Silicon and aluminium leaching kinetics from acidic gold mine tailings

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Abstract. Si and Al were leached from gold mine tailings (GMT) in order to determine if the GMT could be used as precursors for the synthesis of geopolymers. Possible synthesis of geopolymers from GMT would help reduce their potential pollution effects through heavy metal immobilisations. The effect of type of alkali (NaOH/KOH), alkali concentration, temperature, milling and calcination of GMT and solid liquid ratio (S/L) on the leaching of Si and Al was investigated. The optimum conditions were 10 M KOH, S/L of 0.5% m/v and a leaching temperature of 95°C. The leaching obeyed the shrinking core model with the surface chemical reaction being the controlling step. The leaching of Si was linked to the Al leaching since the Si/Al ratio of the leachate was around 2 irrespective of leaching conditions. KOH yielded more Si and Al as compared to NaOH, with 54.7 and 26.7 Si and Al leached respectively from as received GMT. Calcination at 900°C resulted in 18% and 22 % increase in Si and Al yield respectively for KOH based leaching. The successful leaching of Si and Al from GMT using KOH provides opportunities for the geopolymerisation of GMT thereby allowing the minimisation of their pollution effects.

1. Introduction

Geopolymerisation is a process where materials containing Al and Si undergo dissolution and polycondensation of Al and Si species under alkaline conditions to form three dimensional structure which is amorphous or semi crystalline [1]. Geopolymers have been shown to have high strength, low density, thermal and high chemical stability [2]. There is an estimated 600 000 tonnes of gold mine tailings (GMT) dotted around the Gauteng province of South Africa exposing people to pollution effects of these tailings dams [3]. It has been postulated that any alumina-silicate material can undergo geopolymerisation and as such GMT can also be used a precursors for the synthesis of geopolymers. GMT has been shown to contain silica and alumina [4, 5]. With so much GMT it is imperative to turn the waste into useful civil engineering materials through geopolymerisation.

The first step of the geopolymerisation process is thought to be the alkaline dissolution of Si and Al [6]. The leachability and mechanism of leaching of alumina and silica from the mine tailings is therefore an important parameter to be studied as to determine the aluminosilicate material can be used as a precursor for synthesis of geopolymers. A survey of literature does not show the kinetic mechanism and thermodynamics of Si and Al leaching from gold mine tailings. Most geopolymerisation processes look at the use of NaOH only as the alkali [7, 8] and this study seeks to establish the effectiveness of KOH as an alkaline activator.

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The reactivity of a material to synthesise geopolymers is dependent on its capacity to easily dissolve in alkaline media [9]. This paper seeks to establish the reactivity of acidic GMT in geopolymer systems. This paper seeks to establish the kinetics and thermodynamics of aluminosilicate leaching from acidic gold mine tailings. The paper seeks also to establish the effect of type of alkali (KOH/NaOH) on the leaching process. The understanding of these parameters may lead to increased utilisation of GMT as precursors for the synthesis of geopolymers. The effect of solid loading, leaching temperature, alkali concentration, GMT particle size and GMT calcination on the leaching of alumina and silica were also investigated.

2. Materials and Methods

2.1. Materials

The GMT was obtained from a GMT dam in the West Rand of Gauteng province of South Africa. KOH and NaOH were supplied by Rochelle chemicals. Table 1 shows the XRF analysis of the GMT respectively. The pH and SG of the GMT were found to be 3.84 and 2.99 respectively.

| Component | Result |
|-----------|--------|
| MgO       | 5.26   |
| Al₂O₃     | 6.98   |
| SiO₂      | 74.5   |
| SO₃       | 3.05   |
| K₂O       | 1.26   |
| Fe₂O₃     | 7.03   |

The major oxides were found to be SiO₂, MgO, Al₂O₃, K₂O and Fe₂O₃, which were about 95% of the material.

2.2. Equipment

A thermostatic shaker was used for alkaline leaching of silica and alumina from the acidic GMT. X-ray fluorescence (Rigaku ZSX primus II) was used for the determination of metal oxide content of the GMT. Mineralogical structure was determined using an X-ray diffraction technique (Ultima IV Rigaku XRD). Leached Si and Al in the leachate were measured using an Atomic Absorption Spectrometer (AAS) using a nitrous oxide-acetylene flame. FTIR (Fourier transform infrared spectroscopy) Thermoscientific Nicket IS10 was used to characterize the GMT before and after leaching.

2.3. Methods

Leaching experiments were conducted in a thermostatic shaker at a stirring speed of 250 rpm. Silicon and aluminium leaching was optimised parametrically by varying concentration of alkali (KOH/NaOH) from 2 to 10 M, solid liquid loading (S/L) from 2 to 10%, leaching time from 30 to 300 mins, leaching temperature from 50 to 95º C (95º C being the maximum safe temperature of the thermostatic shaker). Optimisation was done with varying one parameter at a time whilst the rest were kept constant. At the end of the appropriate leaching time the slurry was filtered and the filtrate was acidified with HCl before analysing for Si and Al using the AAS.

2.4. Statistics

The results reported are an average of three readings. The error bars in graphs are at 95 confidence interval of the mean.

