration of metal in the solution (g/l)
V_{sol}	Volume of the solution containing the dissolved metal (l)
M_{sd}	Mass of the sample (g), and
G_M	Grade of the targeted metal in the raw sample (%)

2.3. Kinetics analysis

In order to determine the kinetic parameters and mechanism controlling step 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):

$$1 - \frac{2}{3}R - (1-R)^{2/3} = \frac{2MDC}{\alpha\delta r_0^2} t = k_d \quad (9)$$

when the solvent diffuses through liquid film and

$$1 - (1-R)^{1/3} = \frac{6MDC}{\alpha\delta r_0^2} t = k_r t \quad (10)$$

when surface chemical reactions control.

Here 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,

3. Results and discussion

3.1. Leaching processes

3.1.1. Leaching in different alkaline mediums (KOH, NaOH and NH_4OH)

Fig. 4 shows that a maximum of 16% and 1% of nickel was recovered when leaching with NaOH and KOH respectively and a decrease in nickel recovery was observed while increasing the pH of the medium. The opposite behavior was observed when the leaching was performed with NH_4OH ; the higher the pH the higher the nickel recovery. The recovery of nickel became constant at pH 11 where the recovery of nickel was 29%. It was also observed that iron was not dissolved.

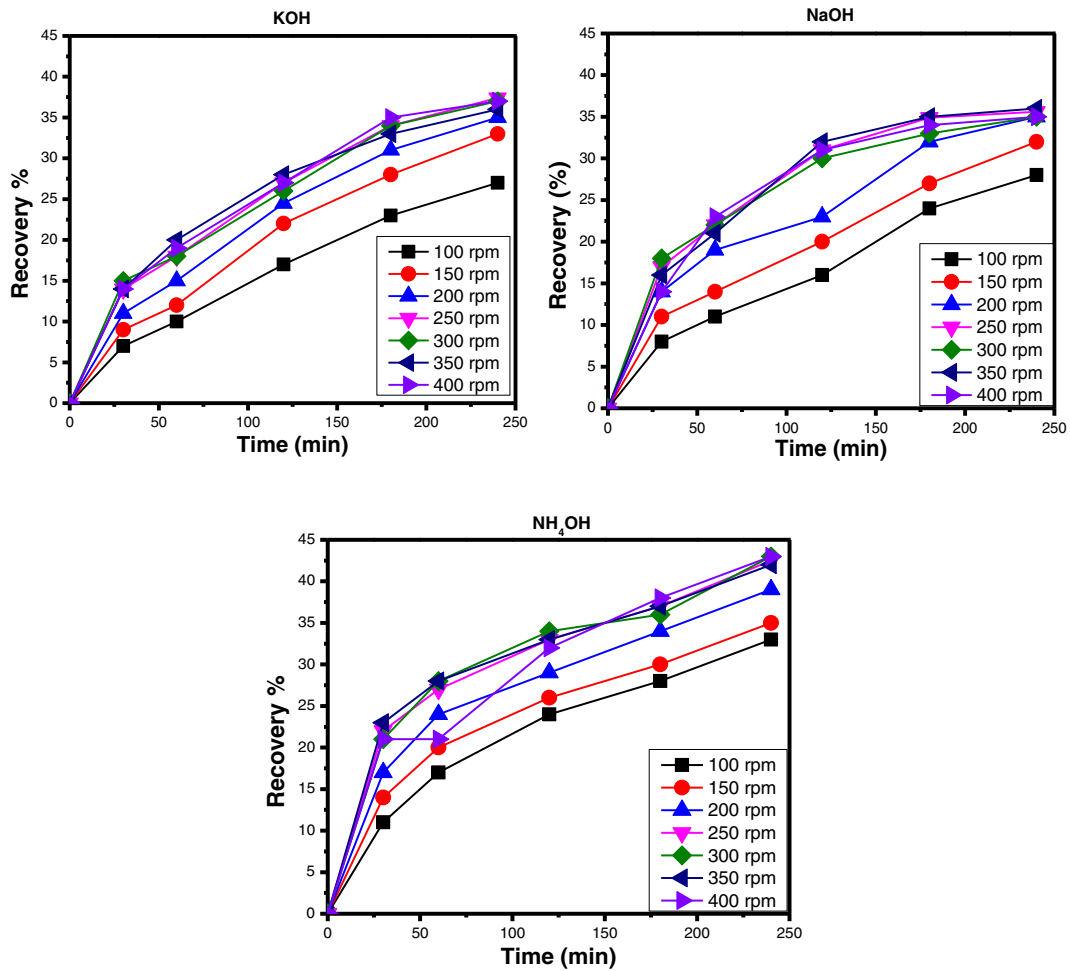


Fig. 11. Effect of stirring speed on nickel leaching (0.1 M EDTA–Na₂S, 25 °C, S/L = 5%, particle size: – 75 μ m, 4 h).

According to the Pourbaix diagram previsions represented in previous works by Ntumba et al. (2014) while studying the thermodynamic of nickel and iron dissolution in hydroxide mediums, and Thompson et al. (2000) while developing the Pourbaix diagrams for multielement systems, it can be concluded that there is a high possibility of forming insoluble species of nickel and iron in NaOH and KOH mediums.

3.1.2. Leaching in different alkaline mediums with EDTA as a complexing agent

From the experimental results in Fig. 5, it is shown that with the use of EDTA there is an upgrading in the recovery of nickel in KOH and NaOH mediums. There is a significant increase to 18% and 22% at a pH of 10 in KOH and NaOH respectively, with not much change in the NH₄OH medium. The presence of iron was observed in all mediums when the EDTA was incorporated. 0.89%, 0.56% and 0.2% of iron was recovered in KOH, NaOH and NH₄OH mediums respectively.

