WASM: Minerals, Energy and Chemical Engineering

Grinding, Flotation and Drying Performance of the Clay-Containing Ores

Nadia Kashif

This thesis is presented for the Degree of
Doctor of Philosophy
of
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July 2024

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Declaration by Author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my research higher degree candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

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Published Works by the Author Incorporated into the Thesis

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Chapter 4:

Kashif, N., Albijanic, B., Xu, J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M.K., 2023. Grinding of highly viscous bentonite containing slurries. Applied Clay Science 232, 106794.

Chapter 5:

Kashif, N., Albijanic, B., Xu, J., McGrath, T., Nazir, M.K., Hitch, M., Tadesse, B., 2024.

Investigating the drying behaviour of clay-containing slurries. Applied Clay Science 260, 107500.

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Abstract

The depletion of higher-grade ores has necessitated the processing of lower grade clay-containing ores, presenting a challenge for the mineral industry. Clay minerals are known to impede various mineral processing operations, including size reduction, classification, separation, and dewatering owing to their distinct size, shape, and properties. However, the specific mechanisms and extents of clay interference remain poorly understood. This research delves into the effects of selected clays on grinding, flotation and drying.

The grinding efficiencies of clay containing ores remains an unexplored area of study. Previous research has demonstrated that clay minerals significantly impact slurry rheology, resulting in increased yield stress and slurry viscosity leading to reduced particle breakage and increased power consumption in grinding operations. This PhD thesis investigated the relations between properties of clay-containing slurries (i.e. rheology, zeta potential and settling behaviour) and grinding efficiency. The findings revealed a detrimental effect of bentonite on ore grinding. The addition of Ca^{2+} ions reduced the repulsive forces between bentonite particles leading to reduced shear forces between particles, reduced slurry viscosity, increased settling rates and improved grinding performance. This effect was particularly pronounced with higher solid percentages of bentonite-containing slurries. Similarly, the study highlighted the adverse influence of kaolin on grinding efficiencies, previously overlooked in clay-containing ores. The introduction of Ca^{2+} intensified this effect, increasing particle agglomeration, viscosity, and significantly reducing the grinding performance, particularly with high clay and solid percentages. The outcome of this thesis emphasized the significance of controlling the concentration of Ca^{2+} ion in plant water sources for optimal grinding of kaolin-containing ores. During flotation, the presence of clay significantly altered recovery and kinetics of a high-density ore (galena) as well as of a low-density ore (sphalerite). The effect of bentonite on slurry rheology was more profound as compared to the effect of same concentration of kaolin, leading to reduced recovery. Increased viscosity during flotation stages led to decreased slurry density, hindering the movement of air bubbles and particles and reducing collisions, ultimately compromising flotation performance. The introduction of Ca^{2+} ions mitigated these effects by reducing the swelling capacity of bentonite, thus improving flotation recovery. But opposite was observed for kaolin containing slurries where Ca^{2+} ions increased the viscosity attributed to the agglomeration of kaolin particles, thus reducing the floatation recovery.

During flotation, the presence of bentonite has a significant effect on slurry rheology, leading to reduced recovery. Although research has explored bentonite's role in flotation, its precise impact on the flotation efficiency of galena and sphalerite remains unquantified. Comparing the flotation behaviours of these minerals is essential due to their significantly different densities. This PhD thesis aims to investigate how bentonite affects the flotation performance of galena and sphalerite and to determine if the density difference between the two minerals influences their flotation results. Findings indicated that bentonite presence led to lower flotation recoveries for both minerals due to increased pulp viscosities. However, the negative effect of bentonite on flotation was mitigated by adding Ca^{2+} ions, which reduced pulp viscosities. Notably, Ca^{2+} ions had a more substantial impact on improving galena's flotation performance compared to sphalerite. These results underscore the intricate relationship between bentonite concentration, mineral densities, and the role of Ca^{2+} ions during flotation processes.

Drying of clay-containing slurries has long been a challenge not only for mineral processing industry but also industries like construction, coatings, and ceramics. Moreover, effective drying of clay-containing slurries plays a crucial role in minimizing costs associated with shipping, handling, storage and downstream processing. A limited information about the drying mechanism of clay containing slurries makes the drying process even more challenging. One of the objectives of this PhD thesis was to study the drying performance and underlying mechanism of bentonite and kaolin-containing slurries. By studying rheological properties, zeta potential and settling behaviours of bentonite and kaolin containing slurries during various drying experiments, it was observed that bentonite was more detrimental as compared to kaolin clay due to its higher capacity of water absorption and water retention. The addition of Ca^{2+} ions reduced the viscosity of bentonite-containing slurries, hence improving the drying performances. On the other hand, the addition of Ca^{2+} did not show a significant improvement in drying performance of kaolin-containing slurries. Three drying regions were observed for both bentonite and kaolin-containing slurries; the first region showed rapid drying due to high moisture, the second region was a moderate phase of reduced drying rates, and the third region was slowed drying rate typically showing the challenge of tightly bound moisture removal. The correlations for drying kinetics of all three regions were also proposed.

In conclusion, the presence of clay minerals can impede the efficiency of mineral processes including grinding, drying and flotation, with a variable extent depending on the clay type and concentration. Bentonite exhibited more pronounced detrimental effects compared to kaolin. The addition of Ca^{2+} ions to bentonite containing slurries alleviated adverse effects, particularly in grinding and flotation. On contrary, the addition of Ca^{2+} ions were found to be detrimental for griding and flotation performance demonstrating the significance to optimize the concentration of Ca^{2+} ions in plant water for kaolin-containing ores.

Key Words

Kaolin, bentonite, clay concentration, quartz, XRD, PSD, synthetic ore, rheology, zeta potential, settling, swelling, viscosity, Ca^{2+}, $CaCl_2$, ppm, minitab, ANOVA, Tukey, grinding, solid percentage, P_{80}, drying, temperature, drying rate, Bingham model, XRF, TGA/ DTA, FTIR, SEM, plastic viscosity, flotation, density of minerals, galena, sphalerite, consistency index, flow index,

Statement of Originality

This thesis has not been submitted for a degree in any University and does not contain material published by another person. The original contributions of this thesis are outlined briefly below:

- A novel approach to study the detrimental effect of calcium on grinding performance of a kaolin-containing ore.
- Comprehensive study to investigate the grinding of highly viscous bentonite containing slurries.
- An investigation into the drying performance of kaolin and bentonite slurries to understand the underlying drying mechanisms.
- A study to investigate the flotation performance of galena and sphalerite in the presence of bentonite to determine if the significant density difference between these two minerals affects their flotation performance.

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Chapter I

Introduction

1. Background

With increasing global demands for a wide range of minerals, the grade and quality of mineral deposits being mined is decreasing rapidly. This unfortunate phenomenon is due to the fact that high-grade deposits have already been exploited and extracted. With the deficiency of high-grade sources, processing of more and more low-grade ores which contain high-clays would be inevitable for next future (Connelly, 2011). In most situations, mining industry is now facing the ores with declining quality, difficult mineralogy and increasingly expensive to process. Australia is not an exception, where mining and mineral processing industry stands as a fundamental pillar in the nation's economy, representing two-thirds (66 %) of all export revenue for the nation (Constable, 2023) and it is a significant source of employment, export income and royalty payments. This sector plays a pivotal role in shaping Australia's economic landscape. According to a study by Jaques et al. in 2002, Australia takes the lead globally in the production of minerals such as bauxite, ilmenite, iron, rutile, and zircon. Furthermore, it ranks as the second-largest producer of gold, lead, lithium, manganese, and zinc. This dominance underscores the significance of the mining and mineral processing industry in sustaining Australia's economic vitality. Therefore, successful and profitable processing of clay-containing ores has become the focus of various studies (Wang, 2016; Basnayaka, 2018; Chen and Peng, 2018).

Grinding of ROM (run of mine) minerals is one of the significant primary beneficiation techniques that is used to separate the valuable minerals from the gangue minerals for other downstream separation techniques like screening, flotation, filtration, thickening etc. Different studies have investigated the relationship between the grinding performance and the viscosity and rheological properties of fine-containing slurries in the absence of clays using laboratory mills (Clarke and Kitchener, 1968; Tucker, 1982; Klimpel, 1982, 1983, 1984; Fuerstenau et al., 1990; Gao and Forssberg, 1993) and industrial mills (Shi and Napier-Munn, 2002). Chipakwe et al. (2020) suggested that use of organic or inorganic chemical grinding aids can be beneficial to reduce the slurry viscosity by altering the surface properties of the valuable mineral or the flow properties of the slurry or the arrangement of particles in the slurry (i.e. agglomeration, dispersion, flocculation). Considering that there is no study investigating grinding performance in the presence of two most common clays (i.e. bentonite and kaolin), this research aims to quantify the influence of kaolin and bentonite on grinding efficiency, particularly in the presence and absence of Ca^{2+} ions, due to their known positive effects on flotation (Basnayaka et al., 2017) and filtration (Basnayaka et al., 2018) efficiencies in the bentonite-containing ores.

Flotation performance is also affected adversely by the presence of clay minerals causing a reduction in both recovery and concentrate grade (Bakker et al., 2009; Tao et al., 2010; Patra et al., 2010; Xing et al., 2019). Challenges arising during flotation include increased slurry viscosity, impaired froth generation, and inadequate loading of valuable minerals on the top of froth (Burdukova et al., 2008; Ndlovu et al., 2011). A lack of reliable approaches to lessen the unwanted effects of clay minerals on flotation efficiency has driven the research to investigate the influence of clay minerals on flotation and to alleviate the negative effects caused by these minerals (Wang et al, 2015). Different clay minerals can cause different problems due to their distinct and complex structures (Wang et al., 2015; Taner and Onen, 2016). Numerous studies have explored issues and mechanisms observed during the flotation of clay-containing ores by considering changes in froth stability (Taner and Onen, 2016, Xing et al., 2019), water absorption and swelling behaviour of clays (Taner and Onen, 2016, Basnayaka, 2018), and increased pulp viscosity (Merve Genc et al., 2012; Patra et al., 2012; Zhang and Peng, 2015). Various techniques considered to mitigate the negative effects of clay minerals on flotation have limitations. These include removing clay minerals before flotation, washing mechanically entrained clay minerals, operating at low air speed, reducing pulp densities, and using weak frothers, viscosity modifiers, or clay binders (Taner and Onen, 2016). The effective strategies to counteract the impact of clay minerals on flotation remains challenging in mineral processing.

Drying is employed to remove water from ores. While various studies have explored the drying of clay-containing minerals in coatings (Nechita, 2021), ceramics (Khalfi and Blanchart, 1999; Oummadi, 2019; Zaccaron et al., 2022;) or desiccation crack formation in different engineering fields (Mohammad et al., 2020) like geotechnical (Li et al. 2009), agricultural (Bronswijk, 1991), environmental geotechnics (Daniel and Brown 1987; Peron et al., 2009a, 2009b, 2009c), a limited work has been done to study the drying behaviour of clay-containing ores in mineral processing. Despite the known influence of Ca^{2+} ions on rheological properties during flotation (Basnayaka et al., 2017), fine particle filtration (Basnayaka et al., 2018), their influence on the drying performance of bentonite and kaolin-containing ores in mineral processing has not yet been investigated.

Given the diverse impact of clay minerals on mineral processing, this study specifically focuses on two distinctive clay types commonly found in Australian mineral deposits: kaolin and bentonite. Therefore, this thesis aims to shed light on the influence of these clays on different processes such as grinding, drying and flotation.

2. Objectives

The primary aim of this thesis is to investigate the negative effects commonly associated with presence of clays during grinding, drying and flotation methods as well as explore potential solutions for mitigating the adverse effects imposed by clay minerals. The sub-objectives of the thesis include:

- To examine the influence of the selected clays on grinding efficiency and mitigation of negative effects by optimising the Ca^{2+} ions concentrations.
- To determine the effect of the selected clays on drying efficiency and to study the effect of Ca^{2+} ions on drying efficiency of clay containing slurries.
- To evaluate the influence of bentonite on the flotation efficiency of galena and sphalerite in the absence and presence of Ca^{2+} ions.

3. Thesis overview

The thesis is divided into seven chapters. **Chapter 1** consists of introduction, objectives, and structure of this thesis. **Chapter 2** shows a critical review of existing literature on the influence of clay minerals on mineral processing as well as discussing the genesis, structure, and classification of relevant clay minerals, highlighting their distinct characteristics and challenges in the mineral processing industry. **Chapter 3** is the published paper about the negative effects of kaolin on the grinding performance and the detrimental effect of calcium on grinding performance of a kaolin-containing ore demonstrating the importance of optimizing Ca^{2+} ions concentrations in plant water for kaolin-containing ores. **Chapter 4** is the published paper about the influence of bentonite on the grinding efficiencies of ores and about the mitigation of these negative effects by adding Ca^{2+} ions. **Chapter 5** is the submitted manuscript to investigate the influence of selected clays on the drying performance of clay-containing slurries in the absence and in the presence of Ca^{2+} ions. **Chapter 6** is the submitted manuscript to examine the flotation performance of galena and sphalerite in the presence of bentonite and the effect of addition of Ca^{2+} ions to alleviate the detrimental effect of bentonite on flotation performance. **Chapter 7** discusses conclusions of this thesis and recommendation for future research.

4. References

Bakker, C.W., Meyer, C.J., Deglon, D.A., 2009. Numerical modelling of non Newtonian slurry in a mechanical flotation cell. Miner. Eng. 22 (11), 944–950.

Basnayaka, L., 2018. Influence of clay on mineral processing techniques. PhD thesis. Curtin University. http://hdl.handle.net/20.500.11937/74929

Basnayaka, L., Subasinghe, N., Albijanic, B., 2017. Influence of clays on the slurry rheology and flotation of a pyritic gold ore. Appl. Clay Sci. 136, 230–238.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2018. Influence of clays on fine particle filtration. Appl. Clay Sci. 156, 45–52.

Bronswijk, J.J.B., 1991. Relation between vertical soil movements and water-content changes in cracking clays. Soil Science Society of America Journal, 55(5): 1220–1226.

Burdukova, E., Becker, M., Ndlovu, B., Mokgethi, B., Deglon, D., 2008. Relationship between slurry rheology and its mineralogical content. 24th Int. Minerals Processing Congress. China Scientific Book Service Co. Ltd., Beijing, China.

Chen, X., Peng Y., 2018. Managing clay minerals in froth flotation—A critical review. Mineral Processing and Extractive Metallurgy Review, 39(5), 289-307. DOI: 10.1080/08827508.2018.1433175

Chipakwe, V., Semsari, P., Karlkvist, T., Rosenkranz, J., Chehreh Chelgani, S., 2020. A critical review on the mechanisms of chemical additives used in grinding and their effects on the downstream processes, Journal of Materials Research and Technology. 9(4) 8148-8162, ISSN 2238-7854

Clarke, B., Kitchener, J.A., 1968. The influence of pulp viscosity on fine grinding in a ball mill. Br. Chem. Eng. 13, 991–995.

Connelly, D., 2011. High clay ores- a mineral processing nightmare. Australian Journal of Mining, July/August Mineral Processing Flotation and Separation. 28-29

Constable, T., 2023. Mining delivers record $455 Billion in export revenue in FY23. Minerals council of Autralia. Media release. https://minerals.org.au/resources/mining-delivers-record-455-billion-in-export-revenue-in-fy23/

Daniel, D.E., Brown, K.W., 1987. Landfill liners: how well do they work and what is their future? In land disposal of hazardous waste: Engineering and Environmental Issues. Edited by S. J. R. A. N. and Jain, R. K. (eds.). Ellis Horwood Publishers, Chickester, West Sussex, England.

Fuerstenau, D.W., Kapur, P.C., Velamakanni, B.V., 1990. A multi-torque model for the effects of dispersants and slurry viscosity on ball milling. Int. J. Miner. Process. 28, 81–98.

Gao, M.W., Forssberg, E., 1993. The influence of slurry rheology on ultra-fine grinding in a stirred ball mill. In: Proceedings XVIII Int. Min. Process. Cong., Sydney. The Australasian Institute of Mining and Metallurgy (AusIMM), Melbourne. 237–244.

Jaques, A.L., Jaireth, S., Walshe, J.L., 2002. Mineral systems of Australia: An overview of resources, settings and processes. Aust. J. Earth. Sci. 49(4), 623-660.

Khalfi, A., Blanchart, P., 1999. Desorption of water during the drying of clay minerals. Enthalpy and entropy variation. Ceramics International. 25, 409-414.

Klimpel, R.R., 1982. Slurry rheology influence on the performance of mineral/coal grinding circuit. Part 1. Min. Eng. 34 (12), 1665–1668.

Klimpel, R.R., 1983. Slurry rheology influence on the performance of mineral/coal grinding circuit. Part 2. Min. Eng. 35 (1), 21–26.

Klimpel, R.R., 1984. Influence of material breakage properties and associated slurry rheology on breakage rates in wet grinding of coal/ores in tumbling media mills. In: Jones, M.J., Oblatt, R. (Eds.), Reagents in the Mineral Industry. I.M.M, London. 265–270.

Li, J.H., Zhang, L.M., Wang, Y., Fredlund, D.G., 2009. Permeability tensor and representative elementary volume of saturated cracked soil. Canadian Geotechnical Journal. 46(8): 928–942.

