Kimberlite weathering: Effects of organic reagents

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Abstract

Kimberlite material is one of the primary sources of diamonds. Accelerated weathering that leads to a physical breakdown of the material over a short period of time has possible benefits in diamond processing such as reduction in the energy consumption when used as a pre-comminution stage. This study investigated accelerated weathering by utilising organic reagents; acetic acid, ethanol, formamide, n-hexane, oxalic acid, and urea, in comparison to the use of Cu^{2+} solution that was previously shown to be very effective in weathering kimberlite. Oxalic acid was the organic agent that showed promising weathering capabilities. However, the use of organic solutions was not as efficient as with Cu^{2+} solutions. Results showed that 67 per cent of the particles passed 12 mm screen size in Cu^{2+} weathering compared to 48 per cent in oxalic acid. It was also found that time of exposure had a small effect on weathering. Increasing the organic chemical concentration twofold, from 0.025 M to 0.5 M, improved weathering by ~ 20 percentage points. Different weathering mechanisms were observed at different solution concentration between oxalic acid (1st to 2nd order) and Cu^{2+} (2nd to 3rd order).

Keywords: Kimberlite, organic weathering, oxalic acid

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1. Introduction

Kimberlite is one of the primary sources of diamonds. Kimberlite processing described by Hodgson (1981) involves crushing the run-of-mine ore in two or three stages followed by a scrubbing stage to wash off fine particles (< 1 mm) which are removed through screening. The washed ore is screened into various size fractions which are sent for further treatment in the DMS circuit. The primary concentration utilises DMS whilst final concentration usually employs grease tables followed by X-Ray sorting. The waste from fines processing is thickened and dumped as tailings and the water is recovered. The coarse stream is sent for re-crushing to ensure that smaller diamonds are liberated before discarding the gangue material.

Kimberlites vary in mineralogical properties but are described as inequigranular textures consisting of crystal and mantle derived xenoliths and xenocrysts (Benvie, 2007). The macrocrysts are imbedded in a fine-grained matrix (groundmass) of second generation primary olivine and/or phlogopite as well as serpentine, perovskite, calcite, chlorite and dolomite (carbonates) and spinels. Weathering process such as carbonation and serpentisation often alter the early formed groundmass minerals. This replaces the primary minerals olivine, phlogopite, monticellite and apatite by clay minerals serpentine, calcite and chlorite.

This study investigates kimberlite weathering with a focus on the accelerated physical breakdown of the material. Accelerated weathering weakens the rock, especially the groundmass or matrix minerals. This leads to a reduction in the comminution effort required to liberate diamonds, which may lead to reduced diamond damage. The energy savings may be by far the greater benefit. This may also lead to completely different processing flowsheet, moving away from multi-stage crushing to a less energy intensive process.

Studies on kimberlite accelerated weathering have been performed utilising cationic salts, i.e. inorganic solutions (Boshoff et al., 2007; Morkel, 2006, 2007). Results showed that swelling clay minerals, especially the smectite species, were responsible for accelerating the breaking down of kimberlite material. The break down occurred as a result of clay structure expansions and the process of exchanging cations. The Cu^{2+} solutions were reported to be the most effective reagents.

This study targets the presence of clays in kimberlite and is the first evaluation of the effect of organic species on kimberlite weathering. Chin (1991), Grim (1968) and Weiss (1989) have shown that organic molecules can be adsorbed onto clay surfaces, which influences the clay interlayer spacing. Clay minerals with the ability to swell, such as smectites and vermiculite, have shown the highest degree of organic species adsorption (Gates, 2004; Tahani et al., 1999).

2. Experimental work

2.1 Material

Kimberlite ore samples were obtained from Finsch Mine, one of the De Beers Consolidated Mines in South Africa. The ore sample was received crushed to -19 +13.2 mm size fraction. Samples were prepared as per test requirement, with mineralogical characterisation determined through cation exchange capacity (CEC), XRD and XRF analysis.