It was also observed that there was an improvement in the thermodynamics of dissolution of both nickel and iron. Therefore the use of the EDTA enhanced the dissolution of both nickel and iron and shows no selectivity behavior.

3.1.3. Leaching in different alkaline mediums with a mixture of EDTA–Na₂S as a complexing and reducing agent respectively

As illustrated in Fig. 6, it is shown that 29, 33 and 31% of nickel was recovered in KOH, NaOH, and NH₄OH respectively with no iron in the solution when leaching using a mixture of EDTA–Na₂S at pH 10. This shows that nickel can be selectively dissolved from the ammonium jarosite precipitate and from the predominance diagram area in Fig. 7,

it can be seen that there is a high possibility of forming soluble species of nickel and insoluble species of iron.

3.2. Optimization of nickel dissolution in the presence of EDTA–Na₂S mixture

3.2.1. Effect of complexing agent concentration

The effect of complexing agent concentration on the dissolution of nickel at room temperature was investigated in the range of 0.05 to 0.2 M EDTA–Na₂S. The results are shown in Fig. 8. Maximum recovery of nickel was obtained with 0.1 M EDTA–Na₂S. It is shown that the recovery of nickel at the concentration of 0.1 M of EDTA–Na₂S mixture solution at 25 °C reached 37.4, 5.4 and 42.5% recovery in KOH, NaOH and NH₄OH respectively with no iron reported after 4 h. Further increases in the concentration of EDTA–Na₂S slightly increase nickel recoveries when using KOH and NaOH. However it might not be beneficial to increase the EDTA–Na₂S concentration above 0.1 M as a further increase in EDTA concentration has no effect on nickel recovery. Under these conditions no iron was detected in the leachate.

3.2.2. Effect of particle size

Particle size plays an important role in the leaching process. Leaching experiments were carried out with particle sizes ranging from <25 μ m to 106 μ m and the results are shown in Fig. 9. Nickel recovery was inversely proportional to particle size in all media. This is due to the increase in surface area with decreasing particle size. It is shown that after 4 h of leaching time, 41, 40 and 43% of nickel was extracted from the particle size of – 25 μ m in KOH, NaOH and NH₄OH respectively.