Merve Genc, A., Kilickaplan, I., Laskowski, J., 2012. Effect of slurry rheology on flotation of nickel sulphide ore with fibrous gangue particles. Can. Metall. Q. 51 (4), 368–375.

Mohammad, N., Meng, W., Zhang, Y., Liu, M., El-Zein, A., Gan, Y., 2020. Desiccation crack formation and prevention in thin bentonite layers. Environmental Geotechnics. 9. 1-14. 10.1680/jenge.19.00112.

Ndlovu, B., Becker, M., Forbes, E., Deglon, D., Franzidis, J.-P., 2011. The influence of phyllosilicate mineralogy on the rheology of mineral slurries. Miner. Eng. 24 (12), 1314–1322.

Nechita, P., 2021. The influence of drying conditions of clay-based polymer coatings on coated paper properties. Coatings. 11, 12. https://doi.org/10.3390/coatings11010012

Oummadi, S., 2019. Drying behaviour of ceramic green bodies: experimental characterization and numerical modelling. Institut de Recherche sur les Céramiques (IRCer)

Patra, P., Bhambhani, T., Nagaraj, D. R., Somasundaran, P., 2012. Impact of pulp rheological behavior on selective separation of Ni minerals from fibrous serpentine ores. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 411. 24–26.

Patra, P., Nagaraj, D.R., Somasundaran, P., 2010. Impact of pulp rheology on selective recovery of value minerals from ores. In: Singh, R., Das, A., Banerjee, P.K., Bhattachalyya, K.K., Goswani,

Peron, H., Delenne, J.Y., Laloui, L., El Youssoufi, M.S., 2009a. Discrete element modelling of drying shrinkage and cracking of soils. Computers and Geotechnics, 36(1–2): 61–69.

Peron, H., Hueckel, T., Laloui, L., Hu, L.B., 2009b. Fundamentals of desiccation cracking of fine-grained soils: experimental characterisation and mechanisms identification. Canadian Geotechnical Journal, 46(10): 1177–1201.

Peron, H., Laloui, L., Hueckel, T., Hu, L.B., 2009c. Desiccation cracking of soils. European Journal of Environmental and Civil Engineering, 13(7–8): 869–888.

Shi, F.N., Napier-Munn, T.J., 2002. Effects of slurry rheology on industrial grinding performance. Int. J. Miner. Process. 65 (3–4), 125–140.

Taner, H., Önen, V., 2016. Control of clay minerals effect in flotation. A review. E3S Web of Conferences. 8. 01062. 10.1051/e3sconf/20160801062.

Tao, D., Zhou, X., Kennedy, D., Dopico, P., Hines, J., 2010. Improved phosphate flotation using clay binder. Separation Science and Technology, 45(5), pp. 604–609.

Tucker, P., 1982. The role of viscosity in the wet-grinding of ores, with special reference to grinding aids. In: Warren Spring Laboratory Report, LR 421 (MP), May.

Wang, Y., 2016. Mitigating the deleterious effect of clay minerals on copper flotation. PhD Thesis. The University of Queensland. https://doi.org/10.14264/uql.2017.49

Wang, Y., Peng, Y., Nicholson, T., Lauten, R. A., 2015. The different effects of bentonite and kaolin on copper flotation". Applied Clay Science 114 48-52. https://doi.org/10.1016/j.clay.2015.05.008

Xing, Y., Xu, M., Guo, F., Luo, J., Zhang, Y., Cao, Y., Gui, X., 2019. Role of different types of clay in the floatability of coal: Induction time and bubble-particle attachment kinetics analysis. Powder Technology, Volume 344, 814-818, ISSN 0032-5910, https://doi.org/10.1016/j.powtec.2018.12.074.

Zaccaron, A., de Souza Nandi, V., Dal Bó, M., 2022. The behaviour of different clays subjected to a fast-drying cycle for traditional ceramic manufacturing. Journal of King Saud University – Engineering Sciences, https://doi.org/10.1016/j.jksues.05.003

Zhang, M., Peng, Y., 2015. Effect of clay minerals on pulp rheology and the flotation of copper and gold minerals. Miner. Eng. 70, 8–13.

Chapter II

Review

1. Introduction

This chapter reviews existing research on both swelling and non-swelling clays, focusing on their negative effects on mineral processing operations and the techniques used to mitigate these effects. It covers the origin, structure, and properties of clay minerals and highlights associated challenges, which hinder operational efficiency, damage equipment, increase reagent consumption, and alter slurry rheology and properties through unfavorable adsorption onto valuable mineral surfaces. And it examines the investigated mitigating techniques and their results in past and recent years. These challenges must be addressed to ensure sustainable and optimized processing of clay-bearing ores in the future. The objective is to integrate this research with existing literature by describing the various approaches explored in prior studies to address the challenges posed by clay minerals in mineral processing operations.

Clay minerals are fine-grained hydrous silicates (Bolt, 1981; Hunter, 1982; Craster, 1999; Murthy, 2002) with unique properties due to their small particle size and layered structure (Ndlovu et al., 2014). These properties, while beneficial in some contexts, complicate mineral processing, necessitating ongoing research to develop effective processing methods. Clay minerals have a wide range of uses due to their versatile properties such as small particle size, colloid and thixotropy, high adsorption capacity and surface area, ion exchange capacity/ cation exchange capacity (CEC), plasticity, cohesion, absorption and desorption, swelling and chemical reactivity and, above all, low cost and nonhazardous nature in handling (Mat, 2023). Some of the most common uses of clay minerals include: soil amendments, ceramics, construction materials, drilling muds: environmental remediation, cosmetics, pharmaceuticals and agriculture (Mat, 2023). Kaolinite is widely used in manufacturing of pottery and porcelain, while some other clay minerals are utilised as extenders in paints and plastics and rubbers (Gupta and Miller, 2010). Smectites are commonly used as binding agents in the preparation of ceramics and in oilwell drilling fluids (Craster, 1999). Another use of smectites is to remove the oil and grease from floors and pet litter trays while acting as an absorbent. Clays find their application in civil engineering as a modifier to alter the movement of water or chemical wastes, for lubrication of cables or pipes and as a waterproofing agent (Hall, 1987; Craster, 1999). Other applications of clays are to decolourise the vegetable oils, wine and in water filtration and purification (Madsen, 1989; Boija, 1992; Craster, 1999).

Clays and clay minerals form under specific geologic conditions, such as soil horizons, sediments, geothermal fields, volcanic deposits, and weathering rocks, primarily where rocks interact with water, air, or steam (Foley, 1999). The formation of clay minerals is a complex process that takes place over extended periods of time as a result of one of the three formation processes; namely inheritance, neoformation, and transformation in three environments weathering, sedimentary, and diagenetic-hydrothermal (Eberl et al., 1984). The behaviour and applications of clay minerals in different fields are predicted by a number of factors (Foley, 1999) that influence the formation process for example climate, drainage patterns, parent rock, topography, vegetation, and time (Huggett, 2005). Weathering of rocks, driven by combined physical and chemical processes, is a primary source resulting in formation of smaller and more stable clay particles (Nelson, 2014), while hydrothermal alteration and sedimentation also play key roles (Keller, 1970; Krekeler, 2004). Diagenesis further transforms minerals into stable forms, essential for forming bentonite and fuller's earth (Craster, 1999). Erosion deposits these minerals in sedimentary environments, making them significant constituents of fine-grained rocks like mudstones, claystones, and shales.

Clay minerals make up a significant portion of sedimentary rocks and soils. They form a major constituent in various environments, such as soils, lakes, estuaries, deltas, and ocean sediments, covering a vast portion of the Earth's surface. Additionally, clays are pervasive in nearly all sedimentary rocks, which constitute around 75% of the Earth's land surface (Huggett, 2005). In fact, clay minerals make up about 40% of the minerals in sedimentary rocks (Nelson, 2014). All these facts make clay minerals an inevitable part of all valuable minerals. However, these associated clay minerals are undesirable and are considered as gangue material because of their detrimental impact on the efficiency of various mining processing operations, including crushing, grinding, screening, flotation, dewatering, filtration, thickening etc.

The adverse effects of clays on various ore processing techniques have been recognized for decades, but their significance has increased in recent times due to the projected depletion of high-grade ore deposits in the future. The focus of mining industry has grown to address the challenges that are associated with exploring the potential cost-effective methods to process clay-containing ores. Despite extensive literature on the influence of clay minerals in the mineral processing industry, there is a lack of proper quantification and understanding of the underlying mechanisms. Additionally, there is very limited research available on grinding and drying of clay-containing ores.

2. Clay minerals

Clay minerals, typically classified as hydrated phyllosilicates, exhibit plasticity and are chemically heterogeneous colloidal particles smaller than 2 µm (Theng, 2012). Composed of hydrous aluminum silicates, they may also contain quartz, feldspars, carbonates, oxides, hydroxides, and organic matter (Luckham and Rossi, 1999). As members of the phyllosilicate family, they exhibit layered structures of silicate tetrahedra and alumina octahedra (Theng, 2012). The varying layer structures and bonding forces among different clay minerals result in diverse properties and behaviours (Brigatti et al., 2013).

2.1. Crystal structure of clay minerals with classifications

Clay minerals possess a layered structure comprising of two main structural units known as silicate tetrahedra sheets “T” and alumina octahedral “O” sheets that form the atomic lattices of clay minerals (Grim, 1968; Bergaya et al., 2006). These units are connected in specific patterns through various forces and bonds and result in macrostructure formation of the clay particles to give a certain set of properties to each clay group (Chen and Peng, 2018).

A tetrahedron contains a central cation bonded to four oxygens, out of which three oxygen atoms are coordinated with other tetrahedrons resulting in an open hexagonal network structure where the basal oxygens become almost coplanar and the apical oxygens points in the same direction. The most common tetrahedron cations are Si^{4+}, Al^{3+}, Fe^{3+} (Figure 1) (Grim, 1968; Wang, 2016; Basnayaka, 2018).

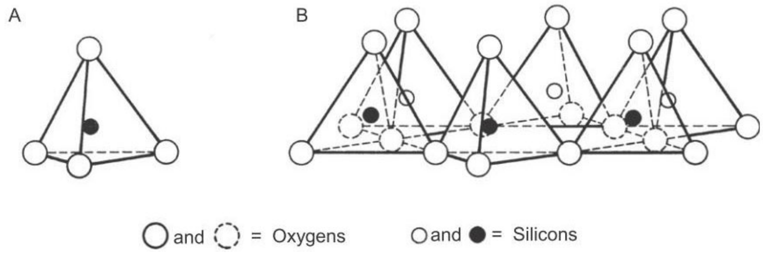


Figure 1. (A) a silica tetrahedron in which the central silicon ion is coordinated to four oxygens; (B) a tetrahedral sheet formed by linking silica tetrahedra through corner-sharing (Grim, 1968).

On the other hand, an octahedron contains a central cation bonded with either oxygen ions or hydroxyl groups in six-fold coordination (Bergaya et al., 2006). These octahedron sheets are linked together to form a lattice by sharing six vertices. The most common octahedron cations found in clay octahedron sheets are Al^{3+}, Fe^{3+}, Mg^{2+}, Fe^{2+}(Figure 2). Octahedron layers are classified as dioctahedral or trioctahedral based on the valency of the central cation; i.e a valency of three refers to dioctahedral or gibbsite-type and a valency of two refers to trioctahedral or brucite (Grim, 1968; Craster, 1999; Wang, 2016; Basnayaka, 2018).

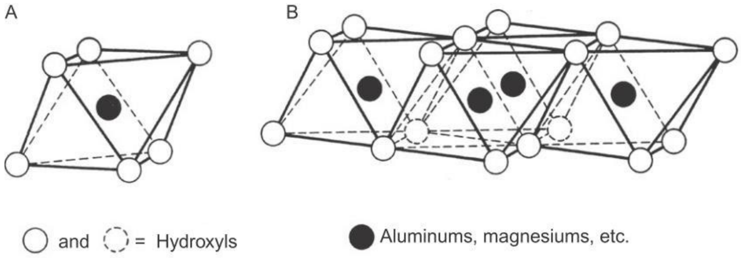


Figure 2. (A) an alumina octahedron; (B) an alumina octahedral sheet. (Grim, 1968).

The formation of clay layers takes place when the basic building blocks “tetrahedron sheets” and “octahedron sheets” share the apical oxygen ions in the tetrahedron sheet and are bonded with each other. All clay minerals have different physical and chemical properties as a result of various combinations of “T” and “O” sheets.

There are several types of clay minerals found in nature (Figure 3). Each of them possesses unique chemical composition and structure. A number of clays namely kaolinite, smectite, illite, chlorite, vermiculite, pyrophyllite and talc group, true (flexible) micas and brittle micas groups, interstratified clay minerals group, sepiolite and palygorskite group, allophane and imogolite group have been described in literature (Dixon and Weed, 1989; Hurlbut and Sharp, 1998; Bergaya et al., 2011; Kumari and Mohan, 2021).

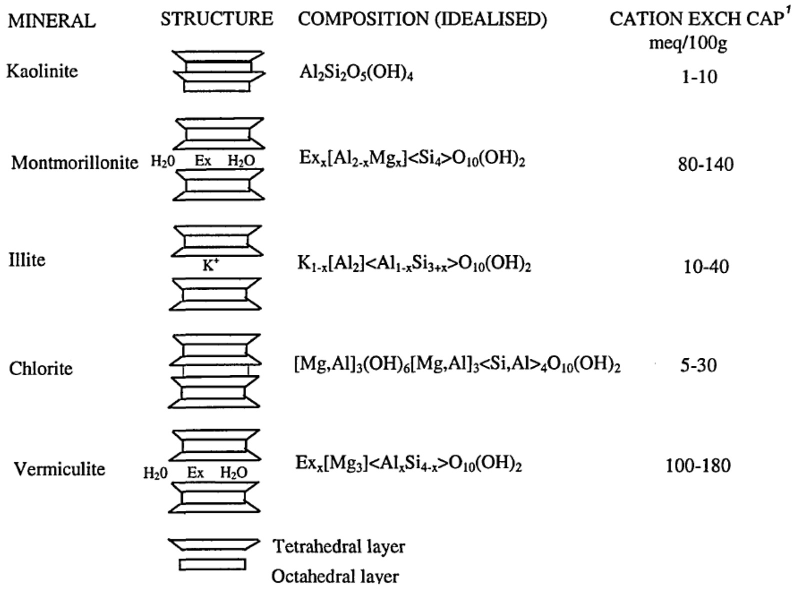


Figure 3. Structural arrangement of different type of clay showing the potential for water adsorption in the interlamellar region of montmorillonite. Ex represents the exchange cations (Bemer, 1971)

The most relevant and prevailing classification of clay minerals is based on the arrangement of T and O sheets in clay layers, interlayer bonding, and the interlayer cations (Deer et al., 1992). Most common layer arrangements in the clay minerals are either 1:1 (T-O) where one "T" sheet is condensed with one "O" sheet (eg. kaolinite) or 2:1 (T-O) where one "O" sheet is sandwiched between two "T" sheets (eg. smectite). These layers are stacked together to form the clay particle through bonding forces (eg. van der Waals forces or hydrogen bonding. (Basnayaka, 2018)

In the 1:1 layered clay (i.e. kaolinite), T and O sheets are bonded together with two strong forces, one is van der Waals attractive forces and other is the strong hydrogen bond. This hydrogen bond exists between the hydrogen atoms in the octahedral sheet of one layer and the oxygen atoms in the tetrahedral sheet of the next layer (Zhang, 2016; Chen and Peng, 2018). That is why this group of clay is non-swelling in water because this strong hydrogen bonding does not allow water to penetrate through the layered structure (Ndlovu et al., 2014; Basnayaka et al., 2017; Basnayaka et al., 2018; Chen and Peng, 2018; Jeldres et al., 2019).

Illites are classified as non-swelling clays with 2:1 layer structured, i.e. one octahedral sheet is sandwiched between two tetrahedral sheets. The presence of anhydrous potassium ions as interlayer cations tightly bound the clay layers prohibiting the penetration of water molecules into interlayers (Luckham and Rossi, 1999; Craster, 1999; Wang et al., 2015; Basnayaka, 2018; Cheng and Peng, 2018).

The smectite group, such as montmorillonite, and vermiculite have a 2:1 (T-O-T) layered structure, with tetrahedral layers on both sides, preventing hydrogen bonding and resulting in layers held together by weak van der Waals forces. This allows water to penetrate, causing the clay to swell and increase viscosity and yield stress even at low concentrations (Luckham and Rossi, 1999; Zhang, 2016). They are known as swelling clays due to their high swelling capacity when exposed to moisture. Both have high cation exchange capacity; smectite expands when hydrated, while vermiculite expands when heated. Figure 4 shows the structures of kaolinite, montmorillonite, and illite.

