Depression and Dewatering Characteristics of Kaolinite in View of the Reprocessing of Ultrafine Colliery Waste

Malibongwe S. Manono

Centre for Minerals Research, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa, malibongwe.manono@uct.ac.za, ORCID 0000-0002-2928-9368

Abstract

Coal holds an important position within South Africa's commodities due to its current role as the primary energy source. Nevertheless, the beneficiation and processing of South African coals result in substantial wastes in the form of discards and ultrafine coal slurries. Previous research has shown the potential of coal ultrafines to serve as an energy resource if suitably beneficiated, given their comparable quality to run-of-mine coal. The issue of long-term environmental impact from these ultrafine coals also comes to the forefront, particularly concerning the substantial sulfidic content in coal ultrafines, which can contribute to the generation of acid rock drainage (ARD). In addressing these complexities, froth flotation is seen as a promising technique for the beneficiation of ultrafine coal waste. However, this technique is not without its challenges. Coal ultrafines often encompass a significant proportion of clay minerals, with kaolinite being a prominent phyllosilicate clay mineral. The prevalence of kaolinite as a gangue mineral in South African coal ultrafines adds an intricate layer to the beneficiation process, as effectively depressing kaolinite during flotation can prove intricate. Efficient depression of kaolinite is thus necessary to separate it from ultrafine coal particles during flotation. Furthermore, considerations of pulp chemistries, such as process water quality in ultrafine coal flotation would be of paramount importance, especially given that there is water scarcity in regions within which coal mining occurs in South Africa. Because of this, the implementation of closed water circuits in flotation and effective dewatering of tailings for water recovery and dry stacking of tailings have gained much prominence owing to the need to minimise water consumption and enhance waste management practice in line with SDG 6, 9, 12, 13, 14 and 15. Therefore, it stands to reason that effective depression of kaolinite during ultrafine coal flotation is crucial in achieving high-quality coal products with reduced impurities with an understanding of the influence of different flotation chemistries. This research considers kaolinite depression and dewatering characteristics in inorganic electrolyte concentrated process water in view of process water recirculation in coal flotation and the need for the dewatering of tailings. Laboratory scale tests such as zeta potential measurements and depressant adsorption studies were considered. Understanding the behaviour of kaolinite in these contexts is vital for sustainable coal processing and environmental stewardship.

Keywords: Coal flotation, coal processing discards, kaolinite flotation, tailings dewatering, water recirculation

Introduction

South African coals contain high amounts of kaolinite, present as gangue mineral, its composition can be as high as 90 wt.%(Mpofu *et al*. 2004). Kaolinite is a clay mineral made up of ultrasmall particles which are too fine to separate using conventional hydrocyclones or screens, due to kaolinite particles passing through all the beneficiation processes during coal beneficiation. It is thus important to selectively depress this kaolinite in fine coal processing through separation processes such as froth flotation where fine clay minerals are rejected to the tails. The nature of the froth flotation process ensures a separation fine particles by manipulating the chemistry of the system through the addition of reagents such as collectors, depressants, flocculants and frothers (Bulatovic, 2007). The manipulation of the pulp chemistries ensures that particles are either hydrophobic or hydrophilic such that the hydrophilic particles attach to air bubbles rising through the pulp and float while the hydrophilic particles remain in the pulp and are rejected out of the system through the tailings stream (Wills and Napier-Munn 2006).

Since flotation is water intensive, previous studies have investigated how process water recirculation and the consequential increase in ionic strength of the plant water affect the overall coal flotation performance and found that the accumulation of inorganic electrolytes affects the mineral surface, reagent action, and pulp chemistry (Arnold and Aplan 1986; Celik and Somasundaran 1986; Yoon and Sabey 1989; Ozdemir 2013; Çelik and Ozdemir 2018; GUNGOREN *et al*. 2020). To induce the depression of clay minerals like kaolinite in coal flotation, depressants such as polysaccharides are added to induce the hydrophilicity of kaolinite. Several studies have revealed factors that may improve the adsorption of polysaccharide type depressants onto clay minerals include an alkaline pH, higher ionic strength of process water and the presence of polyvalent cations in solution (Arnold and Aplan 1986; Yoon and Sabey 1989; Kawatra and Eisele 1992). Ultrafine colliery waste has potential to be a useful energy source due to comparable coal to that of run-of-mine (ROM) coal. Due to the predominant kaolinite minerals and ultrafine size of the coal waste, current conventional South African methods in the coal industry are not able to separate these ultrafine particles, coal waste also contains sulfidic compounds such as pyrite which pose an environmental hazard due to the acid rock drainage (ARD) formation. It is thus suggested to use froth flotation which is being used globally for coal waste. Considering the intensive water use of the flotation process and scarce water availability, water recirculation has become a trend to mitigate fresh water use. This however leads to ion and reagent accumulation in the water, thus changing the water quality which plays an important role in the pulp chemistry and thus flotation performance. This study aims to consider the impact of selected ions at different pH values to the **surface chemistry of kaolinite** in view of the **depression of kaolinite during fine particle coal processing** and **dewatering characteristics of kaolinite laden tailings** emanating out of repurposed coal fine particles.