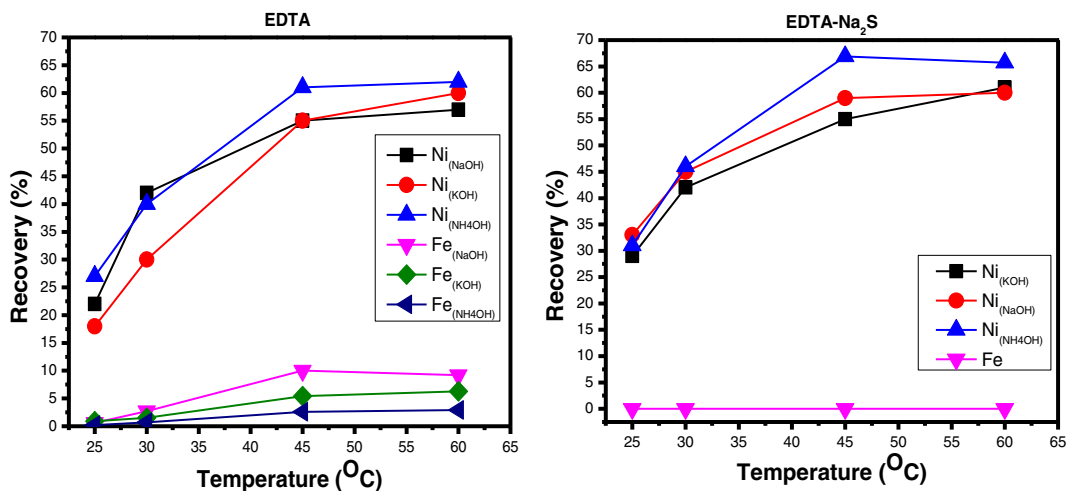


Fig. 12. Effect of temperature on nickel and iron leaching (0.1 M EDTA–Na₂S, 250 rpm, S/L = 5%, particle size: – 75 μm, 4 h).

3.2.3. Effect of solid/liquid ratio

Fig. 10 shows the effect of solid/liquid ratio on the recovery of nickel. Nickel recoveries increased with increasing pulp density between 2% and 5% in all mediums, then decreased with further increases in pulp density. This may be explained by the fact that high pulp density leads to reagent starvation. Therefore, it can be seen that after a pulp density of 5%, 37.5, 35.6 and 42.5% of nickel was extracted in KOH, NaOH and NH₄OH respectively after 4 h.

3.2.4. Effect of stirring speed

Fig. 11 shows that stirring speed has a significant impact on the dissolution of nickel. At an agitation speed of 250 rpm, 37.4%, 35.6%, and 42.5% nickel recoveries were obtained in KOH, NaOH, and NH₄OH with EDTA–Na₂S respectively after 4 h. Stirring increased the diffusion rate of ions in the leaching medium. It can thus be concluded that the dissolution process in alkaline media is diffusion-dependent.