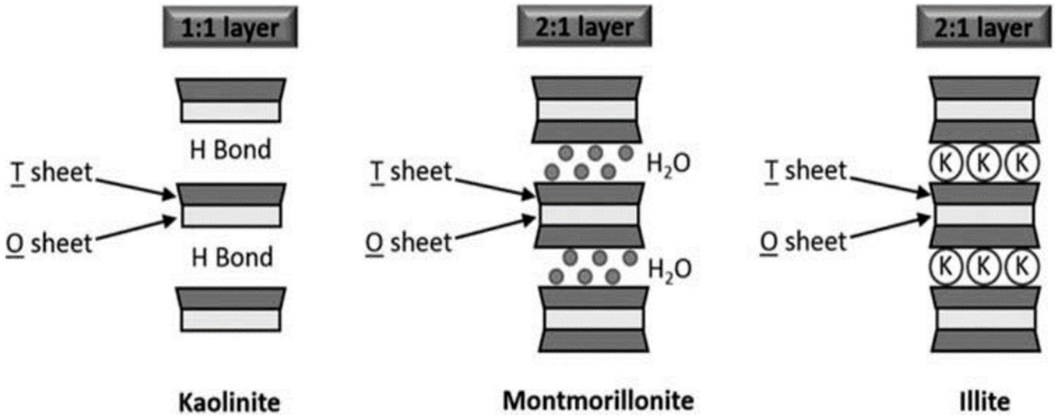


Figure 4. Kaolinite, montmorillonite, and illite structure (Zhang, 2016).

2.2. Properties of clay minerals

Clay minerals exhibit a unique combination of physical and chemical properties that make their presence undesirable in most of the downstream mineral processing and at the same time, make them useful in a variety of other applications (i.e. industrial, domestic or biomedical). Some of the key properties of clay minerals include small particle size (less than 2 μm), high surface area, cation exchange capacity (CEC), plasticity, cohesion, absorption and desorption, swelling capacity of some clays when hydrated, chemical reactivity, non-hazardous for handling, low cost and easy availability, etc (Mat, 2023). The most relevant properties of clay are discussed in detail in this section that are believed to affect the mineral processing operations.

2.2.1. Surface properties of clay minerals

Important surface properties include surface area and surface charges. Clay particles have platy morphology and are anisotropic in nature, therefore, are characterised by the faces of large surface area and smaller thickness (Basnayaka et al., 2017). A less than 2 μm small particle size of clay minerals results in a large surface area per unit mass, making them effective at adsorbing and exchanging ions as well as adsorbing organic compounds. Their high cation exchange capacity increases the possibility to absorb and exchange positively charged ions (i.e. calcium, magnesium, and potassium). This process is known as isomorphous substitution where one structural cation is replaced with another of similar size with lower valency cations; for example, substitution of Si^{4+} with Al^{3+} in tetrahedron sheets or the substitution of Al^{3+} with Mg^{2+} or Fe^{2+} in octahedron sheets (Swartzen-Allen and Matijevic, 1974; Craster, 1999; Johnson et al., 2000). Isomorphous substitution is responsible for the negative electrical charge of clay particles. Adsorption of cations and anions will occur readily in clay minerals to neutralize when the clay is exposed to an electrolyte (Swartzen-Allen and Matijevic, 1974; Cratser, 1999). The clay develops a certain cation exchange capacity (CEC) which is defined as the number of chemical equivalents per unit mass of dry clay. Montmorillonites often exhibit extensive isomorphous substitution, resulting in cation exchange capacity (CEC) values frequently exceeding 100 milliequivalents/ 100 g (see Figure 3).

Surface charge is an important surface property of clay minerals which plays an effective role in all downstream mineral processing operations, especially flotation process. It significantly affects the interaction of clays with other clays or mineral particles in the aqueous solution. It can be observed in Figure 5 that all three groups of clays possess a negative charge across the whole pH range. It represents the overall potential of clay minerals (Chen and Peng, 2018). Latest research shows that the clay particles may have different charges on different faces (basal face surface and edge surface) and these different surface charges decides the final electrostatic interaction between the particles of clay mineral and the valuable mineral. The basal face surface of clay mineral particles is always negatively charged while the charge on the edge surface is decided by the pH of aqueous solution and it can be positive or negative. Broken bond surface exposure on the edges has a potential of adsorbing hydrogen or hydroxyl ions according to the pH of aqueous solution and a variable charge can develop on the edges accordingly (Tombácz and Szekeres, 2004). Different charge features of different clay minerals and surface charge variations with solution pH significantly affect all mineral processing operations in general and flotation in particular (Chen and Peng, 2018).

Electrostatic attraction model says that slime coating can happen only between clay minerals and valuable minerals when they are oppositely charged. On the other hand, slime coating can take place when minerals particles are negatively charged and edges of clay particles carry positive charge. While some other studies have shown the possibility of slime coating when both particles possess low values of zeta potential (Xu et al., 2003). Hence, more detailed investigations are required to understand the role of this deviation in charges.

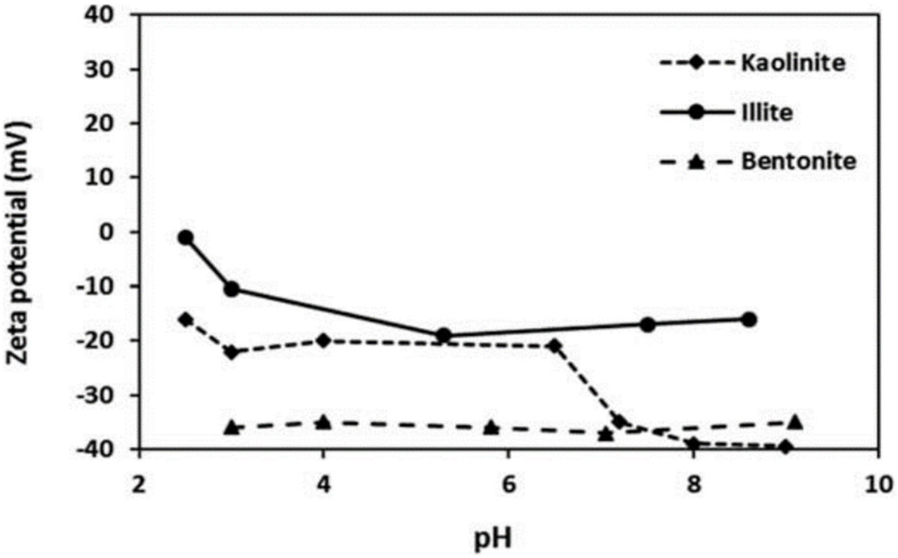
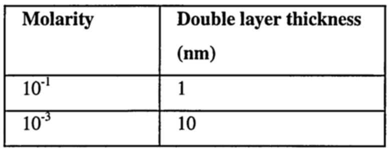


Figure 5. Zeta-potential of kaolinite, illite, and bentonite in DI water (Arnold and Aplan, 1986b).

The term double layer means the presence of two parallel layers of charge around the particle or object. The first layer is the surface charge (either positive or negative) that is composed of ions which are adsorbed onto the surface of object due to chemical interactions. The second layer consists of ions that are attracted to the surface charge due to the Coulomb force, electrically screening the first layer. The second layer is made of free ions and is loosely held with the particle. The electric attraction and thermal motion cause it to move in the fluid prohibiting a firm attachment. It is also known as the diffuse layer. The surface of a clay particle carries a negative charge, which leads to the attraction of positive ions. This zone of attracted positive ions in the solution, alongside the negatively charged clay surface, is referred to as the diffuse double layer (Wan et al., 2020; Estabragh et al., 2020).

The electrical double layer theory can explain the osmotic swelling caused by Na^+ and Li^+ exchanged types of montmorillonite clay (Swartzen-Allen and Matijevic, 1974; Helmy, 1998). The clay platelets with negative charge create a net attraction for cations and a net repulsion for anions, resulting in a positive electrostatic charge in the region near each platelet, therefore repelling the contiguous platelets. The presence of closely acting attractive van der Waals forces (Barclay and Ottewill, 1970) results in an energy minimum at each interplatelet partition which depends on the electrolyte concentration. Alternatively, the charge of the clay double layer completely depends on the imperfections within the clay lattice. To maintain electrical neutrality, the negative lattice charge is balanced by the presence of cations that will stay with the clay during drying and resuspension. The addition of electrolyte will compress the double layer but will not affect its charge (see Table 1).

Table 1. Dependence of diffuse double layer thickness on concentration for a 1:1 electrolyte (Hunter, 1987)



Molarity	Double layer thickness (nm)
10^{-1}	1
10^{-3}	10

2.2.2. Water swelling properties of clay minerals

The behaviour of clay minerals in water containing environment is an important but complex phenomenon. Extensive research has been conducted to understand the structure of water adsorbed on the clay surface, particularly to determine whether its density and arrangement resemble or deviate from bulk water (Low, 1987). The distance to which the effect of the clay surface changes its properties, is also unclear. Water adsorption by clays is characterised as an exothermic process and can be result of either hydration of the exchange cations or the hydration of crystal surface (Cratser, 1999).

Table 2. Characteristic sizes of cations commonly found on montmorillonite surfaces (Mitchell, 1993)

Ion	Dehydrated ion diameter (Å)	Charge density (charge/Å^2)	Hydrated ion diameter (Å)
Sodium (Na^+)	1.90	0.088	11.2
Potassium (K^+)	2.66	0.045	7.6
Magnesium (Mg^{2+})	1.30	0.376	21.6
Calcium (Ca^{2+})	1.90	0.176	19.0

As seen in Table 2, the potassium ion has the least swelling capacity due to the low charge density. When clay is exposed to water, oxygen in siloxane surfaces form hydrogen bonds with the water proton and siloxane surfaces hydrate. In kaolinite clays, alumina and siloxane are the two exposed surfaces. The protons of alumina surface form bonds with oxygen of the water molecule. In smectite, water may penetrate in the interlayers (between the individual structural units). If the moisture content is low, the interlayer cations remain embedded in the hexagonal cavities between the contiguous siloxane surfaces of smectite (montmorillonite) therefore, initial adsorption takes place at the external surfaces only. A stepwise expansion of interlayer spacing occurs, as the moisture content increases hydrating the interlayer cations, leading to a multilayer adsorption of water molecules (Craster, 1999).

It is interesting to note that monovalent and bivalent exchanged clays behave differently under same environment. X-ray diffraction studies show that the Na^+ exchanged clay demonstrates a series of hydration phases, i.e the number of sheets of interlayer water increases with increasing relative humidity. Whereas Ca^{2+} montmorillonite exhibits three or maximum four interlayer water sheets upon complete immersion in water. The phenomenon of Na^+ exchanged clay going through unlimited swelling to larger interlayer spacings is known as osmotic swelling and it is a characteristic of only lithium and sodium clays. Larger monovalent cations (i.e K^+) and exchange cations with higher charge allow for only limited swelling of smectites, typically up to a few water layers (Craster, 1999).

Another reason that kaolinite clays do not show interlayer expansion swelling when encountered with water is the presence of strong hydrogen bonding between Al-OH…O-Si- in adjacent layers within a particle, accompanied by dipole-dipole and van der Waals forces (Theng, 2012).

In smectite (i.e. montmorillonite), the swelling capacity is defined by the particle size, the layer charge and the nature of the exchangeable cation in the interlayer space. As mentioned before, the swelling phenomenon takes place as intra-crystalline swelling (limited amount of adsorbed water), and/ or osmotic swelling (unlimited adsorption of water). This behaviour is attributed to the difference of ion concentrations between close to the clay surface and in clay pores. The exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) are present between montmorillonite unit layers and get hydrated to produce crystalline swelling when exposed to water molecules. Once the maximum number of hydrates are adsorbed, osmotic swelling dominates the swelling mechanisms making surface hydration less significant (Wang et al., 2015).

When montmorillonite clay expands in water, its interlayer surface area becomes available to various external molecules. In aqueous solution with less ions, water molecules can enter and interact with the exchangeable cations in the interlayer spaces and cause hydration. As a result, the clay layers are forced apart in successive steps, to cause clay to swell (Müller-Vonmoos and Løken, 1989).

2.2.3. Agglomeration of clay minerals

Clay minerals are colloidal materials consist of particles less than 2 μm in size and in an ideal aqueous solution they are believed to be in constant motion in random directions. In real mineral suspensions under certain condition, these clay particles become aggregated to form different types of networks because of their anisotropic surface charges. The formation of aggregates results in unwanted effects on the flow properties of clay containing suspensions.

In dilute clay suspension where water volume is large, the interaction of the diffuse double layers keeps the clay particles apart. As the concentration is increased, clay particle come together to form aggregates depending on their relative positions and the relative magnitude of their surface and edge potentials (Luckham and Rossi, 1999). The electrical interaction energy for the three types of aggregation is decided by three different arrangements of the two double layers (Luckham and Rossi, 1999; Baik and Lee, 2010; Wang et al., 2015). The common types of aggregations are shown in Figure 5 (Luckham and Rossi, 1999). Mainly three different patterns of aggregation have been identified as shown in Figure 6 and are known as face-to-face (F–F), edge-to-face (E–F), and edge-to-edge (E–E) (Arnold and Aplan, 1986b; Luckham and Rossi, 1999; Chen and Peng, 2018).

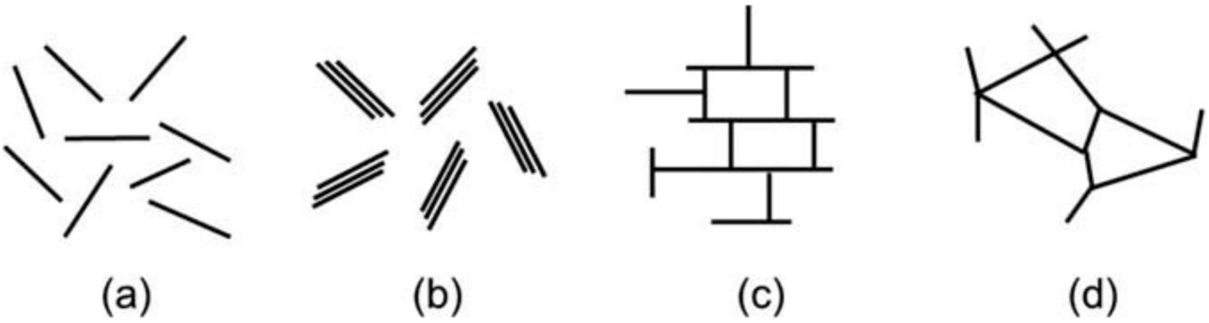


Figure 6. Aggregation of clay particles: (a) dispersed, (b) F–F, (c) E–F, (d) E–E (Luckham and Rossi, 1999).

Gupta et al. (2011) observed the domination of silica face-alumina face interaction for kaolinite particle aggregation at low pH during their work for kaolinite suspensions. As a result of this F-F association, the stacking of kaolinite layers is increased, promoting the E-F (edge-silica face and edge-alumina face) and F-F (silica face-alumina face) aggregations with increasing pH (Figure 7). As the system pH increases, Gupta et al. (2011) observed a lower degree of consolidation and the EE association as evident from the cryo-SEM images of the kaolinite aggregates. It is attributed to the fact that the silica tetrahedral face of kaolin is negative at a pH > 4, while at pH < 6 the alumina octahedral face is positive and negative at pH < 6 and pH > 8 respectively, whereas the edge surface charge is decided by the pH of the system (Gupta and Miller, 2010).

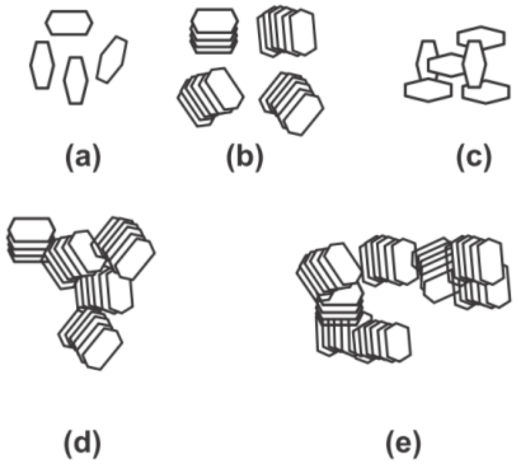


Figure 7. The formation of aggregate structures in kaolinite suspensions, as (a)dispersed, (b)FF, (c) EF, (d) EE, and (e) a combination of (b), (c) and (d), depending on the solution chemistry of the suspension (Gupta et al., 2011).

Bentonite studies revealed that an acidic pH results in the formation of a card-house network where E(+)-F(−) interaction dominates. While alkaline pH gave rise to a band-like network structure through F(−)-F(−) interactions (see Figure 8 (Lagaly, 1989)). A stiff gel like aggregation was observed when the solid contents were above 3.5 wt.% for the sodium montmorillonite (Abend and Lagaly, 2000).

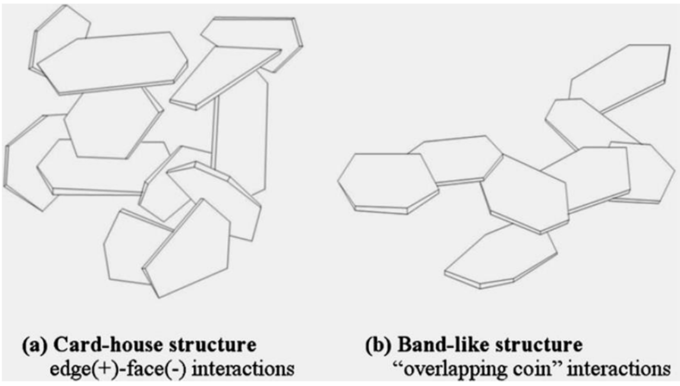


Figure 8. Cartoon of bentonite microstructures (Lagaly, 1989).