Methods

Mineral Sample Preparation

A kaolinite powder-like sample of analytical grade was provided from a supplier in Cape Town. The sample was then screened according to the appropriate sizes required for zeta potential measurements, sodium carboxy methyl cellulose (CMC) adsorption tests and particle flocculation tests. Particle sizes between -75 to 38 µm were used for CMC adsorption tests and flocculation tests while -38 µm were used for the zeta potential studies as these have been chosen to be suitable for these tests (October *et al*. 2019).

Reagents

De-ionised water was used to prepare single salt solutions of sodium chloride (NaCl), magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$), sodium hydroxide (NaOH) and hydrochloric acid (HCl) for pH control, and sodium carboxymethyl cellulose as depressant.

Single Salt Solution Preparation

In order to study the effect of selected ions or water quality on the depression and dewatering characteristics of kaolinite, single salt solutions of NaCl, $MgCl_2$ and $CaCl_2$ in concentrations of 0.01 mol/L were used. These single salt solutions were prepared using de-ionised water as the baseline. These salts were supplied by Merck and were of analytical grade.

pH Modifiers

Buffer solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for pH adjustment.

Depressant Preparation

CMC, SENDEP-30E, supplied by Senmin, was used as a depressant. A stock solution of 1% (w/v) was prepared by adding 1 g of CMC in 100 mL of deionised water in a beaker and stirred for 3 h on a magnetic stirrer until completely dissolved. The stock solution was refrigerated at the end of every test day and a new batch was prepared every 5 days to ensure it does not expire (Dzingai *et al.* 2020).

Acid and Phenol Solution Preparation for CMC Adsorption

The DuBois calorimetric method used for the determination of the adsorption of CMC requires the use of sulfuric acid and phenol. To prepare the solutions used in the DuBois calorimetric method, concentrated sulfuric acid (H_2SO_4) was poured into a test beaker under a fume hood. The volume was measured according to the number of tests performed daily since the acid could not be reused the following day. For the phenol preparation, 5 g of phenol salt were weighed and added to a 100 mL glass beaker with de-ionized water under a fume hood (du Bois *et al.*, 1956). The contents were transferred to a volumetric flask and closed with a cap to ensure that the fumes are not released. The solution was then magnetically stirred until full dissolution of phenol salt was achieved. The phenol solution was placed in the fume hood and used daily as needed.

CMC Adsorption on Kaolinite

Adsorption of CMC onto kaolinite was measured by determining the concentration of the CMC that remained in suspension. A tool used to measure this is the UV spectrophotometer which is based on the theory of ultraviolet rays being absorbed by a substance and this results in an apparent spectrum. This theory is based on Beer's law explained by Mayerhöfer and Popp (2019), relating absorbance and concentration as shown in Eq (1), A is the absorbance and c, is the concentration(c). Another essential element is the wavelength determined at the highest absorbance which is used in absorption studies to be able to determine the concentration (L).

$$A = \varepsilon L c \qquad (1)$$

For the adsorption tests performed, four calibration curves were first generated for all water types, i.e., deionised water, NaCl, $MgCl_2$ and $CaCl_2$. The samples were poured into beakers at a volume of 30 mL, CMC was then added from 1 mL to 5 mL in increments of 1 mL in five separate beakers for each water type. The contents were then mixed. Using a syringe, 1 mL per sample was measured out into test tubes and then transferred to the fume hood.

Following the DuBois calorimetry method, 2 mL of a phenol solution and 10 mL of sulfuric acid were added to the test tubes with CMC samples. The reaction is almost immediate and is exothermic giving off a warm touch to the test tubes. The samples were left in the fume hood for 40 min to allow the reaction to come to completion. When the reaction time was over, small amounts of the samples were poured into quartz cuvettes for absorbance measurements in a UV-Vis spectrophotometer. Maximum absorbances were recorded and observed in the 483–489 nm frequency range. This was slightly different to the 490 nm frequency for CMC reported by du Bois *et al.* (1956) but close and this might be due to residual components in the industrial make-up of CMC, SENDEP-30E.