2.2 Weathering

Samples of 300 g Finsch ore, -16 +13.2 mm size fraction, were immersed in 1 L of solution in flat bottomed plastic containers (250 × 140 × 70 mm). Particles were spread in a single layer with no physical contact to each at room temperature (~ 25 ºC) and immersed in 0.5 M solution concentration for a period of 6 days. Reagents tested were; ethanol, n-hexane, formamide, oxalic

acid, urea and acetic acid as well as distilled water and 0.5 M Cu^{2+} in chloride form for comparison purposes. After the test, the weathered samples were air dried for 1 day. The particle size distribution was then determined. The effect of exposure time; 2, 6, 15, and 30 days was investigated at 0.5 M oxalic acid concentration. The effect of concentration on weathering was determined with 0.025, 0.1, and 0.5 M oxalic acid for 6 days.

2.3 Kinetic evaluation

Utilising oxalic acid and Cu^{2+} as the weathering medium on a 300 g -16 +13.2 mm material, 50 ml of the weathering solutions was extracted at intervals 0, 4, 24, 72, 360 and 720 hours for ICP analysis. The tested solution concentrations were 0.025, 0.1 and 0.5 M. ICP analysis measured the quantity of Na^+ released into the solution with time. ICP analysis was performed at Set Point Laboratories in Johannesburg, South Africa.

3. Results and discussion

3.1 Ore characterisation

The XRD analysis results indicated that the ore contained ~ 35, 5, 7, 8, 11, 7, and 8 per cent smectite, serpentine, mica, calcite, dolomite, plagioclase, and pyroxene, respectively, and had a CEC value of 28.21 cmol/kg. According to Morkel (2006), a correlation can be drawn between CEC and the smectite content, which can predict the weathering behaviour. Kimberlite that contains around 30 per cent swelling clay minerals will show rapid weathering in cation solutions compared to very low weathering in distilled water (Morkel, 2006). The Finsch ore was therefore a suitable ore sample for accelerated weathering test. XRF results displayed fairly high amounts of Mg and Ca of 19.6 and 13.2 per cent, respectively.

3.2 Weathering

Weathering tests were evaluated by a particle size distribution after weathering and compared to the initial particle size of 100 per cent passing -16 +13.2 mm (-16000 +13200 µm). Less or no information could be gathered on the d_{80} or d_{50} values. Therefore, a reference of the amount of particles passing 12 mm (12000 µm) was adopted from Morkel (2006), so as to compare the results.

All the organic media tested improved weathering compared to the water that produced the least weathered product of ~ 25 per cent passing 12 mm (Figure 1a and 1b). Oxalic acid produced a promising weathering of 48 per cent passing 12 mm that was slightly more than the rest of the organics. The effect of oxalic acid on mineral weathering has been confirmed by Varadachari et al. (1994). The combined action of H^+ attack as well as oxalate complex formation on dissociation is one of the reasons highlighted by Barman et al. (1992), Bigham et al. (2001), Chin and Mills (1991).
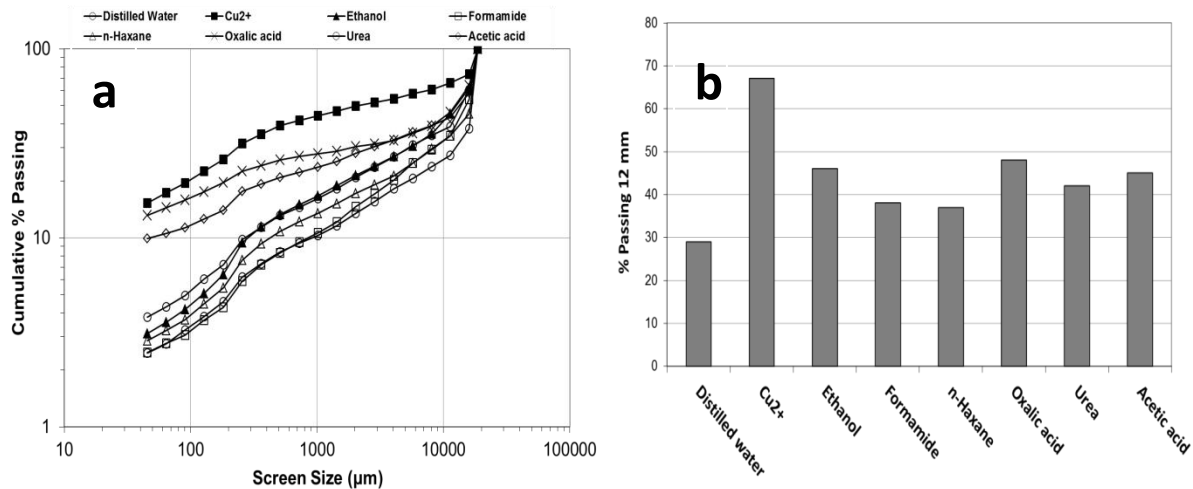