One more factor that affects formation of network structure is the solid percentage. Low solid percentage do not support aggregate formation and the result is a pulp with Newtonian fluid behaviour. Pulp viscosity is increased with formation of small aggregates as the solid percentage is increased (Chen and Peng, 2018).

Several factors can strongly influence the tendency of clay particles to aggregate. These include high clay percentage, high ionic strength (concentration of ionized salts), and the presence of surfactants and organic polymers. The type of compensating cations also plays a significant role in the aggregation/dispersion behaviour. Cations with strong hydration, such as Li^+ with a small radius, induce the dispersion of aggregates into small nanoparticles. Additional structural details, such as the charge heterogeneity of the clay surfaces, and the redox state of iron (Fe^{2+} or Fe^{3+}), also have an important impact on the dispersion or flocculation of clay particles (Bergaya et al., 2011).

3. Rheology of clay-containing slurries

The study of rheological behaviour of slurries is of paramount importance because most of the mineral processing techniques involve the processing of ore in the form of slurries (Ndlovu et al., 2013). Rheological behaviour of slurries in known to influence the mineral processing operations significantly because the flow of the slurries is greatly defined by the rheological principles.

Rheology is the study of how materials deform and flow when subjected to a shear stress. In a slurry of high concentration, particles tend to aggregate or flocculate, immobilizing the suspending medium and resulting in the development of yield stress. Yield stress represents the minimum applied stress required to initiate flow in a particulate system. Essentially, it is a macroscopic representation of the shear strength of inter-particle forces within a particulate network (Nasser and James, 2007), providing insight into the complexity of the structures formed in solutions. Viscosity, on the other hand, is defined as the ratio of shear stress to shear rate and indicates the ease of flow in the suspension once the complex structures collapse. Both yield stress and viscosity are crucial in understanding the flow behaviour and structural properties of materials (Wang et al., 2015).

The rheological behaviour of slurry is profoundly influenced by various properties of mineral particles, including their concentration, morphology, swelling capacity, surface charges, and mode of aggregation. Clay minerals, due to their anisotropic shape and charge heterogeneity have the potential to significantly modify the rheological properties of slurries (Mueller et al., 2010). In the presence of clay, the apparent viscosity and yield stress of the slurry tend to increase. However, the extent of these alterations in rheological properties may vary depending on the specific type of clay present (Zhang and Peng, 2015). Swelling smectite clays, like montmorillonite, have been reported to be more influential on slurry rheology compared to non-swelling clays (Ndlovu et al., 2013; Basnayaka, 2018).

Clay particles tend to form network structure by aggregating in three distinct orientations—edge-edge (E-E), edge-face (E-F), and face-face (F-F), especially in acidic pH conditions (Rand and Melton, 1977). The network structure formation alters the pulp rheology. E-E and E-F aggregations form voluminous structures, increasing viscosities in clay slurries, typical in swelling smectite clays like montmorillonite (Swartzen-Allen and Matijevic, 1974; Luckham and Rossi, 1999). However, F-F aggregation creates a thicker, flaky structure, preventing significant increases in viscosity as seen in kaolinite clays (Basnayaka, 2018).

Rheological behaviour of a slurry is described as the relationship between applied shear stress and the resultant shear rate. Newtonian slurries exhibit a linear relationship between the applied shear stress and the shear rate where the slurry viscosity (μ) is defined by the gradient of the line. Equation (1) describes the behaviour of a Newtonian slurry and shows that the Newtonian slurries have constant viscosity at any shear rate (King, 2002).

$$\tau = \mu\gamma \qquad \text{Equation 1}$$

where, τ is the applied shear stress, μ is the slurry viscosity, and the γ is the shear rate. This relationship becomes non-linear in the presence of colloidal or microscopic particles and exhibit non-Newtonian slurry properties (King, 2002).

In general, suspensions can demonstrate either Newtonian or non-Newtonian behaviour. Non-Newtonian slurries include dilatant, plastic, pseudo-plastic, and Bingham behaviors (Barnes, 1999). A Newtonian fluid maintains a constant viscosity across the entire range of shear rates, whereas non-Newtonian fluids exhibit varying viscosity values based on the shear rate (Klimpel, 1999; He et al., 2004). Therefore, for non-Newtonian fluids, the viscosity at any given point is referred to as the "apparent viscosity. Mineral suspensions typically exhibit Bingham or pseudo-plastic behaviour, and researchers often use the Bingham model (Equation 2), Casson model (Equation 3), and Herschel-Bulkley model (Equation 4) to estimate viscosity and yield stress (Hunter, 2000).

Bingham model $\tau = \tau_y + \eta_{pl}\dot{\gamma}$ Equation 2

Casson model $\tau^{1/2} = \tau_y^{1/2} + (\eta_{pl}\dot{\gamma})^{1/2}$ Equation 3

Herschel-Bulkley model $\tau = \tau_y + \mathrm{K}\,(\dot{\gamma})^n$ Equation 4

where η_{pl} symbolises the plastic viscosity (the slope of the shear stress-shear rate curve above the yield point, indicating the viscosity of the slurry when projected to an infinite shear rate). $\dot{\gamma}$, τ_y, τ , K and n are the shear rate, the yield stress, the shear stress, the consistency index, the flow behaviour index respectively. Figure 9 presents the relationships between shear stress and shear rate for Newtonian and non-Newtonian slurries.

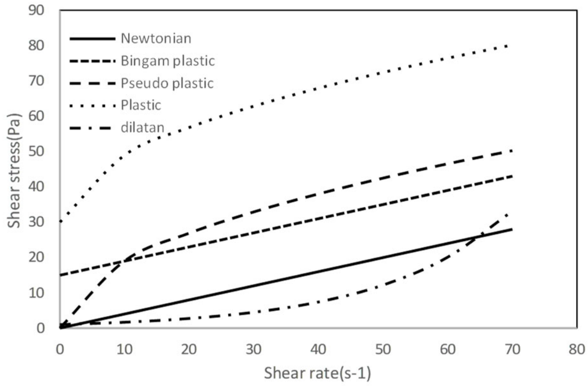


Figure 9. Rheological behaviour of Newtonian and non-Newtonian slurries (King, 2002).

Due to the hydration of interlayer cations in suspensions containing smectites, there is an effective increase in the volumetric fraction of the suspension, which is associated with a relatively high yield stress and a significant increase in viscosity (Burdukova et al., 2008a). It should be noted that suspensions with similar viscosities may not always have the yield stresses in same case. In the study of muscovite and vermiculite flow behaviour, it was found that the Bingham viscosities of vermiculite, muscovite, and quartz were quite similar. However, there was a significant difference in their yield behaviour, primarily attributed to the surface charge and inter-particle orientation of the edges and faces that occur in solutions (Ndlovu et al., 2011a).

In addition to solid loading, particle size distribution, surface charge distribution, and particle morphology, particle-particle interaction also plays a significant role to determine the rheological behaviour of concentrated suspensions. Particle-particle interaction, which is strongly affected by the chemical factors such as pH and the presence of dispersing agents (Ndlovu et al., 2011a; Ndlovu et al., 2011b; Papo et al., 2002) determines the aggregate structure, and finally the flow behaviour of clay suspensions. The reverse process for aggregation is identified as dispersion in the absence of yield stress (see Figure 10).

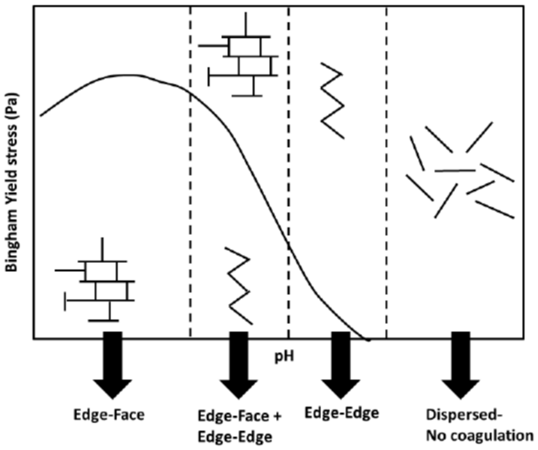


Figure 10. The effect of pH on the Bingham yield stress (Rand and Melton, 1977; Ndlovu et al., 2011a).

4. Challenges encountered in mineral processing of clay-containing ores

The presence of clays with valuable minerals has been a great challenge for mining industry because of the unfavourable effects of presence of clay on various mineral processing operations such as crushing, grinding, gravity separation, filtration, flotation, leaching and drying however, in spite of notable research in this field, the mechanism of these undesirable effects still needs more understanding and interpretation. Though a lot of work has been done to study the influence of clay mineral on flotation efficiency of different ores including gold and copper but there is no information available on impact of clays on flotation separation efficiency of complex ores (specially with different densities). Furthermore, the effect of clay minerals on grinding and drying efficiencies has not been examined.

The presence of clays can influence the efficiency of different unit operations from size reduction to final recovery (such as grinding and flotation) in mineral processing plants. Clays are observed to bridge the openings of crushers and blinding of screens in initial separation stage. Other negative effects become operative at later stage mineral processing, including increased viscosity as the first detrimental effect (Basnayaka et al., 2017, 2018; Chen and Peng, 2018). Clay minerals consist of very fine particles (even less than 2 μm) and therefore, are characterised by very poor settling rates. High viscosity impedes the efficiency of grinding operations, particularly when wet grinding medium is involved because in that case grinding mills are supposed to operate at lesser solid percentages. In such case grindability is significantly reduced due to the limited movement of grinding medium (for example grinding balls during ball mill operation) (Basnayaka et al., 2017). Some other studies have revealed that increase in viscosity and yield stress is associated with some of the clay groups and not for others (Zhang and Peng, 2015; Basnayaka, 2018, Chen and Peng, 2018).

4.1. Flotation performance

Flotation is a physicochemical mineral processing method used to separate valuable minerals from gangue. This technique, introduced in early 20th century, enables the processing of low grade and complex ore bodies (Wills and Napier-Munn, 2006). It involves preferential attachment of valuable mineral particles to the air bubbles and transport them to the top of a flotation cell. Chemical conditioning of the pulp can enhance the floatability of valuable minerals. Various mechanisms involved in the process of flotation include bubble-particle attachment, bubble-particle detachment, entrainment, and slime coating etc (Wills and Napier-Munn, 2006). Though the flotation process is not fully understood, a comprehensive literature is available on the underlaying mechanisms (Sutherland and Wark, 1955; Glembotskii et al., 1972; King, 1982; Leja, 1982; Jones and Woodcock, 1983; Ives, 1984; Schulze, 1984; Fuerstenau et al., 1985). Separation of different minerals particles during flotation process depends on the differences in their ability to adhere to air bubbles. More hydrophobic particles are more likely to attach to air bubbles, and chemical reagents (i.e collectors, activators) are used to regulate the hydrophobicity of valuable commodity particles (Basnayaka, 2017).

As mentioned before, mineral flotation involves a combination of chemical and physical interactions in a three-phase system consisting of particles, air, and water (Bulatovic, 2007). To begin with, a slurry from the impeller/stator system enters the flotation cell, where it undergoes turbulence and circulates back to the impeller. Simultaneously, small bubbles are introduced in the impeller/stator region and disperse throughout the flotation cell through the bulk fluid flow. As a result of the collision between hydrophobic particles and bubbles, a froth is formed by the attachment of particles onto the bubbles (Ata et al., 2004). The presence of clay ores affects froth and pulp phases leading to a reduced flotation performance (Basnayaka, 2018). Some of the negative effects posed by the clay particles during flotation of clay-containing mineral slurries are given in Section 4.1.

The main mechanisms working behind the negative effects of clay-containing slurries include 1) increased apparent viscosity and the yield stress of the pulp (Bakker et al., 2009; Shabalala et al., 2011), 2) tendency of clay particles to coat the surface of both valuable mineral surfaces and air bubbles (Tao et al., 2010), 3) high entrainment of fine clay particles during flotation (Patra et al., 2010; Vasudevan et al., 2010; Jorjani et al., 2011), 4) consumption of flotation reagents (Connelly, 2011), 5) either increasing or decreasing froth stability (Dippenaar, 1988; Bulatovic, 2007; Farrokhpay, 2011; Basnayaka, 2018).

The efficiencies of flotation are reduced because of the high viscosity factor associated with clay particles (Basnayaka et al., 2017). It is important to note that the extent of the mentioned effects may vary depending on the specific type of clay present. Although the effect of clay minerals on flotation is attributed to their anisotropic shape, charge, complex rheological effects, and large surface area, the exact mechanisms responsible for these effects have not been conclusively identified. Furthermore, increased power is required to maintain the slurry agitation as increased viscosity and rheological modifications alter the hydrodynamics within the flotation cell, necessitating (Bakker et al., 2009; Basnayaka, 2018).

Slime coating is another strong reason behind the negative effects of presence of clay with valuable minerals. Clay particles tend to cover the surface of valuable minerals (Basnayaka et al., 2017, 2018; Chen and Peng, 2018) resulting in restricted collector adsorption during flotation process. As a fact, most clays being hydrophilic in nature form a shield of clay particles over the valuable mineral surface supressing adversely the collector adsorption on the valuable minerals (Gaudin et al. 1960; Edwards et al. 1980; Bremmell et al. 2005). As a result, bubble–particle attachment possibility becomes limited that finally reduce both the mineral flotation and concentrate grade. Some studies have shown a significant role of electrostatic forces between the minerals and clay particles in deciding the slime coating (Chen and Peng, 2018). Type of clay minerals, the properties of mineral/clay particles, the concentration of ions in water, pulp pH etc are some of the other factors to affect clay coating mechanisms. An extensive reduction in flotation concentrates grades is observed due to high entrainment of fine clay particles. This effect becomes more intense in the presence of electrolytes and results in poor mineral grade.

Increased viscosity and yield stress result in a drop in flotation recovery having detrimental effects on the hydrodynamics in flotation cells as can be seen in Figure 11. It can be assumed that increased viscosity results in restricted mobilisation of clay particles and poor circulation of bubbles that can reduce the likelihood of collision between bubbles and clay particles resulting in ineffective flotation performance.

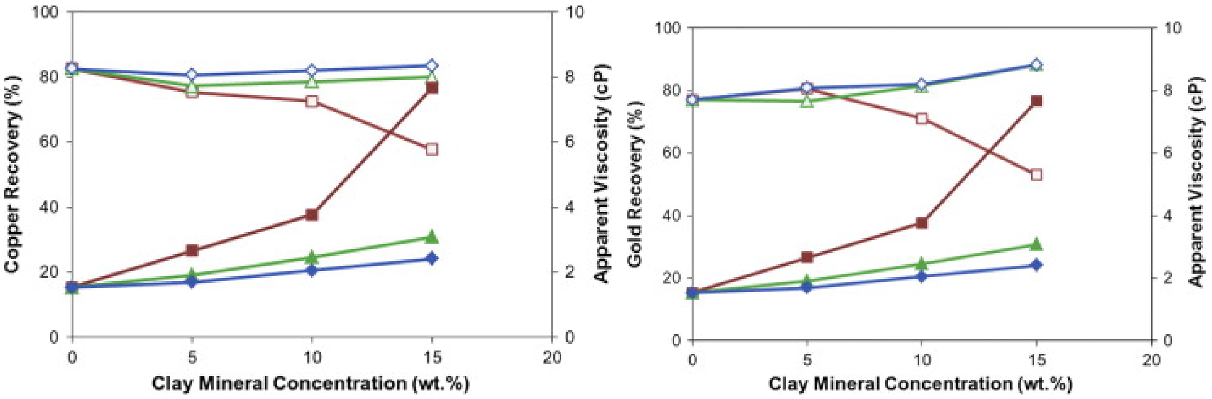


Figure 11. Effect of clay minerals on copper and gold recovery (hollow points) and apparent viscosity (solid points) of flotation slurries: snobrite (◊), Q38 (△), bentonite (□). (Zhang and Peng, 2015)

4.1.1. Rheological behaviour of clay containing slurries

Rheology is a measure of the particle-particle aggregations and interactions of particles in a slurry under applied stress (Farrokhpay, 2012). The differential movement of mineral and gangue particles within the slurry forms the basis of rheological measurements. Clay mineral particles have the potential to modify the rheological properties of the processed slurry due to their very fine particle size, anisotropic surface charges, and shape, swelling capacity, the formation of voluminous structures (Ndlovu et al., 2014). Slurries with certain clay concentrations can exhibit non- Newtonian behaviour modifying the hydrodynamics within a flotation cell (Bakker et al., 2010), adversely affecting the mechanisms of gas dispersion, bubble coalesce and gas holdup involved in flotation process due to increased yield stresses and apparent viscosities (Shabalala et al., 2011). Additionally, the possibility of bubble-particle collision and attachment is reduced under increased rheological properties. Hence, the mobility of bubbles and particles is affected, leading to a reduced flotation performance. (Bakker et al., 2009).

The clay type plays a significant role in deciding the degree of modification of hydrodynamics in flotation cell because different clay types have distinctive properties. Multiple studies have confirmed swelling smectite clays, for instance, can have a significant impact on slurry rheology, even with a relatively low solid concentration of 5%, leading to a notable reduction in flotation efficiency (Zhang and Peng, 2015a; Zhang and Peng, 2015b; Cruz et al., 2015b). On the other hand, non-swelling clays such as kaolinite will become effective above 10% of solid percentage (see Figure 12 for the difference).