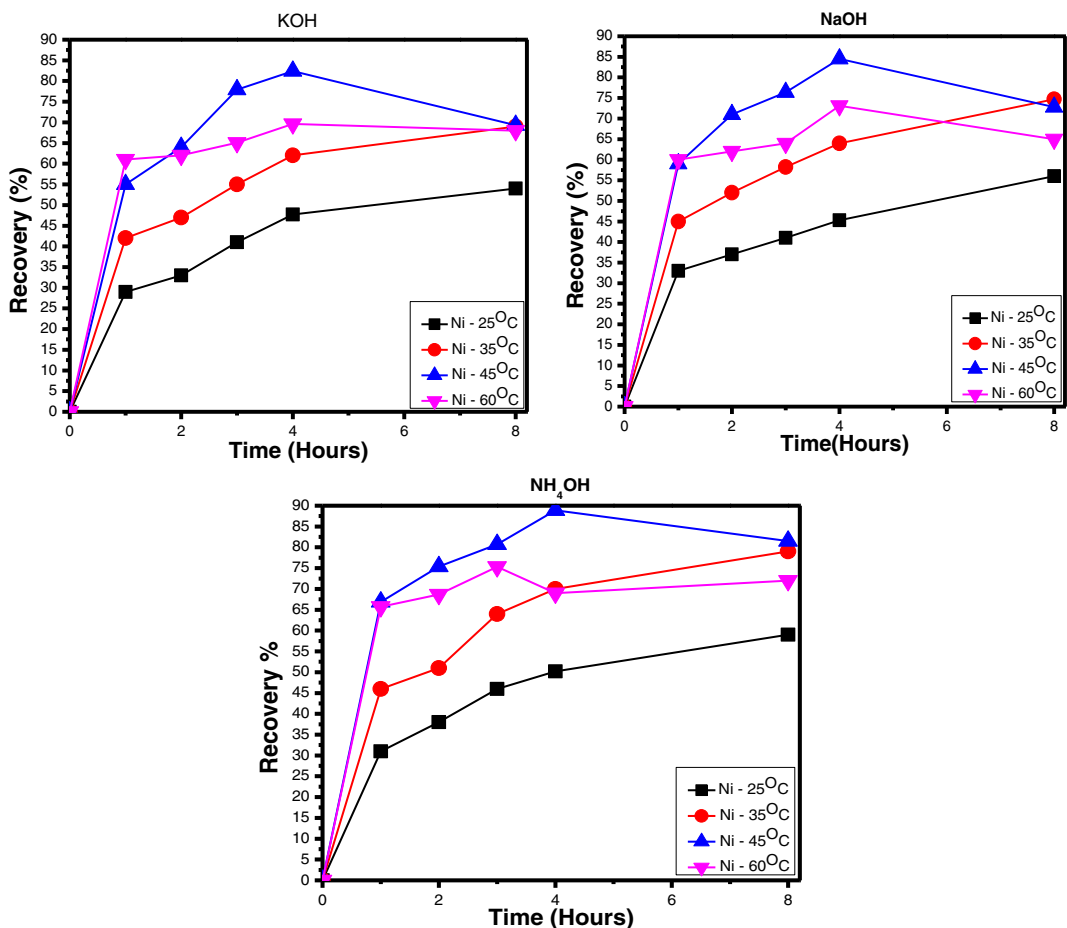


Fig. 13. Effect of time on nickel and iron leaching (0.1 M EDTA–Na₂S, 250 rpm, S/L = 5%, 45 °C, particle size: – 75 μm).

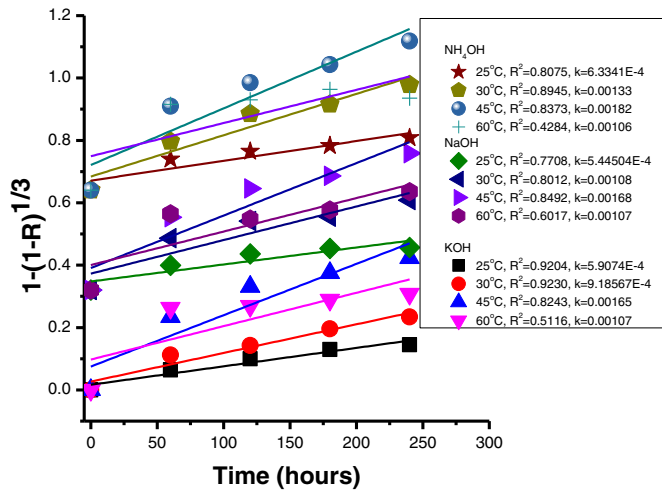


Fig. 14. Plot of Eq. (10) with time at various temperatures (0.1 M EDTA–Na₂S concentration, S/L = 5%, 250 rpm, particle size: – 75 μm).