Figure 1: The particle size distribution (a) and the % passing 12 mm (b) after weathering for 6 days in Cu2+, ethanol, formamide, n-hexane, oxalic acid, urea and acetic acid at 0.5 M.

From Figure 1, despite the fact that oxalic acid was a better organic agent, the Cu^{2+} medium showed superior weathering results of 67 per cent passing 12 mm (~ 20 per cent higher than oxalic acid). According to Morkel (2006), Cu^{2+} has the ability to adsorb not only at interlayers of the particle crystal structure but also on other sites such as crystal edges. This process reduces the surface energy that reduces the energy required to produce fresh crack surfaces during weathering. Organics adsorb into the interlayer space causing an expansion and are held by coulombic as well as van der Waals forces (Lerf, 2004). Therefore, organic species are limited to the interlayer space whereas inorganics can also adsorb onto other alternative sites.

The effect of time on weathering was tested utilising oxalic acid as this particular organic solution had shown positive results. Figure 2a and 2b shows no significant improvement in weathering with increased exposure time. Only a 10 percentage point increase was realised by a 2 to 30 days increment.
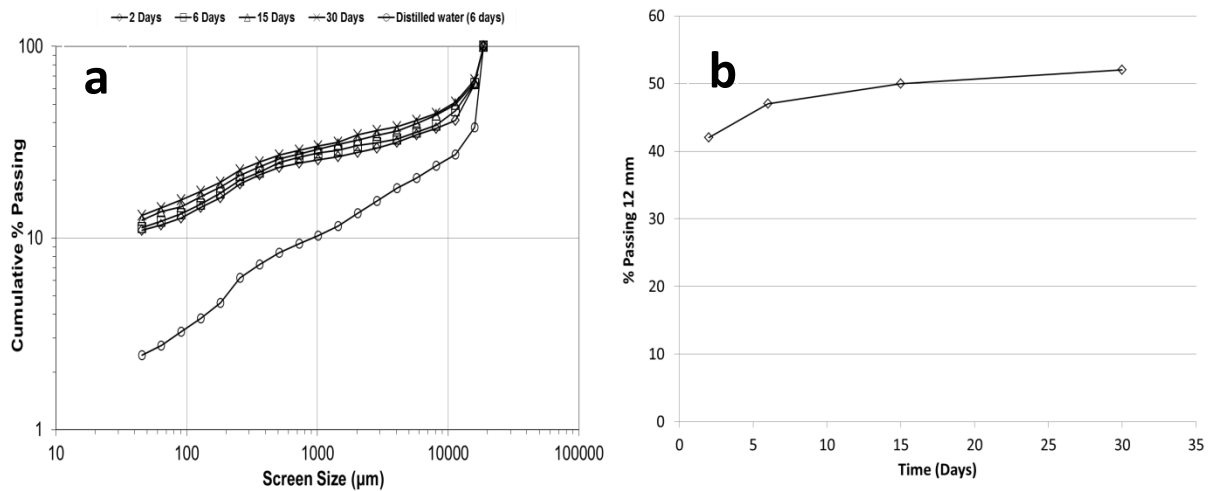

Figure 2: Results of the effect of exposure time in 0.5 M oxalic acid (a) and the % passing 12 mm (b).