Osmotic and crystalline swelling of smectites (i.e. montmorillonite) produces a gelatinous sludge when hydrated and swells by more than twenty times of its original size (Luckham and Rossi, 1999). While kaolin-type clays the effect of kaolin-type clay is attributed to their very fine particle size and different modes of particle aggregations explained in the section "aggregation behaviour of clays".

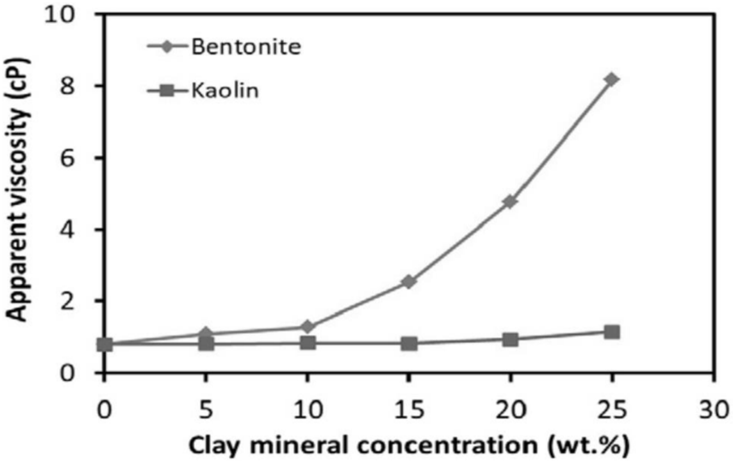


Figure 12. Apparent viscosity as a function of clay mineral concentration in Telfer clean ore at a shear rate of 100 s^{-1} (Wang, 2016)

4.1.2. Effect of clay particles on froth stability

Froth structure is defined by the froth stability and mobility and provides a significant insight of the visual assessment of a froth. Three common types of froth are found in literature: namely; ideal, runny and sticky/ viscous (Moolman et al., 1995a). An ideal froth is characterised as closely packed bubbles with clear spaces on top of some of the bubbles by a balance between too low viscosity with high coalescence and too stable with low coalescence. A runny froth with too high-water content and smaller average bubble size will cause the mineralized bubbles to rupture before they can be carried over the weir of the flotation cell and mineral particles become detached and fall back into the pulp (Moolman et al., 1995b). In a viscous froth, mineral content is too high in the surface froth with large bubbles, without the little spaces on top of the bubbles (Moolman et al., 1996; Wang et al., 2015).

Froth stability is the rate of bubble coalescence and bubble bursting. Froths characterised by comparatively low coalescence and small average bubbles increase the recovery of attached particles as well as the recovery of gangue minerals by entrainment (Wang and Peng, 2013). The drainage rate of liquid in the froth phase is also impeded by the increasing froth stability leading to increased recovery of suspended gangue mineral particles entrained in the concentrate (Farrokhpay, 2011; Wang and Peng, 2014; Wang et al., 2015). An adequately stable froth is important for optimum flotation performance (Farrokhpay, 2011). Unstable bubbles in a froth will break and drop the collected mineral particles back in the pulp. An overly stable froth is difficult to handle and transport and result in higher entrainment and reduced concentrate grade (Basnayaka, 2018). Some important factor that can affect the froth behaviour include pH value, drainage, amount of solids in the froth and the frother concentration (Aktas et al., 2008; Farrokhpay, 2011). Two methods of froth stability measurement are found in literature (1) measuring the height of the froth column at the dynamic equilibrium of froth forming and decaying, (2) measuring the rate of decaying of froth (Basnayaka, 2018).

Available literature provides contradictory information on the influence of clay on the froth behaviour. Clay minerals are known to increase or decrease the froth stability. The adsorption of frother onto the clay mineral surfaces can decrease the froth stability (Miller et al., 1983). Clay aggregates can increase the solids in froth through entrainment leading to increased stability of the froth column. Froth stability was reported to increase in the vicinity of kaolin clay and to decrease by adding bentonite clay (Wang et al., 2015b). A decrease in froth stability in presence of bentonite can be attributed to increased apparent viscosity leading to poor dispersion of bubbles. While the rise in froth stability in presence of kaolin clay is attributed to the entrainment of kaolin particles. On contrary, a study by Farrokhpay et al., (2016) showed that both kaolin and bentonite increased the froth stability. The contradictory observations available in literature regarding the impact of clay on froth stability, demand more in depth and comprehensive investigation to validate and clarify the effects (Basnayaka, 2018).

4.1.3. Mechanical entrainment

Entrainment is a mechanical mass transfer process that takes place simultaneously along with true flotation during mineral flotation. During entrainment, particles suspended in water between bubbles are carried into the flotation froth to the bottom of the froth column and subsequently transferred to the concentrate (Gaudin, 1957; Wang et al., 2015a). Entrainment does not involve chemical selectivity like true flotation where a direct attachment between particles and bubbles takes place. Entrainment is a two-step process, first the particles in the region just below the pulp/ froth interface rise upwards to the froth phase and then the particles entrained in the froth get transported to the concentrate lauder with water (Wang et al., 2015). Both valuable and gangue minerals experience entrainment but the entrainment of gangue particles reduce the concentrate grade (Basnayaka et al., 2017). Important factor affecting entrainment include water recovery, particle shape, particle size, solid percentage, gas flow rate, rheology and the froth structure, particle size and froth stability being predominant (Smith and Warren, 1989; Wang et al., 2015a).

Entrainment of clay particles into the concentrate can mainly be attributed to the very fine particle size. Particles less than 30 µm have significant potential to be entrained (Smith and Warren, 1989). Another study specifies the particle size as smaller than 50 µm for ready recovery by entrainment (Wang et al., 2015). The normal size range of clay mineral particles is between 2-10 µm, making them inevitable for entrainment. Furthermore, some recent studies have revealed that clay network structures are an added factor to enhance the clay entrainment (Cruz et al. 2015b, 2015c; Zhang et al., 2015b; Wang et al., 2015; Basnayaka, 2018).

In a study of copper-gold flotation, it was observed that the entrainment of kaolinite was due to the formation of loose edge-edge association of kaolin aggregates in the suspension (Zhang et al., 2015b). These E-E and E-F kaolin aggregations were more susceptible to transfer into froth due to the low density of voluminous honeycomb structure (Cruz et al., 2015a; Chen and Peng, 2018). Contrary to flotation recovery where bentonite clay demonstrates more adverse effects, it exhibits a lesser impact in terms of entrainment (Zhang and Peng 2015a; Zhang et al., 2015b; Wang et al., 2015; Basnayaka, 2018).

4.1.4. Slime coating effect of fine clay particles

Slime coating is another negative effect of fine clay particles that becomes of profound importance hindering the flotation process performance. The faces of clay mineral particles (basal planes) have a negative charge due to isomorphous substitution and is independent of the solution pH whereas charges on the edges are pH dependant (Schoonheydt and Johnston, 2006). However, clay particles carry a net negative charge under most pH conditions of flotation. Therefore, electrostatic attraction is developed between the clay particles and the positively charged surface of valuable minerals giving rise to slime coating of the mineral surface. As a result, the adsorption of reagents is restricted preventing the bubble particle attachment.

The negative surface charge of sulfide minerals (pyrite, chalcopyrite) does not allow surface coating by negatively charged clay particles (Chen and Peng, 2018). But it has been observed that oxidization makes sulfide surfaces positively charged permitting this coating to occur. The flotation efficiency of galena, coal, and bitumen flotation was reported to be redcued due to slime coating of clays (Arnold and Aplan, 1986a; Quast et al., 2008; Tao et al., 2010). In another study by Peng and Zhao (2011), it was found that chalcocite flotation was impeded due to slime coating of bentonite particles as the surfaces of chalcocite particles were oxidised during grinding and turned positively charged. On the other hand, chalcopyrite was not oxidized to the level of chalcocite, not allowing the bentonite coating at investigated pH levels. A similar response from kaolinite clays was observed in chalcocite recovery (Zhao and Peng, 2014). A significant reduction in flotation recovery of galena was observed at pH 5 as compared with pH 10 attributed to negative effects of slime coating of bentonite (Chen et al., 2017a).

4.2. Dewatering performance

Thickening is one of the widely used dewatering techniques to remove water from solids. The basic principle involved is the gravitational sedimentation of particles within a cylindrical tank, where the thickened slurry settles as the underflow, and the clarified liquid overflows from the peripheral launder (Wills and Napier-Munn, 2006). A typical thickener tank is strategically designed with one or two radial arms to rake the solids towards the centre leading them to the outlet, giving an efficient slurry consolidation and separation. Additives known as “flocculants” are commonly used to improve aggregation of particles, contributing to more effective separation (Basnayaka, 2018).

An optimal thickening process performance demands a faster settling behaviour of solids. However, clay minerals in tailing slurries of hydrometallurgical processes tend to impair settling rates (Mpofu et al., 2004; McFarlane et al., 2005; Harris et al., 2018; Liu et al., 2018) by reducing the terminal velocities due to the fine particle size, anisotropic shape, and low density of clay minerals. Particularly, smectite type clays exhibit extremely low settling rates in water environment due to their high swelling capacity. Presence of swelled clay increases the viscosity of thickener underflow and makes the pumping of slurries a challenging process (Mpofu et al., 2005). Another problem encountered by the thickener tank is the overflow with high solid content that contaminates the downstream processes with solids and reduces the efficiency (Connelly, 2011; Basnayaka, 2018). Addition of polymer flocculants to flocculate the slow settling particles is found to be inefficient for clay-containing slurries, especially in the presence of smectite clays (i.e. montmorillonite) (Addai-Mensah et al., 2007).

Filtration is another widely adopted dewatering technique employed in the mineral processing industry where a pressure difference is applied to a slurry through a filter medium, typically a filter cloth, causing solids to be retained within the system. Filtration rate is significantly hindered by the presence of very fine particles as they tend to reduce the porosity and permeability of the formed filter cake, resulting in low filterability (Besra et al., 1999). A reduced filterability negatively impacts the throughput rates of large-scale mineral processing operations, such as those in the iron ore industry. Additionally, the amount of moisture retained in the filter cake is of paramount importance, particularly in the context of transportation and storage. High retained moisture not only increases transportation costs but also poses a risk of tailing dam failure (De Kretser and Boger, 1992).

Even a small amount of clay minerals can significantly reduce the filtration rate due to their unique properties, such as anisotropic shape, very fine particle size, and swelling characteristics. The existing literature provides insufficient information on the specific effects of clay minerals on filtration performance. Although, it is known that even small amount of clay minerals can significantly reduce the filtration rate due to their unique properties of fine particle size, anisotropic shape, swelling characteristics and network formation tendency, but the influence of different types of clay on filtration may vary, as each clay type possesses its distinct properties. For example, only at high solid percentages, the very fine kaolin clay particles can reduce the permeability and filtration efficiency by reducing the effective flow diameter (Aksu et al., 2015). On the other hand, bentonite clay can impede filtration performance by increasing retained moisture and reducing the filtration rate even at very small amounts. These effects primarily arise from the significant swelling of bentonite particles, which can swell by over twenty times due to hydration (Aksu et al., 2015).

4.3. Effect of clay minerals on gravity separation

Gravity separator devices employ the difference in densities among feed materials to effectively separate valuable minerals. Knelson and Falcon concentrators are widely used examples of centrifugal gravity concentrators in modern days due to their environmental friendliness and cost-effective installation and operation. The Knelson or Falcon concentrators find their most common application in the gold processing industry, because of their remarkable efficiency in recovering up to 96% of free liberated gold with a size coarser than 30µm (Silva, 1986).

Although, the alteration of slurry rheology in the presence of clay is known to reduce the settling rates of particles in highly viscous environment leading to a reduced efficiency of gravity separation methods, but the influence of clays on gravity separation techniques remains an area with limited research. The sensitivity of gravity concentration devices such as jigs, tables, and spirals is adversely affected by an increase in apparent viscosity leading to reduced settling rates of particles (Wills and Napier-Munn, 2006).

The increased viscosity of clay-containing minerals suspensions can affect the efficiency of gravity separation devices (Wills and Napier-Munn, 2006). The voluminous structures formed in clay-containing suspension can hinder the percolation of pregnant solutions during heap leching (Tremolada et al., 2010; Connelly, 2011). Preg-robbing is also of concern that is associated with clayey ores. The low settling rates of clay-containing ores can lead to the overflowing water with high solid content in thickener tanks, contaminating downstream processes like solvent extraction (Connelly, 2011). Moreover, pumping of clay-containing mineral suspensions can also be challenging as the elevated viscosity of the slurry in thickener underflows can hinder the pumping operation (Mpofu et al., 2004).

Despite limited research, some studies suggest that centrifugal gravity concentrators can be effectively used in de-sliming of clay-containing ores. Lyubomir et al., (1993) reported that clay minerals, being less dense materials, can be separated from denser materials when subjected to high shear rates and agitation in centrifugal gravity concentrators.

The Knelson concentrator finds extensive application in present processing plants, especially in the gold mining industry. Two methods have been defined in literature to assess the performance evaluation of Knelson concentrators; namely, GRG (Gravity Recoverable Gold) test, introduced by Laplante et al. (2000) and another method involves the use of performance curves and performance criterion, as proposed by Coulter and Subasinghe (2004). The performance of Knelson concentrator was found to be unaffected by the presence of bentonite clay particles. No significant influence of presence of any type of clay was observed by Basnayaka (2020). A possible reason can be that the clay particles did not enter the concentrated bed inside the concentrate bowl but were rejected to the tailings instead.

5. Mitigation of negative effect of clays on mineral processing

Researchers have explored various remedial measures to alleviate the negative effects of clay in minerals processing. These include addressing issues like slime coating, modifying pulp rheology, and controlling entrainment, all of which contribute to poor process performance. For example, to achieve better flotation performance, coated clay particles must be removed from valuable mineral either chemically or mechanically. Three techniques of mechanical removal of coated particles are found in literature i.e. i) high-intensity agitation, ii) hydrocyclone desliming, iii) ultrasonic vibration. (Yu et al., 2017a, 2017b) reported improvement in flotation performance of coal by employing high-intensity agitation in the conditioning stage of the kaolin-containing pulp. A further increase in clay coating was observed when the agitation was less than the optimal value.

Using hydrocyclones is a common practice to remove coated clay particles from before flotation. For example, a significant increase in the flotation of boron minerals was observed by Celik et al. (1998) when hydrocyclone was used for desliming of boron minerals, that were heavily coated with clay minerals. A high shear environment was also found to assist the removal of coated clay particles (Oats et al., 2010) as well as ultrasonic treatment is another beneficial physical method to remove the coated clay particles.

Use of chemical dispersants is another useful method to restrict the slime coating by incorporating repulsive forces between the minerals and the clay particles. For example, coal flotation from clay containing ore was improved by using an inorganic anionic dispersant known as lignosulfonate (Liu and Peng, 2015). Lignosulfonate was also found effective by Wei et al. (2013) while working with clay containing copper-gold ore flotation. Another study showed that slime coating can be reduced by using polyaminoaldehyde, a polymer of low molecular weight that acts as clay binder (Tao et al., 2010).

Increased apparent viscosity and the yield caused by the clay particles can be dealt with by adding inorganic dispersants to improve the flotation performance. For example, addition of sodium polyphosphate as a dispersant notably lowered the slurry viscosity of a kaolin suspension (Papo et al., 2002). Similarly, another study showed significant reduction in viscosity of bentonite-containing slurry, by using polyphosphate dispersant (Goh et al., 2011), especially at higher pH levels. Furthermore, Cruz et al. (2015a, 2015c) reported slurry modification, leading to an improvement in flotation performance in the presence of electrolytes. Commercially available biopolymers are also useful dispersants, that are commonly used for the flotation of clay-containing mineral suspensions. Addition of PIONERA F-100 biopolymer to the flotation circuits has been reported to improve the gold recovery by 5%.

Mechanical entrainment of clay particles occurs mainly due to the fine particle size and the low-density voluminous structures, that means an aggregated denser clay particle would have lesser chance of entrainment. Therefore, the addition of polymer flocculants is used to encourage the aggregation of fine clay particles to denser structures. For examples, by adding high molecular weight polyethylene oxide flocculent to kaolin containing pulp, Liu and Peng (2014) observed a significant reduction in kaolin particles entrainment attributed to the aggregation.

5.1. Effect of Ca^{2+}

Studies have shown that adding Ca^{2+} ions to clay-containing slurries significantly reduces the swelling properties of smectite-containing ores, thereby lowering slurry viscosity (Basnayaka et al., 2017). The presence of Ca^{2+} ions improves the rheological properties of these slurries, mitigating the detrimental effects of various clays during flotation (Basnayaka et al., 2017) and fine particle filtration (Basnayaka et al., 2018).

Conversely, the presence of Ca^{2+} ions in kaolinite containing ores increased the slurry's shear stress and viscosity attributed to the formation of kaolin agglomerates in the presence of Ca^{2+}

(Cruz et al., 2013). The double layer around kaolin particles was influenced by the addition of Ca^{2+} ions due to the replacement of existing monovalent ions with bivalent Ca^{2+}.