3.2.5. Effect of temperature on the nickel leaching

As the temperature has a direct thermodynamic effect on the dissolution of nickel in different alkaline mediums, the effect of temperature on the leaching behavior was investigated in the range of 25–60 °C. Results presented in Fig. 12 show that at 45 °C, 57%, 60%, and 62% of nickel with 9.2%, 6.3%, and 2.9% of iron were recorded when leaching with NaOH, KOH, and NH₄OH respectively in the presence of EDTA only while 60%, 61%, and 65.7% of nickel with no iron were recorded in NaOH, KOH, and NH₄OH respectively in the presence of EDTA–Na₂S combined.

3.2.6. Effect of time

The effect of time on the dissolution of nickel in 1 M NaOH, KOH, and NH₄OH solution in the presence of 0.1 M EDTA–Na₂S was investigated at 45 °C and the results are shown in Fig. 13. Recovery of nickel increased with time up to 82.4%; 84.5%, and 88.9% by leaching with NaOH, KOH and NH₄OH respectively for 4 h, after which it decreased.

3.3. Kinetics analysis

By comparing the R² values of plots from Figs. 14 and 15, Fig. 15 shows a good correlation between the experimental data and Eq. (9). This indicates that the leaching kinetics can be described by the SCM

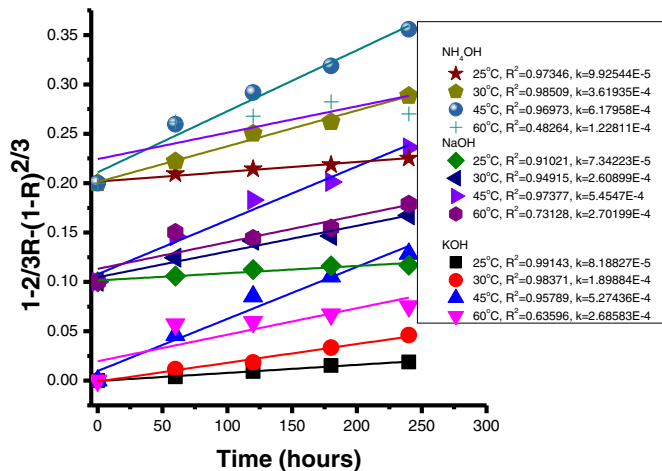


Fig. 15. Plot of Eq. (9) with time at various temperatures (0.1 M EDTA–Na₂S concentration, S/L = 5%, 250 rpm, particle size: – 75 μm, 4 h).

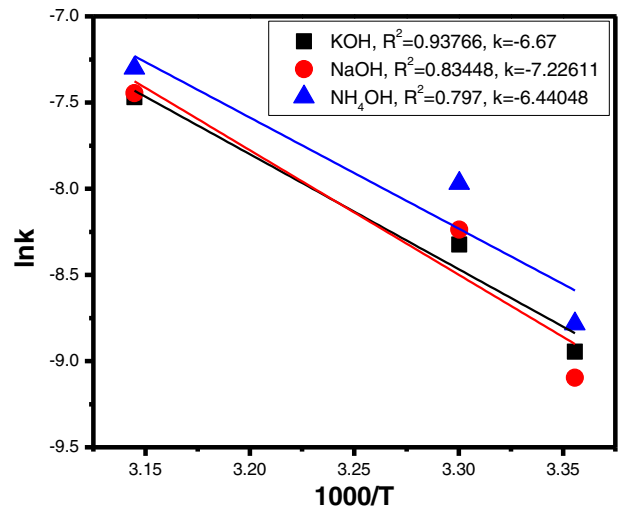


Fig. 16. Arrhenius plot for the dissolution process (0.1 M EDTA concentration, S/L = 5%, 250 rpm, and particle size: – 75 μm).

with an ash layer diffusion control and that the dissolution is temperature dependent (Habashi, 1999).