Varying solution concentration indicated that no significant difference between a 0.025 M and a 0.1 M oxalic acid concentration (Figure 3a and 3b). However, an increase of ~ 20 percentage points was realised with the change in concentration from 0.025 M to 0.5 M oxalic acid.
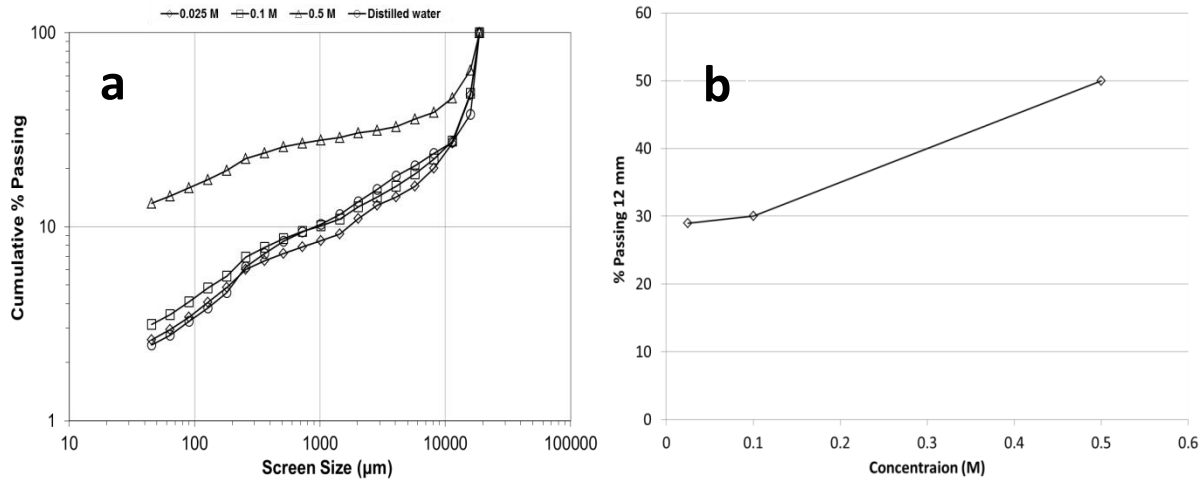

Figure 3: The product of the effect of oxalic acid concentration on weathering (a) and the % passing 12 mm (b).

3.3 Kinetic evaluation

Similar to the work by Morkel (2006), evaluating the weathering kinetics of oxalic acid and Cu^{2+} media, the nth-order kinetic model (Equation 1) was utilised. The rate of initial Na^+ dissolution in the first 72 hours is shown in Figures 4a and 4b .

$$\frac{dC}{dt} = -k(C - C_\infty)^n$$

[1]