Bivalent cations are known to create a thinner electrical double layer compared to monovalent cations. This thinner electrical double-layer brings particles closer together, initiating agglomeration processes. Bivalent cations create a thinner electrical double layer than monovalent cations (Pavel, 2002), causing particles to come closer together and initiate agglomeration. These agglomerates retain significant amounts of water (Pavel, 2002), reducing the water layers between particles and increasing the slurry viscosity (Barbato et al., 2008).

Basnayaka et al. (2018) studied the negative effects of presence of clay minerals on the filtration efficiency of fine particle slurries during their research work. They investigated the effect of addition of hydrophobic reagent, DAH (i.e. dodecylamin hydrochloride) and Ca^{2+} ions on the filtration efficiency of clay (bentonite and kaolin) containing pyritic gold ore (Basnayaka et al., 2018). Studies by (Basnayaka et al., 2018) showed improvement in filtration rate of kaolin containing ores by adding DAH while the addition of Ca^{2+} was found beneficial for bentonite containing ores.

5.2. Effect of pH

It has been observed that as the pH of kaolinite containing suspension is raised from 5 to 6, the initial F-F lamellar tactoid formation of lower suspension shear-yield stress is changed to E-F formation of thicker edge surfaces with a maximum shear-yield stress at pH 5-5.5 (Wang et al., 2015, Wang, 2016). A further increase in pH, decreases the F-F and E-F association and the shear-yield stress attributed to lower magnitude of surface charge density on edge surfaces and face surfaces leading to a complete dispersion with a minimal shear-yield stress (Gupta et al., 2011). Further study of the influence of pH on the viscosity of 35 wt.% kaolinite suspension revealed that the viscosity of kaolinite suspension exhibited a shear thinning behaviour at both pH 3.4 and 8.3. It should be noted that pH 8.3 resulted in a significantly higher viscosity than pH 3.4 illustrating a higher aggregation of kaolinite suspension at pH 3.4 and higher dispersion at pH 8.3 (Zhang et al., 2012).

During the study of the aggregation behaviour of Na-bentonite suspensions as a function of pH at constant ionic strength, F-F association were found to be virtually independent of pH while

E-E associations, at the p.z.c edges (pH~7) were observed to be most attractive. In suspensions with sufficiently high ionic strength, mainly E-E interaction was responsible for formation of "house-of-cards" gel structure. Steady-state viscometry also confirmed a significant decrease in yield stress, by up to an order of magnitude, from pH 3 to pH 7. However, the rate of decrease was much slower in the pH range of 7 to 11 (Duran et al., 2000).

5.3. Effect of dispersants

Polymers, while acting as dispersants, have the potential to modify the strength of the interparticle forces and rheological behaviour of mineral suspensions through their adsorption on clay minerals that occur both at basal and edge surfaces of clay minerals (Lee et al., 1991; Wang, 2016), leading to modification in the network structures of clay minerals. Dispersant (polymers) keep them apart by producing repulsive forces between the particles through adsorption on the particle surface. For example, Goh et al. (2011) observed a smaller yield stress and complete dispersion of bentonite slurry a pH > 6 by adding polyphosphate attributed to a reduction in the attractive forces between clay particles. Another study of using sodium polyphosphate (PP) and tripolyphosphate (TPP) as dispersing agents for pure kaolin suspensions by Papo et al. (2002) showed a steady decay in viscosity by increasing the amounts of both dispersants. A further increase in dispersants' amount beyond the adsorption saturation limit resulted in destabilization, flocculation and higher viscosity due to suspension coagulation due to excess concentration of dispersant in the solution.

Polymers can perform as flocculants also. In this role they tend to induce clay aggregates by neutralising the charges and connecting the particles. A number of studies are available on using polymers as flocculants (Zbik, 2006; Nasser and James, 2007; Tunc et al., 2008; Du et al., 2010). The dewatering behaviour of the smectite clays was improved by adding polyacrylamide-acrylate copolymer (PAM) together with adequate concentrations of hydrolysable metal ions (Ca^{2+}, Mn^{2+}) (Mpofu et al., 2005). Another study showed that the addition of non-ionic polyethylene oxide flocculant improved dewatering of smectite clays (Addai-Mensah et al., 2007). Electroosmotic dewatering also proved to be beneficial for the dewatering behaviour of clay containing slurries (Harris et al., 2018; Basnayaka, 2018).

Addition of filtering aids (i.e. surfactants and flocculants) can effectively reduce the adverse effects of fine particles on filtration performance (Sastry et al., 1983). Studies have shown promising results in iron-containing ore filtering processes where polyacrylamide flocculants were used to improve filtration rates and reduce moisture content (Amarante et al., 2002). Polyacrylamide flocculants aid in agglomerating bentonite clay particles, leading to an improved filtration rate (Hocine et al., 2017).

Additionally, Hung et al. (2017) reported that the filtration of kaolin clay can be increased by using cationic hydrophobic reagents. An electrostatic bonding is promoted between the cationic hydrophobic molecules particles and the negative surfaces of kaolin clay particles, making kaolin clay particles surfaces hydrophobic. Thus a higher filtration rate is achieved as a result of repulsion between water and the hydrophobic clay surfaces (Hung et al., 2017).

5.4. Effect of salts

The ionic strength of the solution plays a crucial role in the stability of the network structure of clay mineral particles. It was observed by Cryo-SEM that in case of tap water, kaolinite layers formed elongated strings of E-E association that were not closely joined. On the other hand, kaolinite layers aggregated in sea water as cross-linked three-dimensional F-F orientations through E-E and E-F associations, leading to high porosity, as shown in Figure 13 (Zhang et al., 2015b).

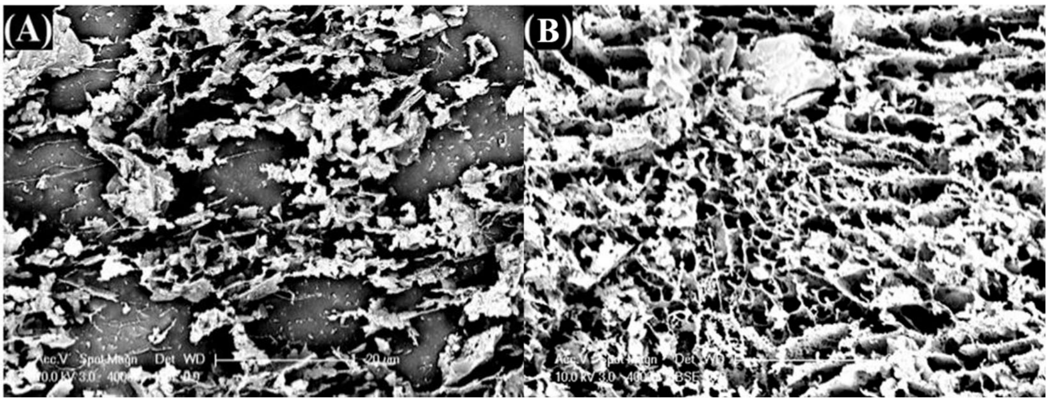


Figure 13. Cryo-SEM images of pulp in the presence of 15 wt.% kaolinite at the magnification of 4000× in tap water (A) and sea water (B) (Wang, 2016).

As shown by Lagaly and Ziesmer (2003) for montmorillonite, the absence of salts or very low salt concentrations, results in increased viscosity and yield stress. The presence of salts leads to reduced viscosity by increasing the freedom of the particles and by decreasing the thickness of the diffuse ionic layer (Figure 14). It is attributed to the adsorption of cations that reduces the attractive E(+)-F(-) association, increase the net repulsive F-F association with a lower yield stress and break the network structure (Lagaly and Ziesmer, 2003).

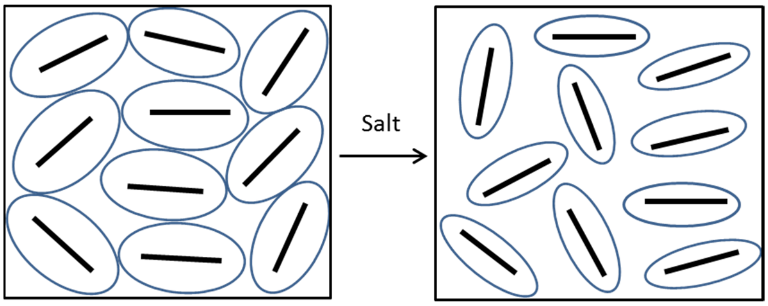


Figure 14. When the thickness of the diffuse ionic layers decreases at higher salt concentration, the particles again become more mobile (Permien and Lagaly, 1994).

In a study conducted by Heller and Keren (2001), it was observed that a free electrolyte clay suspension exhibited a notably high apparent viscosity due to the presence of E-E associations between Na-rich montmorillonite platelets. However, at higher concentrations of NaCl, F-F associations became dominant, resulting in a lower apparent viscosity. Similarly, Suzuki et al. (2005) observed a decrease in the expansion ratio of bentonite aggregates with an increasing concentration of NaCl. The introduction of even small amounts of calcium ions had a significant impact on the type of aggregation attributed to their participation in the lamellae and stacks of layers to promote band-like networks (Figure 2.11B). At higher concentration of calcium ions, the bands contracted, leading to the formation of smaller aggregates and eventually particle-like structures, causing disruption of the network (Figure 15) (Permien and Lagaly, 1994).

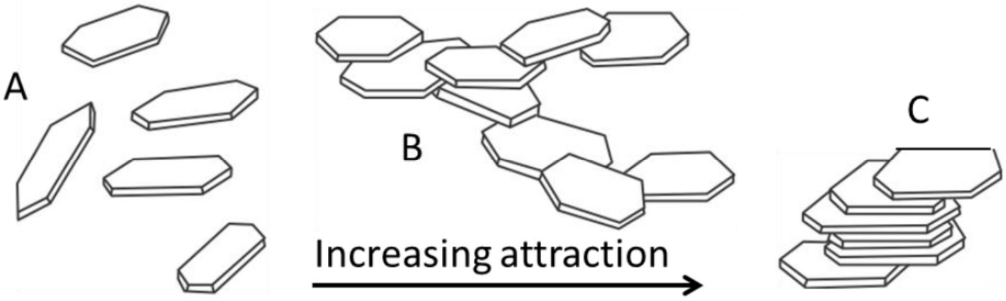


Figure 15. Aggregation of the clay mineral layers with increasing attraction: (A) single layers, (B) band-type aggregates, (C) compact particles (Permien and Lagaly, 1994).

Cation exchange plays an important role when it comes to the interaction between clay, especially 2:1 phyllosilicates are profoundly influenced by the cation exchange selectivity which is largely controlled a factors like the type, valence, charge density, size, and concentration of cations (Ho and Lee, 1998; Herbert et al., 2008).

Usually, cations with higher valence have a greater capacity to replace other cations, while the replacing capacity increases with size for cations of same valence. Studies have shown that montmorillonite exhibits a preference for Ca^{2+} and Mg^{2+} over Na^{+}, and a preference for Ca^{2+}over Mg^{2+} (Fletcher et al., 1984). The affinity of montmorillonite was observed to be more for Ca^{2+} and K^{+} than for Na^{+} (Di Maio, 1996). The order for cation exchanging capacity is typically defined as: $Na^{+} < K^{+} < Mg^{2+} < Ca^{2+}$ (Pusch, 2001). Therefore, Ca^{2+} will replace Na^{+} when Na-bentonite is exposed to Ca^{2+} solutions converting it to Ca-bentonite (Chun-Ming et al., 2013). Attraction between the particles is increased when Na^{+} ions are replaced by K^{+} and Cs^{+} ions, attributed to strong adsorption of these cations in the Stern layer (Liu and Lu, 2006b). Selectivity for the weakly hydrated cation K^{+} is extensively increased due to the layer collapse (Laird and Shang, 1997). A study by Shainberg et al. (1988) showed that Mg^{2+} was less effective than Ca^{2+} to prevent the collapse of the aggregates.

6. Conclusions

This literature review confirms that the majority of studies on the impact of clays on mineral processing mainly focus on flotation. Clays primarily cause issues by altering pulp rheology and causing slime coating, which affect flotation efficiency. These effects vary with the type of clay. Although some mechanisms are understood, current solutions are insufficient, especially for clays that swell and change slurry rheology. Research on clays' impact on complex ore flotation, particularly minerals with different densities, is lacking. Further research is needed to find effective solutions to mitigate clay's adverse effects on mineral processing. Therefore, in this thesis for this study work we have selected two minerals with different densities (galena (SG 7.6g/cc) and sphalerite (SG 3.9g/cc)) were selected for the study of rheological behaviours as impacted by the presence of two types of clays (kaolin and Na-bentonite). The study presented possible solutions to mitigate the negative effects caused by the presence of clays and introduced new approaches to address these challenges. Additionally, the existing literature provides minimal to no information on the adverse effects of clay minerals on grinding and drying efficiencies in mineral processing. Therefore, this thesis examines the grinding and drying performances of synthetic ores with kaolin and Na-bentonite, explores the possible mechanisms behind these effects, and proposes mitigating techniques.

7. References

Abend, S., Lagaly, G., 2000. Sol-gel transitions of sodium montmorillonite dispersions. Appl. Clay Sci. 16, 201-227.

Addai-Mensah, J., 2007. Enhanced flocculation and dewatering of clay mineral dispersions. Powder Technol. 179, 73–78.

Aksu, I., Bazilevskay, E., Karpyn, Z.T., 2015. Swelling of clay minerals in unconsolidated porous media and its impact on permeability. Geo Res. J. 7, 1–13.

Aktas, Z., Cilliers, J.J., Banford, A.W., 2008. Dynamic froth stability: particle size, airflow rate and conditioning time effects. Int. J. Miner. Process. 87, 65–71.

Amarante, S.C., Araujo, A.C., Valadao, G.E.S., Peres, A.E.C., 2002. Cake dewatering of some iron ore industrial products. Miner. Metall. Process 19 (3), 161.

Arnold, B. J., Aplan, F. F., 1986b. The effect of clay slimes on coal flotation, part II: the role of water quality. International Journal of Mineral Processing, 17(3–4), pp. 243–260.

Arnold, B., Aplan, F., 1986a. The effect of clay slimes on coal flotation, part I: the nature of the clay. International Journal of Mineral Processing, 17(3), 225–242.

Ata, S., Ahmed, N., Jameson, G.J., 2004. The effect of hydrophobicity on the drainage of gangue minerals in flotation froths. Miner. Eng. 17, 897-901.

Baik, M.H., Lee, S.Y., 2010. Colloidal stability of bentonite clay considering surface charge properties as a function of pH and ionic strength. Journal of Industrial and Engineering Chemistry 16, 837-841.

Bakker, C.W., Meyer, C.J., Deglon, D.A., 2009. Numerical modelling of Non-Newtonian slurry in a mechanical flotation cell. Miner. Eng. 22 (11), 944–950.

Bakker, C.W., Meyer, C.J., Deglon, D.A., 2010. The development of a cavern model for mechanical flotation cells. Miner. Eng. 23 (11–13), 968–972.

Barbato, C.N., Nele, M., Pinto, J.C., Silvia, C. A. F., 2008. Studies of kaolin rheology. X Jornadas Argentinas de Tratamiento de Minerales. San Juan, Argentina. 1-10.

Barclay, L., Ottewill, R., 1970. Measurement of forces between colloidal particles, Discussions Faraday Society 1 138-171.

Barnes, H.A., 1999. The yield stress—a review or ‘παντα ρει’—everything flows? J. Non-Newtonian Fluid Mech. 81, 133-178.

Basnayaka, L., 2018. Influence of clay on mineral processing techniques, PhD Thesis. Curtin University.

Basnayaka, L., Albijanic, B., Subasinghe, N., 2020. Performance evaluation of processing clay-containing ore in Knelson concentrator. Miner. Eng. 152, 106372.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2017. Influence of clays on the slurry rheology and flotation of a pyritic gold ore. Appl. Clay Sci. 136, 230–238.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2018. Influence of clays on fine particle filtration. Appl. Clay Sci. 156, 45–52.

Bemer R. A., 1971. Principles of chemical sedimentology, International series in the earth & planatery sciences, Me Graw-Hill, 166.

Bergaya, F., Jaber, M., Lambert, J.-F., 2011. Clays and clay minerals. In Rubber-Clay Nanocomposites, M. Galimberti (Ed.). https://doi.org/10.1002/9781118092866.ch1

Bergaya, F., Theng, B.K.G., Lagaly, G., 2006. Handbook of clay science, Elsevier Science, Burlington.

Besra, L., Sengupta, D.K., Roy, S.K., 1999. Particle characteristics and their influence on dewatering of kaolin, calcite and quartz suspensions. Int. J. Miner. Process. 59, 89– 112.

Boija, R., Martin, A., Duran, M.M., Luque, Y.M., 1992. Kinetic study of the anerobic purification of a cheese factory waste water, Rev. Esp. Cienc Tecnol. Ailment. 32,19-32.

Bolt G.H., Bruggenwert, M.G.M., 1981. Composition of the soil:, Soil chemistry A: basic elements, Elsevier.

Brigatti, M.F., Gal´an, E., Theng, B.K.G., 2013. Chapter 2 – structure and mineralogy of clay minerals. In: Faïza, B., Gerhard, L. (Eds.), Developments in Clay Science, 5. Elsevier, Amsterdam, Netherlands, 21–81.