Fig. 16 shows that the Arrhenius plot is a straight line constructed with the $\ln k$ versus $1/T$ for the k values determined from Eq. (9) and its slope is $(-E_a/R)$. The activation energies E_a = 38.4, 35.3 and 31.53 kJ/mol were calculated using the Arrhenius equation in KOH, NaOH and NH₄OH respectively.

3.4. Analysis of residues

Residues were analyzed and compared to the feed to see the impact of medium after leaching. From Fig. 17 there is not much change of the feed structure compared to the residues coming from NH₄OH but a remarkable change was observed with the patterns of residues from KOH and NaOH.

3.5. Conclusions

- 1) Nickel can be selectively leached from ammonium jarosite precipitate using alkaline medium in the presence of a mixture of complexing and reducing agents. Optimum conditions are pH 9–

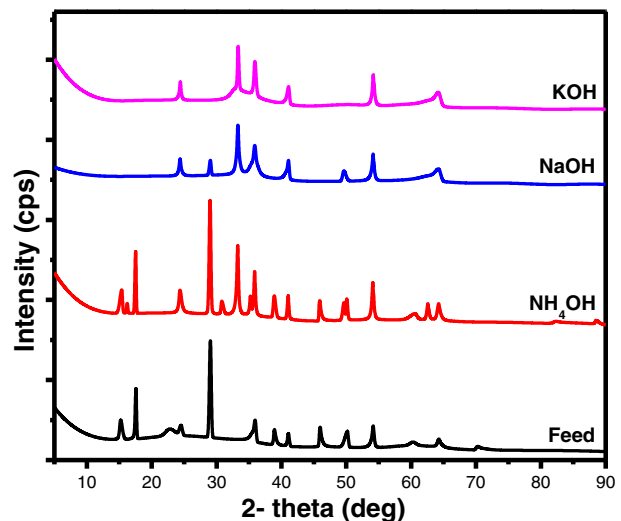


Fig. 17. Comparison of XRD pattern of the feed to the residues in different mediums.

- 10, $T = 45\text{ }^{\circ}\text{C}$, $t = 4\text{ h}$ and 0.1 M EDTA– Na_2S concentration while stirring at 250 rpm using $<25\text{ }\mu\text{m}$ particle size. Under these conditions, no iron was reported to the leachate.
- 2) Nickel leaches poorly from Jarosite precipitate in alkaline mediums only and in alkaline mediums plus EDTA.
 - 3) The kinetic study shows that the dissolution of nickel increases with an increase in temperature, leaching time, particle size, S/L ratio 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. Dissolution of nickel from jarosite precipitate obeys the shrinking core model supported by the process which is diffusion controlled.