where C is the concentration in solution at time t, k the rate constant, C_∞ is the equilibrium concentration (assumed in this study as the concentration after 720 hours) and n is the apparent reaction order..
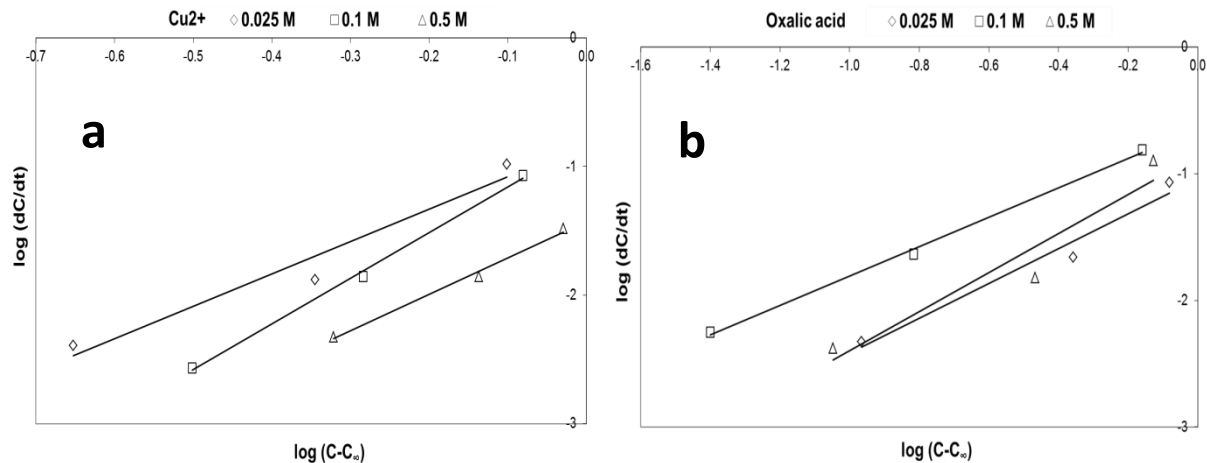
Figure 4: Na+ dissolution rate in 0.025 M, 0.1 M, and 0.5 M of Cu2+ (a) and oxalic acid (b) media.

Regression results are shown in Table I. The R^2 for both Cu^{2+} and oxalic acid concentrations showed a good fit to the equations. For Cu^{2+}, the order of reaction for 0.025 M concentration was closer to 2 indicating the possibility of a second order reaction type whilst for 0.1 M and 0.5 M indicated a different mechanism. For oxalic acid, the reaction order at lower concentrations 0.025 and 0.1 M were closer to 1 and this indicated the possibility of a first order mechanism. At a higher oxalic concentration, the order was closer to two.

Table 1: Results of fitting kinetic equation 1 on Na+ dissolution in Cu2+ and oxalic acid tests.

Concentration	Equation	R^2	n	k
Cu^{2+}				
0.025	y = 2.520x − 0.829	0.951	2.52	6.745
0.1	y = 3.555x − 0.804	0.998	3.56	6.368
0.5	y = 2.844x − 1.426	0.993	2.84	26.668
Oxalic acid				
0.025	y = 1.374x − 1.042	0.968	1.37	11.015
0.1	y = 1.162x − 0.646	0.997	1.16	4.425
0.5	y = 1.540x − 0.855	0.917	1.54	7.161

Oxalic acid is known to dissolve minerals by proton attack. This attack causes a release of cations from the ore's crystal structure which then forms cation-organic complexes with the oxalic anion known as oxalates (Chen et al., 2000). The rate of organic acid dissolution is controlled by surface reactions that involve dissolution of cations which is accompanied by the precipitation of secondary minerals that form a passive layer that slows down further dissolution (Barman et al., 1992; Drever and Stillings, 1997; Fiantis et al., 2010).

4. Conclusion

The effectiveness of kimberlite weathering utilising organic species was investigated on a 30 % smectite containing Finsch kimberlite. The weathering was assessed by a particle size distribution analysis and results compared to the starting size of 100 per cent passing -16 +13.2 mm. Amongst the organic media tested, oxalic acid was the better organic agent resulting in a product of 48 per cent passing 12 mm. Oxalic acid effect was attributed to proton attack on the structural cations but also limited by oxalate salts precipitated on the surface. However, oxalic acid was 20 percentage points less effective than Cu^{2+} containing solution. This was due to the differences in weathering mechanisms between the two types of media. Inorganic cations not only adsorbing onto interlayer spaces, as is the case with organic solutions, but also on other alternative sites such as crystal edges.

5. Acknowledgements

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