Bremmell, K. E., Fornasiero, D., and Ralston, J., 2005, “Pentlanditelizardite interactions and implications for their separation by flotation.” Colloids and Surfaces A: Physicochemical and Engineering

Aspects, 252(2–3), pp. 207–212

Bulatovic, S.M., 2007. Handbook of flotation reagents: chemistry, theory and practice: Flotation of sulphide ores Boston. Elsevier, Oxford.

Burdukova, E., Becker, M., Ndlovu, B., Mokgethi, B., Deglon, D., 2008a. Relationship between slurry rheology and its mineralogical content, 24th Int. Minerals Processing Congress. China Scientific Book Service Co. Ltd., Beijing, China, pp. 2169-2178.

Celik, M.S., Elma, I., Hancer, M., Miller, J.D., 1998. Effect of insitu ultrasonic treatment on the floatability of slime coated colemanite. In: Proceedings of the International Mineral Processing 7th Symposium.

Chen, T., Zhao, Y., Li, H., Song, S., 2017a. Effects of colloidal montmorillonite particles on froth flotation of graphite, galena and fluorite. Physicochem. Probl. Mi. 53(2), 699–713.

Chen, X., Peng, Y., 2018. Managing clay minerals in froth flotation—a critical review. Miner. Process. Extr. Metall. Rev. 39(5), 289-307.

Chun-Ming, Z., Wei-Min, Y., Yong-Gui, C., Bao, C., Yu-Jun, C., 2013. Influence of salt solutions on the swelling pressure and hydraulic conductivity of compacted GMZ01 bentonite. Engineering Geology 166, 74-80.

Connelly, D., 2011. High clay ores: a mineral processing nightmare. Aust. J. Min. 28–29.

Coulter, T., Subasinghe, G.K.N., 2004. A mechanistic approach to modelling Knelson concentrators. Miner. Eng. 18, 9-17.

Craster, B., 1999. Studies of the modification of ion and water movement through clays and shales. Doctoral, Sheffield Hallam University (United Kingdom).

Cruz, N., Peng, Y. and Wightman, E., 2015a. Interactions of clay minerals in copper–gold flotation: Part 2 — Influence of some calcium bearing gangue minerals on the rheological behaviour. International Journal of Mineral Processing 141: 51-60.

Cruz, N., Peng, Y., Farrokhpay, S., Bradshaw, D., 2013. Interactions of clay minerals in copper-gold flotation: Part 1-Rheological properties of clay mineral suspensions in the presence of flotation reagents. Miner. Eng. 50-51, 30-37.

Cruz, N., Peng, Y., Wightman, E. and Xu, N., 2015c. The interaction of pH modifiers with kaolinite in copper–gold flotation. Minerals Engineering 84: 27-33.

Cruz, N., Peng, Y., Wightman, E., Xu, N., 2015b. The interaction of clay minerals with gypsum and its effects on copper–gold flotation. Miner. Eng. 77, 121-130

De Kretser, R.G., Boger, D.V., 1992. The compression, dewatering and rheology of slurried coal mine tailings. Proceedings 5th Australian Coal Science Conference, Newcastle, Australia, pp. 422–429

Deer, W.A., Howie, R.A., Zussman, J., 1992. An introduction to rock forming minerals. Longman Scientific & Technical, Essex.

Di Maio, C., 1996. Exposure of bentonite to salt solution: osmotic and mechanical effects. Geotechnique 46, 695-707.

Dippenaar, A., 1988. The effect of particles on the stability of flotation froth. (Report No. 81) IMM, South Africa

Dixon, J.B., Weed, S.B, 1989. Minerals in soils environnents, 2nd Edition, Soil Sci. Society of America, Madison, USA.

Du, J., Morris, G., Pushkarova, R.A., Smart, R.S.C., 2010. Effect of Surface Structure of Kaolinite on Aggregation, Settling Rate, and Bed Density. Langmuir 26, 13227-13235.

Duran, J.D.G., Ramos-Tejada, M.M., Arroyo, F.J., Gonzalez-Caballero, F., 2000. Rheological and electrokinetic properties of sodium montmorillonite suspensions - I. Rheological properties and interparticle energy of interaction. J. Colloid Interface Sci. 229, 107-117.

Eberl, D. D., Farmer, V. C., Barrer, R. M., 1984. Clay mineral formation and transformation in rocks and soils [and discussion]. Philos Trans R Soc Lond A 311(1517):241–257.

Edwards, C. R., Kipkie, W. B., and Agar, G. E., 1980, “The effect of slime coatings of the serpentine minerals, chrysotile and lizardite, on pentlandite flotation.” International Journal of Mineral Processing, 7(1), pp. 33–42.

Estabragh, A.R., Soltani, A., Javadi, A.A., 2020. Effect of pore water chemistry on the behaviour of a kaolin–bentonite mixture during drying and wetting cycles, European Journal of Environmental and Civil Engineering, 24:7, 895-914, DOI: 10.1080/19648189.2018.1428691

Farrokhpay, S., 2011. The significance of froth stability in mineral flotation- a review Adv. Colloid Interface Sci. 166, 1–7.

Farrokhpay, S., 2012. The importance of rheology in mineral flotation: a review. Miner.Eng. 36, 272–278.

Farrokhpay, S., Ndlovu, B., Bradshaw, D., 2016. Behaviour of swelling clays versus non-swelling clays in flotation. Miner. Eng, 96-97, pp. 59-66.

Fletcher, P., Sposito, G., Levesque, C.S., 1984. Sodium-Calcium-Magnesium Exchangereactions on a montmorillonitic soil .1. binary exchange-reactions. Soil Sci. Soc. Am. J. 48, 1016-1021.

Foley, N., 1999. Geology, Energy & Minerals Science Center. USGS. https://www.usgs.gov/publications/environmental-characteristics-clays-and-clay-mineral-deposits accessed on 1st July 2024

Fuerstenau, M.C., 1985. Chemistry of flotation. AIMME, New York.

Gaudin, A. M., 1957, Flotation, New York: McGraw-Hill.

Gaudin, A. M., Fuerstenau, D. W., Miaw, H. L., 1960. Slime-coatings in galena flotation. CIM Bulletin, 53, 3.

Glembotskii, V.A., Klassen, V.I., Plaksin, I.N., 1972. Flotation, primary sources, New York.

Goh, R., Leong, Y.-K., Lehane, B., 2011. Bentonite slurries—zeta potential, yield stress, adsorbed additive and time-dependent behaviour. Rheologica Acta, 50(1), 29–38.

Grim, R.E., 1968. Clay Minerology, 2nd ed. McGraw-Hill, NY, 596.

Gupta, V., Hampton, M.A., Stokes, J.R., Nguyen, A.V., Miller, J.D., 2011. Particle interactions in kaolinite suspensions and corresponding aggregate structures. J. Colloid Interface Sci. 359, 95-103. https://doi.org/10.1016/j.jcis.2011.03.043.

Gupta, V., Miller, J. D., 2010. Surface force measurements at the basal planes of ordered kaolinite particles. J. Colloid Interface Sci. 344, 362−371. https://doi.org/10.1016/j.jcis.2010.01.012.

Hall P.L., 1987. Clays, their significance, properties origins and uses, In: A handbook of determinative methods in clay mineralogy, Ed. M.J. Wilson, Blackie, 22.

Harris, A., Nosrati, A., Addai-Mensah, J., 2018. The influence of pulp and interfacial chemistry and mode of electrical power input on electroosmotic dewatering of Naexchanged smectite dispersions. Appl Clay Sci. 162, 214-222.

He, M.Z., Wang, Y.M., Forssberg, E., 2004. Slurry rheology in wet ultrafine grinding of industrial minerals: a review. Powder Technol. 147, 94-112.

Heller, H., Keren, R., 2001. Rheology of Na-rich montmorillonite suspension as affected by electrolyte concentration and shear rate. Clays Clay Miner. 49, 286-291.

Helmy, A.K., 1998. The limited swelling of montmorillonite, Journal of Colloid and Interface Science, 207,128-129.

Herbert, H.-J., Kasbohm, J., Sprenger, H., Maria Fernandez, A., Reichelt, C., 2008. Swelling pressures of MX-80 bentonite in solutions of different ionic strength. Physics and Chemistry of the Earth 33, S327-S342.

Ho, C.C., Lee, K.C., 1998. The role of metallic cations on the colloidal stability of tin tailings slurries. Colloids and Surfaces a-Physicochemical and Engineering Aspects 141, 19-27.

Hocine, T., Benhabib, K., Bouras, B., 2017. Comparative study between new polyacrylamide-based copolymer poly(AM-4VP) and a cationic commercial flocculant: application in turbidity removal on semi-industrial pilot. J. Polym. Environ

Huggett, J.M., 2005. CLAY MINERALS, Editor(s): Richard C. Selley, L. Robin M. Cocks, Ian R. Plimer, Encyclopedia of Geology, Elsevier, 9780123693969, 358-365. https://doi.org/10.1016/B0-12-369396-9/00273-2.

Hung, K., Pan, L., Yoon, R.H., 2017. A capillary flow model for filtration. Min. Eng. 115,88–96.

Hunter, R.J., 1982. Adv. Colloid Interf. Sci. 17, 197.

Hunter, R.J., 1987. Foundations of colloid science, 1, Oxford Science Publications, 332.

Hunter, R.J., 2000. Foundations of colloid science. Oxford University Press, Oxford.

Hurlbut, C.S., Sharp, W.E., 1998. Dana’s minerals and how to study them (After Edward Salisbury Dana), fourth ed. John Wiley & Sons, Inc., New York, 248–257.

Ives, K.J., (ed.) 1984. The scientific basis of flotation, Martinus Nijoff Publishers, The Hague.

Jeldres, R. I., Uribe, L., Cisternas, L. A., Gutierrez, L., Leiva, W. H., Valenzuela, J., 2019. The effect of clay minerals on the process of flotation of copper ores - A critical review. Applied Clay Science 170, 57-69.

Johnson S.B., Franks G.V., Scales P.J., Boger D.V., Healy T.W., 2000. Surface chemistry-rheology relationship in concentrated mineral suspension. International Journal of Mineral Processing 58:267-304

Jones, M.H., Woodcock, J.T., 1983. Decomposition of alkyl dixanthogens in aqueous solutions, Int. J. Min. Proc., 10, 1.

Jorjani, E., Barkhordar, H.R., Tayebi Khormani, M., Fazeli, A., 2011. Effects of aluminosilicate minerals on copper–molybdenum flotation from Sarcheshmeh porphyry ores. Miner. Eng. 24, 754–759.

Keller, W.D., 1970. Environmental aspects of clay minerals. J. Sediment. Petrol., 40: 788--813.

King, R.P., 1982. The principles of flotation, S. fr. I.M.M.

King, R.P., 2002. Introduction to practical fluid flow. First ed. Butterworth Heinemann, Oxford.

Klimpel, R.R., 1999. The selection of wet grinding chemical additives based on slurry rheology control. Powder Technol. 105, 430-435.

Krekeler, M.P., 2004. Improved constraints on sedimentary environments of palygorskite deposits of the Hawthorne formation, Southern Georgia, from a detailed study of a core. Clays Clay Miner. 52, 253–262.

Kumari, N., Mohan, C., 2021. Basics of clay minerals and their characteristic properties. 10.5772/intechopen.97672.

Lagaly, G., 1989. Principles of flow of kaolin and bentonite dispersions. Appl. Clay Sci. 4, 105-123.

Lagaly, G., Ziesmer, S., 2003. Colloid chemistry of clay minerals: the coagulation of montmorillonite dispersions. Adv. Colloid Interface Sci. 100, 105-128.

Laird, D.A., Shang, C., 1997. Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 phyllosilicates. Clays Clay Miner. 45, 681-689.

Laplante, A. R., Woodcock, F. C., Huang, L., 2000. A laboratory procedure to characterise gravity recoverable gold, Trans. Soc. Min. Metall. Explor. 308, 53–59.

Lee, L.T., Rahbari, R., Lecourtier, J., Chauveteau, G., 1991. Adsorption of polyacrylamides on the different faces of kaolinites. J. Colloid Interface Sci. 147, 351-357.

Leja, J., 1982. Surface chemistry of froth flotation, Plenum Press, New York.

Liu, D., Edraki, M., Berry, L., 2018. Investigating the settling behaviour of saline tailing suspensions using kaolinite, bentonite, and illite clay minerals. Powder Technol. 386, 228-236

Liu, D., Peng, Y., 2014. Reducing the entrainment of clay minerals in flotation using tap and saline water. Powder Technol. 253, 216–222.

Liu, D., Peng, Y., 2014. Reducing the entrainment of clay minerals in flotation using tap and saline water." Powder Technology, 253, 216–222.

Liu, D., Peng, Y., 2015. Understanding different roles of lignosulfonate in dispersing clay minerals in coal flotation using deionised water and saline water. Fuel, 142, 235–242.

Liu, X.D., Lu, X.C., 2006b. A Thermodynamic Understanding of Clay-Swelling Inhibition by Potassium Ions. Angewandte Chemie International Edition 45, 6300-6303.

Low, P.F., 1987. The clay water interface. In Proceedings International Clay Conference, Denver, Colarado. Eds: L.G Schultz and H. van Olphen, 247-256.

Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite suspensions. Adv. Colloid Interf. Sci. 82 (1–3), 43–92.

Lyubomir; K., Luis, B., Metodi, M., 1993. Sulphides and gold recovery from slime by gravity methods at the Asarel refining factory. Godishnik na Minno-Geolozhkiya Universiteta = Annual of the University of Mining and Geology 39, Part 2(Pages 123- 128.

Madsen M., Schlundt, J., 1989. Low technology water purification by bentonite clay flocculation as performed in Sudanese villages: bacteriological examinations, Water Research, 23, 873-882.

Mat, M., 2023. Clay minerals. Geologyscience. https://geologyscience.com/minerals/clay-minerals/#Uses_of_Clay_Minerals accessed on 1st July 2024.

McFarlane, A., Bremmell, K., Addai-Mensah, J., 2005. Microstructure, rheology and dewatering behaviour of smectite dispersions during orthokinetic flocculation. Miner. Eng. 18, 1173–1182.

Miller, J.D., Lin, C.L., Chang, S.S., 1983. MIBC adsorption at the coal/water interface. Colloids Surf. 7 (4), 351–355.

Mitchell, J.K., 1993. Fundamentals of soil behaviour, 2nd edition, John Wiley and Sons, 113-BO.

Moolman, D., Aldrich, C., Van Deventer, J., Bradshaw, D., 1995a. The interpretation of flotation froth surfaces by using digital image analysis and neural networks. Chem. Eng. Sci. 50, 3501-3513.

Moolman, D.W., Aldrich, C., van Deventer, J.S.J., Stange, W.W., 1995b. The classification of froth structures in a copper flotation plant by means of a neural net. Int. J. Miner. Process. 43, 193-208.

Moolman, D.W., Eksteen, J.J., Aldrich, C., vanDeventer, J.S.J., 1996. The significance of flotation froth appearance for machine vision control. Int. J. Miner. Process. 48, 135-158.

Mpofu, J.P., Ralston, J.A., 2004. Flocculation and dewatering behaviour of smectite dispersions: effect of polymer structure type, Minerals Engineering, 17 (3), 411-423, ISSN 0892-6875, https://doi.org/10.1016/j.mineng.2003.11.010.

Mpofu, P., Mensah, J.A., Ralston, J., 2005. Interfacial chemistry, particle interactionsand improved dewatering behaviour of smectite clay dispersions. Int. J. Miner. Process. 75,155–171.

Mueller, S., Llewellin, E.W., Mader, H.M., 2010. The rheology of suspensions of solid particles. Proc. Roy. Soc. A 466, 1201–1228.

Müller-Vonmoos, M., Løken, T., 1989. The shearing behaviour of clays. Appl. Clay Sci. 4, 125-141.

Murthy, V.N.S., 2002. Geotechnical engineering, principles and practices of soil mechanics and foundation engineering. Marcel Dekker. Inc.

Nasser, M.S., James, A.E., 2007. Effect of polyacrylamide polymers on floc size and rheological behaviour of kaolinite suspensions. Colloids and Surfaces a-Physicochemical and Engineering Aspects 301, 311-322.

Ndlovu, B., Becker, M., Forbes, E., Deglon, D., Franzidis, J.-P., 2011a. The influence of phyllosilicate mineralogy on the rheology of mineral slurries. Miner. Eng. 24, 1314-1322.

Ndlovu, B., Farrokhpay, S., Bradshaw, D., 2013. The effect of phyllosilicate minerals on mineral processing industry. Int. J. Miner. Process. 125, 149–156.

Ndlovu, B., Forbes, E., Farrokhpay, S., Becker, M., Bradshaw, D., Deglon, D., 2014. A preliminary rheological classification of phyllosilicate group minerals. Miner. Eng. 55, 190–200.

Ndlovu, B.N., Forbes, E., Becker, M., Deglon, D.A., Franzidis, J.P., Laskowski, J.S., 2011b. The effects of chrysotile mineralogical properties on the rheology of chrysotile suspensions. Miner. Eng. 24, 1004-1009.

Nelson, S.A., 2014. Weathering & clay minerals. Tulane University. EENS 2110.

Oats, W.J., Ozdemir, O., Nguyen, A.V., 2010. Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation. Miner. Eng. 23 (5), 413–419.

Papo, A., Piani, L., Ricceri, R., 2002. Sodium tripolyphosphate and polyphosphate as dispersing agents for kaolin suspensions: rheological characterization. Colloids and Surfaces A: Physicochemical and Engineering Aspects 201, 219-230.