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References

- Alison, E.L., 2010. Review of metal sulphide precipitation. *Hydrometallurgy* 104, 222–234.
- Babcan, J., 1971. Synthesis of jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. *Geol. Zb.* 2 (22), 299–304.
- Canterford, J., 1978. Leaching of some Australian nickeliferous laterites with sulphuric acid at atmospheric pressure. *Proceedings of the Australasian Institute of Mining and Metallurgy*. AusIMM, pp. 19–26.
- Curlook, W., 2004. Direct Atmospheric Leaching of Saprolitic Nickel Laterite Ores With Sulphuric Acid. s.l. TMS, Warrendale. pp. 385–398.
- Das, G., Anand, S., Acharya, S., Das, R., 1995. *Hydrometallurgy* (38), 263–276.
- Dutrizac, J., 2004a. The behaviour of the rare earths during the precipitation of sodium, potassium and lead jarosites. *Hydrometallurgy* 11–30.
- Dutrizac, J., 2004b. The behaviour of the rare earths during the precipitation of sodium, potassium and lead jarosites. *Hydrometallurgy* (73), 11–30.
- Dutrizac, J., Jambor, J., 2000. Jarosites and their application in hydrometallurgy. *Rev. Mineral. Geochem.* 405.
- Dutrizac, J., Bautist, R., Plenun, E., 1984. *Hydrometallurgy Process Fundamentals*. pp. 125–169.
- Georgiou, D., Papangelakis, V., 1998. Sulphuric acid pressure leaching of a limonitic laterite: chemistry and kinetics. *Hydrometallurgy* (49), 23–46.
- Gupta, C., Mukherjee, T., 1990. *Hydrometallurgy in Extraction Process*. CRC Press, Florida.
- Habashi, F., 1980. *Principles of Extractive Metallurgy*. Science Publishers, Quebec.
- Habashi, F., 1999. *Kinetics of Metallurgical Processes*. Nancy St-Pierre, Quebec.
- Karbanee, N., Van Hille, R., Lewis, A., 2008. Controlled nickel sulfide precipitation using gaseous hydrogen sulfide. *Ind. Eng. Chem. Res.* 47 (5), 1596–1602.
- Lamy, R.M., 2007. A Fundamental Evaluation of the Atmospheric Pre-leaching Section of the Nickel–Copper Matte Treatment Process, s.l. University of Stellenbosch.
- Liu, K., Chen, Q., Hu, H., 2009. Comparative leaching of minerals by sulphuric acid in a Chinese ferruginous nickel laterite ore. *Hydrometallurgy* (98), 281–286.
- María, P.A., Jordi, C., María, M., Javier, G., 2009. Arsenic removal by goethite and jarosite in acidic conditions and its environmental implications. *J. Hazard. Mater.* (171), 965–972.
- Migdisov, A., Williams-Jones, A., Lakshtanov, L., Alekhin, Y., 2002. Estimates of the second dissociation constant of H_2S from the surface sulfidation of crystalline sulfur. *Geochim. Cosmochim. Acta* 66 (10), 1713–1725.
- Moradkhani, D., et al., 2012. Selective zinc alkaline leaching optimization and cadmium sponge recovery by electrowinning from cold filter cake (CFC) residue. *Hydrometallurgy* 84–92.
- Nheta, W., Makhatha, M., 2013. Leaching of Nickel from a Jarosite Precipitate with Hydrochloric Acid (Johannesburg (South Africa), s.n.).
- Ntumba, E., Mulaba, A., Nheta, W., 2014. Ni Recovery Using KOH, NaOH, and NH_4OH in the Presence of EDTA and Na_2S from Jarosite Precipitated from a PGM Plant. The Southern African Institute of Mining and Metallurgy, Rustenburg.
- Robert, W.P., 1999. Chelant extraction of heavy metals from contaminated soils. *J. Hazard. Mater.* (66), 151–210.
- Roeland, J., Dijkhuis, E., 2009. The Minimisation of Copper Losses During Iron and Aluminium Precipitation from Zinc Leach Liquors. Technical University of Delft, Netherlands.
- Tatiana, A.K., et al., 2006. Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochim. Cosmochim. Acta* (70), 2163–2190.
- Teik-Thye, L., Peng-Cheong, C., Kok-Hui, G., 2005. Process evaluation for optimization of EDTA use and recovery for heavy metal removal from a contaminated soil. *Chemosphere* 58, 1031–1040.
- Thompson, W., Kaye, M., Bale, C., Pelton, A., 2000. Pourbaix diagrams for multielement systems. In: Revie, R.W. (Ed.), *Uhlig's Corrosion Handbook*, 2nd ed. John Wiley & Sons, Inc. (s.l.).
- Whittington, B., Johnson, J., 2005. Pressure acid leaching of arid-region nickel laterite ore. Part III: effect of process water on nickel losses in the residue. *Hydrometallurgy* (78), 256–263.