3. Results and Discussion
3.1. Effect of solid loading and alkali type

Figure 1 shows the variation in yield of silicon and aluminium with solid loading and type of alkali

Leaching with KOH yielded more Si and Al as compared to NaOH based leaching. This was because the leaching with KOH is more alkaline as compared to NaOH and these results were in agreement with some similar experiments but on different materials [10]. More Si was leached than Al and this may be due to that there is more silica than alumina in the GMT (Table 1) although there have been suggestion that the intrinsic dissolution of Si is higher than Al [10]. There was a decrease in Si and Al yield with an increase in solid loading (S/L) and this may be due to reagent starvation at high S/L [11] leading to a decrease mass transfer efficiency. Though geopolymerisation reactions occur at high S/L (25-50%), the low S/L of 0.5% can still be used as an indication of the reactivity of a possible geopolymeric material.

3.2. Effect of alkali concentration

Figure 2 shows the variation of Si and Al yield with alkali concentration. There was an increase in Si and Al yield with increase in alkali concentration from 5 to 10 M. The reaction for the dissolution of Si and Al can be written as in equation 1

\[ \text{Al} - \text{O} + 7(\text{OH}) \rightarrow \text{Al(OH)}_4^- + \text{OSi(OH)}_3^- \quad (1) \]

From equation 1 the increase in alkali concentration favours higher OH\(^-\) ions which then favour the forward reaction leading to more Si and Al dissolution. However at 15 M alkali concentration there was drop in Si and Al yield (though insignificant as the concentrations at 10 and 15 M were within the error limits). This was due to that at 15 M the slurries became very viscous and leading to an impediment in the mass transfer process.
3.3. Effect of leaching temperature

Figure 3 shows the variation of Si and Al yield with temperature.

![Graph showing variation of Si and Al yield with temperature](image)

**Figure 3.** Variation of yield with temperature (Time 300 mins, agitation speed 250 rpm, S/L 0.5% m/v, alkali concentration 10 M).

There was an increase in Si and Al yield with an increase in temperature. The increase in temperature provided thermal energy to overcome activation energy for the dissolution process. One interesting phenomenon was that though the Si/Al ratio of GMT was 9.4, the leachates of both KOH and NaOH had a Si/Al ratio of about 2. This then shows that the dissolution of Si depends on the dissolution of Al.

3.4. Effect of milling

Figure 4 shows the variation in yield of Si and Al with milling time.

![Graph showing variation of Si and Al yield with milling time](image)

**Figure 4.** Variation in yield with milling time (Time 300 mins, agitation speed 250 rpm, S/L 0.5% m/v, alkali concentration 10 M, leaching temperature 95ºC)

Milling resulted in at least a 10% increase for Si yield for KOH based leaching using a GMT sample milled for 2 h. Milling resulted in a decrease in particle size.

3.5. Effect of GMT calcination

Figure 5 show the variation in Si and Al yield with calcination at 750 and 900ºC for 1 h respectively
Figure 5. Variation in yield with milling time (Time 300 mins, agitation speed 250 rpm, S/L 0.5% m/v, alkali concentration 10 M, leaching temperature 95ºC)

For the KOH based leaching there was 18 and 22% increase in Si and Al yield respectively with the use of GMT calcined at 900ºC as compared to as received GMT. The reason for this is shown in Figure 6.

Figure 6. XRD diffractograms of raw GMT and GMT after milling and calcination

Calcination resulted in the decrease in the intensity of the silica peak around 28º accompanied with the significant reduction in the pyrite peak at around 50º. This therefore meant the crystallinity of the GMT was reduced leading to increase in the amorphous content which meant more Si and Al could be leached

3.6. Kinetics of Si and Al leaching (KOH based)

Figure 7. Chemical surface reaction plots for Si (Time 300 mins, agitation speed 250 rpm, S/L 0.5% m/v, KOH concentration 10 M)
The kinetics of Si and Al leaching were tested using KOH since it gave the highest yield. Figures 7 and 8 show the leaching kinetic plots based on surface chemical reaction of the shrinking core model.

**Figure 8.** Chemical surface reaction plots for Al (Time 300 mins, agitation speed 250 rpm, S/L 0.5% m/v, KOH concentration 10 M)

The leaching of Si and Al was controlled by the surface chemical reactions between the alkali and Si and Al [12]. The equation for the plot is represented as

\[ 1 - (1 - X)^{1/3} = k \cdot t \]

(2)

Where \( X \) is the fraction leached, \( k \) is the reactant constant, \( t \) is time. Equation 2 was chosen to represent the leaching of Si and Al using KOH because the equation representing phenomenon when solvent diffusion through liquid film is the slowest step had correlation coefficients below 0.5 and were not plotted.

**4. Conclusion**

Si and Al can successfully be leached from GMT using KOH and hence GMT can be used as a precursor for the synthesis of geopolymers. KOH leaching is more effective than NaOH leaching. The optimum leaching conditions are a time of 300 mins, agitation speed of 250 rpm, S/L of 0.5% m/v, KOH concentration 10 M and 95°C. The leaching of Si and Al obeys the shrinking core model where the surface reaction is the controlling step. Calcination increases the amorphous content resulting in the increase of Si and Al yield. Milling of GMT reduces particle size and increases surface area resulting in the increase in Si and Al yield. This research therefore provides insight into the possible solidification of gold mine tailings using alkaline activation.

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