The measured absorbances were recorded alongside the corresponding CMC concentrations. Calibration curves were then used in the adsorption studies to obtain residual CMC in solution following kaolinite adsorption to CMC. A total of 16 samples were prepared for the four water types: de-ionised (DI), NaCl, $CaCl_2$ and $MgCl_2$ and at four different pH values, namely, pH 4, 6, 8, and 10. To start, the waters were poured into 16 flasks as marked appropriately according to water type and pH to be tested, 3 mL of CMC and 3 g of kaolinite of 38–75 µm particle size were added to 30 mL of water then mixed, the mixture was then adjusted to required pH values. The top of the flasks was covered with tin foil and placed in an Ecobath shaker at a controlled temperature of 20°C and speed of 141 rpm for 15 min. After 15 min in the water bath, a plastic syringe was used to draw out enough slurry such that 1 mL filtered solution can be collected to be analysed for residual CMC. A 0.45 µm filter was attached at the end of the syringe and the filtrate was collected in a sample container. The sample was then poured into a test tube at an amount of 1 mL and the DuBois colorimetric procedure was followed as already described by adding 2 mL of phenol and 10 mL of sulfuric acid and allowing the reaction to come to completion, after which the samples were poured into cuvettes for absorbance measurements. The concentration of CMC in solution for unknown samples was then calculated using measured absorbances and generated calibration curves. Adsorption tests were done in triplicate to minimise experimental error.

Zeta Potential Determination

To analyse the electrokinetic behaviour of the particle suspension, zeta potential measurements were conducted. An amount of 30 mL of four water types were poured into four beakers, DI, NaCl, $MgCl_2$ and $CaCl_2$, an amount of 3 g kaolinite was added to the solutions and mixed. The four samples were then taken for zeta potential tests. This process was repeated four times for the following pH values, 4, 6, 8, and 10. Using a pipette, a small amount of the suspension was poured into a folded capillary cell and closed tightly. The cell was wiped on the outside to ensure that no solution was leaking or flowing out of the cell, then inserted into a Malvern Zeta-sizer which was then closed. On the desktop, the Malvern Zeta-sizer application was opened and set up by selecting the mineral of interest (kaolinite), the parameter to be measured (zeta potential), dispersant (water), cell (folded capillary cell), measurement (automatic, 3 times), data processing (general/default), the ok and start prompts were then selected to start the analysis. The machine read a single sample three times as selected and reported the potential in mV together with a graph showing the total potential versus the total counts. The cell was removed from the machine and flushed using de-ionised

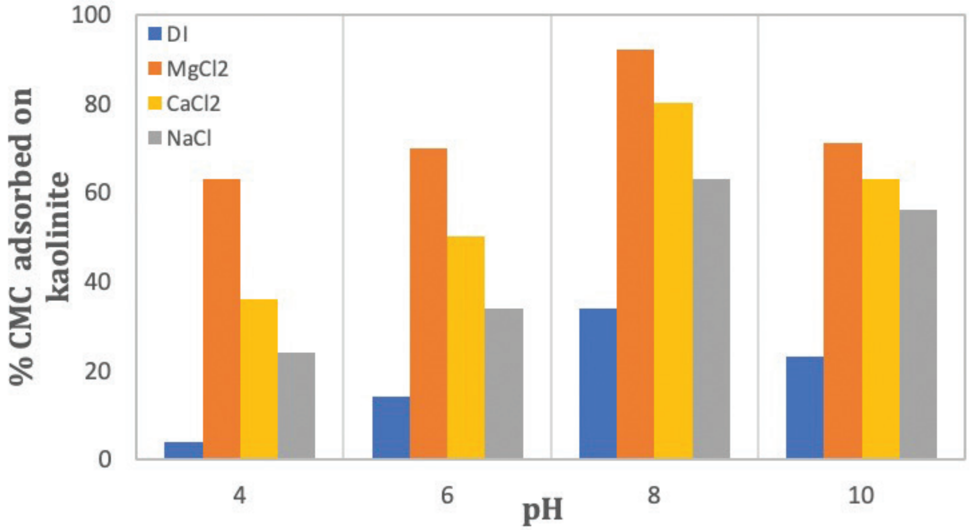

Figure 1 CMC Adsorption onto Kaolinite at varying pH.

water to ensure that the next sample was not contaminated. The zeta potential studies were repeated two times for each test condition to increase the accuracy of results.

Results and Discussion

Effect of Solution Chemistry and pH on CMC Adsorption

Fig. 1 shows a comparison of CMC adsorption to kaolinite at pH 4, 6, 8, and 10 for different water types.

$MgCl_2$ shows the best adsorption performance across all pH values. This trend is followed by $CaCl_2$. NaCl and de-ionised (DI) water both showed lower adsorption performance with NaCl showing better performance than DI. It can also be seen that for all water or solution types, the adsorption of CMC on kaolinite increased as pH increased from 4 to 8 and then took a deep at pH 10. The results shown in Fig. 1 also show that the divalent ions from $MgCl_2$ and $CaCl_2$ showed better adsorption performance of CMC to kaolinite compared to the monovalent NaCl and the DI, these observations agree with the literature that polyvalent ions are effective at improving depressant adsorption to minerals (Laskowski *et al.* 2007; Burdukova *et al.* 2008; Manono *et al.* 2019).

Effect of Solution Chemistry and pH on the Zeta Potential of Kaolinite

Fig. 2 shows a comparison of the zeta potential of kaolinite at pH 4, 6, 8, and 10 for different water types.

It can be seen from Fig. 2 that both $MgCl^2$ and $CaCl^2$ had less negative zeta potential values and closest to the isoelectric point (0 mV) when compared to NaCl and DI water. These results agree with the observed higher percentage adsorption for CMC to kaolinite; these trends are similar to earlier work on talc by (Manono *et al.* 2020). $CaCl_2$ resulted in a more negative zeta potential than $MgCl_2$ after pH 8, this can be attributed to the different speciation occurring as the pH changes. The DI water showed the most negative magnitude in zeta potential at pH 6 and 7 and less negative lower than NaCl above pH 7. The zeta potential trend suggests that kaolinite particles are more flocculated in $CaCl_2$ and $MgCl_2$ and thus kaolinite dewatering would be more effective in divalent cations and possibly even better in the presence of CMC as CMC has been shown to possess flocculant-polymer-like properties (Sharma *et al.* 2006; Salehizadeh *et al.* 2018; Guo *et al.* 2021).

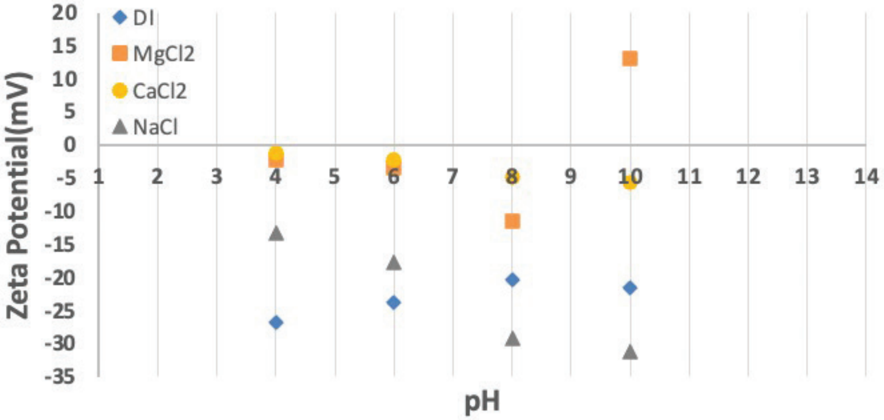

Figure 2 *Zeta potential of Kaolinite at varying pH.*

Conclusions

The effect of different ionised water and varying pH on **CMC adsorption to kaolinite** was studied. De-ionised water was doped with three salts $MgCl_2$, $CaCl_2$, and NaCl at 0,01 M separately, and depressant CMC was added and measured for adsorption to kaolinite, pH was also varied at 4, 6, 8, and 10 to observe it effect. **Zeta potential** was measured to assess the inherent repulsive forces of the kaolinite particles in the different waters at varying pH values: 4, 6, 8, and 10 in the absence of the depressant. **Adsorption studies** and **zeta potential measurements** were necessary in terms of predicting the effects that **varying pH and inorganic electrolytes** would have on the **hydrophilicity, depression and flocculation of kaolinite** particles.

Adsorption studies showed that water containing Mg^{2+} resulted in the best adsorption performance across all pH values followed by Ca^{2+}, Na^+, and DI performed poorly. **Zeta potential results** showed that both Ca^{2+} and Mg^{2+} water types had zeta potential values lower and closest to the isoelectric point (0 mV) when compared to Na^+ and DI water types in agreement with the observed higher percentage adsorption of CMC to kaolinite.

This study showed that CMC adsorption increased with **alkaline pH** although a threshold was seen. Both divalent ions Mg^{2+} and Ca^{2+} showed the best adsorption performance and less negative zeta potential compared to Na^+ and DI water. Thus, process water with Ca^{2+} and Mg^{2+} ions may be recommended for CMC adsorption to kaolinite at ~pH 8; this could result in the necessary depression of kaolinite particles in ultrafine colliery waste beneficiation through froth flotation and may also impart better flocculation or dewatering behaviour on kaolinite bearing tailings after flotation.

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