Patra, P., Bhambhani, T., Nagaraj, D.R., Somasundaran, P., 2010. Effect of morphology of altered silicate minerals on metallurgical performance: transport of Mg silicates to the froth phase. In: Pawlik, M. (Ed.), Proceedings 8th UBC-McGill-UA International Symposium on the Fundamentals of Mineral Processing: Rheology and Processing of fine Particles. The Canadian Institute of Mining, Metallurgy and Petroleum,Vancouver, British Columbia, Canada, pp. 31–42.

Pavel, V., Zdeněk, C., Jiří, K., 2002. Thinning of kaolin slurry, Národní konference s mezinárodní úcastí Inženýrská Mechanika 13. – 16. 5., Svratka, Ceská republika

Peng, Y., and Zhao, S., 2011. The effect of surface oxidation of copper sulfide minerals on clay slime coating in flotation. Miner. Eng. 24(15), 1687–1693.

Permien, T., Lagaly, G., 1994. The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds. I: Flow behaviour of sodium-bentonite in water-alcohol. Clay Miner. 29, 751-760.

Pusch, R., 2001. Experimental study of the effect of high porewater salinity on the physical properties of a natural smectitic clay. SKB.

Quast, K., Ding, L., Ralston, J., Fornasiero, D., 2008. Effect of slime clay particles on coal flotation, in Proceedings of the Chemeca: Towards a Sustainable Australasia, Newcastle.

Rand, B., Melton, I.E., 1977. Particle interactions in aqueous kaolinite suspensions: I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. J. Colloid Interface Sci. 60 (2), 308–320.

Sastry, K.V.S., Kawulok-Englund, H.Y., Hosten, C., 1983. Comparative study of vacuum filtration behaviour of iron ore concentrate slurries, Min. Eng. 35 (10) 1432–1436

Schoonheydt, R., Johnston, C., 2006. Chapter 3 surface and interface chemistry of clay minerals. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science, first ed. Elsevier Science, Amsterdam, The Netherlands, 87–113.

Schulze, H.J., 1984. Physio-chemical elementary processes in flotation. Elsevier Science Publishing Co., Amsterdam.

Shabalala, N.Z.P., Harris, M., Filho, L.S.L., Deglon, D.A., 2011. Effect of slurry rheology on gas dispersion in a pilot-scale mechanical flotation cell. Miner. Eng. 2 (13), 1448–1453.

Shainberg, I., Alperovitch, N., Keren, R., 1988. Effect of magnesium on the hydraulic conductivity of Na-smectite-sand mixtures. Clays Clay Miner. 36, 432-438.

Silva, M.A., 1986. Placer gold recovery methods, Special publication.

Smith, P. G., and Warren, L. J., 1989, Entrainment of particles into flotation froths. Min. Proc. Ext. Met. Rev. 5(1–4), 123–145.

Sutherland, K.L., Wark, I.W., 1955. Principles of flotation, Australian IMM.

Suzuki, S., Prayongphan, S., Ichikawa, Y., Chae, B.G., 2005. In situ observations of the swelling of bentonite aggregates in NaCl solution. Appl. Clay Sci. 29, 89-98.

Swartzen-Allen, S., Matijevic', E., 1974. Surface and colloid chemistry of clays, Chemical Reviews, 74, 385-400.

Tao, D., Dopico, P.G., Hines, J., Kennedy, D., 2010. An experimental study of clay binders in fine coal froth flotation. Proceedings of the International Coal Preparation Congress, Lexington, USA, 478–487.

Theng, B.K.G., 2012. Chapter 1 — the clay minerals. In: Theng, B.K.G. (Ed.), Developments in Clay Science. vol. 4. Elsevier, 3–45.

Tombácz, E., Szekeres, M., 2004. Colloidal behavior of aqueous montmorillonite suspensions: the specific role of pH in the presence of indifferent electrolytes. Applied Clay Science, 27(1), 75–94

Tremolada, J., Dzioba, R., Bernardo-Sanchez, A., Menendez-Aguado, J.M., 2010. The preg-robbing of gold and silver by clays during cyanidation under agitation and heap leaching conditions. Int. J. Miner. Process. 94, 67–71.

Tunc, S., Duman, O., Uysal, R., 2008. Electrokinetic and rheological behaviors of sepiolite suspensions in the presence of poly(acrylic acid sodium salt)s, polyacrylamides, and poly(ethylene glycol)s of different molecular weights. J. Appl. Polym. Sci. 109, 1850-1860.

Vasudevan, M., Nagaraj, D.R., Patra, P., Somasundaran, P., 2010. Effect of altered silicates in flotation performance: role of changes in pulp rheology. In: Pawlik, M. (Ed.), Proceedings 8th UBC-McGill-UA International Symposium on the Fundamentals of Mineral Processing: Rheology and Processing of Fine Particles. The Canadian Institute of Mining, Metallurgy and Petroleum, Vancouver, British Columbia, Canada,pp. 21–30

Wan, Y., Guo, D., Hui, X., Liu, L., Yao, Y., 2020. Studies on hydration swelling and bound water type of sodium- and polymer-modified calcium bentonite, Advances in Polymer Technology, 9361795, 11. https://doi.org/10.1155/2020/9361795

Wang, B., Peng, Y., 2013. The behaviour of mineral matter in fine coal flotation using saline water. Fuel 109, 309-315.

Wang, B., Peng, Y., 2014. The interaction of clay minerals and saline water in coarse coal flotation. Fuel 134, 326-332.

Wang, L., Peng, Y., Runge, K., and Bradshaw, D., 2015a, A review of entrainment: mechanisms, contributing factors and modelling in flotation. Minerals Engineering, 70, 77–91.

Wang, Y., 2016. Mitigating the deleterious effect of clay minerals on copper flotation. PhD Thesis. The University of Queensland. https://doi.org/10.14264/uql.2017.49

Wang, Y., Peng, Y., Nicholson, T., Lauten, R. A., 2015. The different effects of bentonite and kaolin on copper flotation. Applied Clay Science 114 48-52. https://doi.org/10.1016/j.clay.2015.05.008

Wang, Y., Peng, Y., Nicholson, T., Lauten, R. A., 2015b, The different effects of bentonite and kaolin on copper flotation. Applied Clay Science, 114, 48–52.

Wei, R., Peng, Y., and Seaman, D., 2013. The interaction of lignosulfonate dispersants and grinding media in copper–gold flotation from a high clay ore. Minerals Engineering, 50–51, 93–98.

Wills, B. A., Napier-Munn, T., 2006. Wills' mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery. Retrieved from https://ebookcentral.proquest.com

Xu, Z., Liu, J., Choung, J. W., and Zhou, Z., 2003, Electrokinetic study of clay interactions with coal in flotation. International Journal of Mineral Processing, 68(1–4), 183–196.

Yu, Y., Cheng, G., Ma, L., Huang, G., Wu, L., Xu, H., 2017a. Effect of agitation on the interaction of coal and kaolinite in flotation. Powder Technol. 313(Supplement C), 122–128.

Yu, Y., Ma, L., Wu, L., Ye, G., Sun, X., 2017b. The role of surface cleaning in high intensity conditioning. Powder Technol. 319 (Supplement C), 26–33.

Zbik, M., 2006. SEM evidence of structural re-arrangement from gelling to aggregation in Birdwood kaolinite. Colloids and Surfaces a-Physicochemical and Engineering Aspects 287, 191-196.

Zhang, L., Lu, Q., Xu, Z., Liu, Q., Zeng, H., 2012. Effect of polycarboxylate ether comb-type polymer on viscosity and interfacial properties of kaolinite clay suspensions. J. Colloid Interface Sci. 378, 222- 231.

Zhang, M., 2016. The effect of clay minerals on copper and gold flotation. PhD Thesis. The University of Queensland.

Zhang, M., Peng, Y., 2015. Effect of clay minerals on pulp rheology and the flotation of copper and gold minerals. Miner. Eng. 70, 8–13.

Zhang, M., Peng, Y., Xu, N., 2015a. The effect of sea water on copper and gold flotation in the presence of bentonite. Miner. Eng. 77, 93-98.

Zhang, M., Xu, N., Peng, Y., 2015b. The entrainment of kaolinite particles in copper and gold flotation using fresh water and sea water. Powder Technol. 286, 431-437.

Zhao, S., Peng, Y., 2014. Effect of electrolytes on the flotation of copper minerals in the presence of clay minerals. Miner. Eng. 66–68. 152–156.

Chapter III

Detrimental effect of calcium on grinding performance of a kaolin-containing ore

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Abstract

The presence of kaolin in ores may cause many problems in mineral processing industries. However, no study was conducted investigating the influence of kaolin on grinding efficiencies in any clay-containing ores. The primary objective of this research is to investigate the influence of kaolin on the grinding efficiency in the absence and the presence of Ca^{2+}; the reason is that the presence of Ca^{2+} had already a positive effect on flotation and filtration of various clay containing ores. The experiments were performed using a rod mill to determine the grinding performance of the kaolin-containing ores by determining P_{80}. The zeta potential measurements and the settling tests of pure kaolin were used to study the surface properties and the settling behaviour of pure kaolin particles. The rheology tests were used to analyse the changes in the slurry rheology of the products obtained after grinding the kaolin-containing ores. The results showed that the additions of Ca^{2+} ions reduced the repulsion forces between kaolin particles as confirmed by the zeta potential measurements as well as reduced settling rates. As a result, the agglomeration between kaolin particles increased, leading to the increase in the slurry shear stress (i.e., viscosity) and thus reducing the grinding performance significantly. The grinding performance was reduced by the addition of Ca^{2+} ions when there was a high clay percentage (40%) and a high solid percentage (70%). This paper demonstrated the importance of controlling Ca^{2+} concentrations in plant water to maximize the grinding performance of kaolin-containing ores.

Key words: Kaolin; grinding; rheology; zeta potential

1. Introduction

The presence of clay minerals with valuable minerals is unavoidable in many ore bodies. In this case, the associated clay minerals are considered as gangue and are known to reduce the efficiency of various processes involved in mining operations, for example, crushing, grinding, flotation, dewatering, filtration etc. Profitable mining of clay-containing low-grade ores is the focus of recent research in the mineral processing industry because of the foreseen depletion of high-grade ore deposits. The primary source of a clay formation is the weathering of rocks; physical weathering is the fragmentation of rocks and chemical weathering is a chemical change or decomposition of rocks and minerals. When combining both physical and chemical weathering, more stable and small clay particles are formed (Nelson, 2014). Clay minerals are phyllosilicate minerals consisting of alumino or hydrous silicates and they have particle sizes of less than 2 μm (Theng, 2012). Silica tetrahedral (T) and alumina octahedral (O) sheets are the two main structural units to form atomic lattices of all clays groups (Grim, 1968). The final macrostructure formation can be kaolin, smectite, and illite (Cruz 2016; Zhang 2016, Chen and Peng, 2018), depending on the arrangement and the bonding forces between these sheets (Brigatti et al. 2013).

Although smectites are considered the most detrimental clay group, kaolin becomes equally problematic under certain conditions. Smectites are very determinetal considering that the structural units are bonded together with weak van der Waals forces permitting water molecules to penetrate between interlayer spacing, resulting in a volumetric increase by water-swelling of this clay (Luckham and Rossi, 1999; Zhang, 2016). However, kaolin is a non-swelling clay mineral. The 1:1 (T to O) layer arrangement of silica tetrahedral (T) sheets and alumina octahedral (O) sheets in the kaolin group of clays result in two effective bonding forces; van der Waals and a strong hydrogen bond between the hydrogen atoms of the octahedral sheet of one layer and the oxygen atoms of the tetrahedral sheet of the adjacent layer (Zhang 2016, Chen and Peng, 2018). When exposed to water, the presence of this strong hydrogen bond resists the water molecules penetration through the layered structure resulting in a non-swelling characteristic of kaolin clays (Chen and Peng, 2018; Jeldres et al., 2019; Basnayaka et al., 2017; Basnayaka et al., 2018, Ndlovu et al., 2014).

Kaolin did not affect the slurry viscosity during mineral flotation but resulted in high gangue entrainment (Zhang and Peng, 2015). Wang and Peng (2014) and Cruz et al (2015) studied this effect during their flotation experiments and observed that kaolin clays were transferred to flotation concentrates, resulting in improved froth stability. Cruz et al (2015) reported reduced concentrate grade due to flotation entrainment while flotation recovery remained unaffected. Therefore, one of the major problems associated with kaolin group clay minerals in flotation is the significant gangue entrainment whereas high viscosity can become a concern at high concentrations (Chen and Peng, 2018). These flotation results show that the presence of kaolin can be equally detrimental not due to the water swelling capacity like bentonite but due to the face-face agglomerations and then entrainment in flotation concentrate resulting in reduced grades.

Face to face aggregation of clay platelets in kaolin-containing slurries form thick and large flakes resulting in reduced viscosity, due to the insufficient units available to make a gel like network and less free surface available for particle interactions (Luckham and Rossi, 1999).

Recently introduced high-resolution Cryo-SEM technique (Du et al., 2010) has provided an insight of network structure formed in kaolin-containing slurries which showed face to face, edge to face and edge to edge aggregations of kaolinite crystals ((Ndlovu et al., 2014; Rand et al., 1980; Zhang and Peng, 2015). Face to face aggregations probably play an important role in the rheological behaviour of kaolin-containing suspensions (de Kretser et al., 1998).

However, the addition of Ca^{2+} to kaolin containing slurries can increase the pulp viscosity. This research by Cruz et al (2015) is supported by the investigations done by Abdi and Wild (1993) and Wild et al. (1993) who described that interaction between added Ca^{2+} and kaolin in the slurry can result in an increased pulp viscosity due to the formation of a gel-like structure. The addition of Ca^{2+} cations can get adsorbed on clay surfaces, altering the double layers around kaolin particles and thus contributing to the formation of undesirable network structures (Abdi and Wild, 1993, Wild et al., 1993).

The adverse effects of the presence of kaolin on filtration efficiency are attributed to the very fine particle size of less than 2 μm being one of the major contributing factors. Basnayaka et al (2018) found that kaolin can increase the specific cake resistance, filter medium resistance and final cake moisture content (Benna et al., 2001). Face to face agglomeration of kaolin particles along with their anisotropic structure, and positive surface charge properties increased the resistance to fluid flow (Besra et al., 1999), resulting in decreased effective capillary radius flow channels (Basnayaka et al, 2018). Kaolin increased the filter medium resistance by four times probably due to the blinding of filter medium pores with fine clay particles (Basnayaka et al, 2018). Additionally, kaolin clay increased the filter cake moisture content by about 8% which was reduced from 33.7 to 22.7% after the addition of dodecyl amine hydrochloride i.e. the surfactant. Similarly, the specific cake resistance of the gold-bearing pyritic ore was increased from 4.68×10^{13} to 8.27×10^{13} m^{-2} in the presence of 10% kaolin which was reduced to
7.54×10^{13} m^{-2} after the addition of dodecyl amine hydrochloride. Therefore, the addition of this compound to kaolin containing ores was reported to improve filtration efficiency by mitigating the negative effects (Basnayaka et al, 2018).

The presence of kaolin did not affect the performance of the Knelson concentrator as reported by Basnayaka et al (2020). It might be because the particles of kaolin got rejected to the tailings instead of entering the concentrated bed inside the concentrate bowl due to the high centrifugal force.

A variety of strategies are used to reduce the deleterious effects of clay minerals on the flotation process that may include the addition of reagents to modify the pulp rheology or surface properties of the clay particles to prevent their attachment to the valuable minerals. Another option is to reduce the solid percentage of the slurry to reduce the slurry viscosity which, on the other hand, lead to reduced metal production. Thirdly, the possibility is to remove clays by physical methods before the flotation stage (Jeldresa et al, 2019). A recent study by Yu et al., 2017a, 2017b on coal with kaolin found that intense agitation during conditioning can improve the process efficiency. Hydrocyclone desliming was found to be more effective than using dispersants (Oats et al., 2010; Quast et al., 2008) but this method can be useful if the valuable minerals are present in negligible quantities otherwise valuable minerals could be lost with slimes in large amounts. Ultrasonic pre-treatment studies were found promising in the case of boron flotation (Celik et al., 1998) but this technique needs industrial-scale trials to be comparable with high-intensity agitation and desliming by hydrocyclones.

Even though the effect of kaolin has been studied for flotation, filtration and Knelson concentrations, no adequate information is available on the effect of kaolin on grinding performances. Therefore, the primary objective of this research is to analyse the influence of kaolin on grinding efficiency in the absence and presence of Ca^{2+} ions. The selection of Ca^{2+} ions for this experimental work is based upon the fact that Ca^{2+} ions have been reported to have positive effects in flotation (Basnayaka et al, 2017) and filtration (Basnayaka et al, 2018) of ores containing different clays such as bentonite clay minerals. `

2. Materials and Methods

2.1. Synthetic ore

The synthetic ore for the solid percentage of 70% contained 900 g of ground quartz and 100 g of kaolin (i.e. 10% of kaolin ore) as well as 600 g of ground quartz and 400 g of kaolin (i.e. 40% of kaolin ore). In the case of the solid percentage of 40%, 495 g of ground quartz was mixed with 55 g of kaolin to obtain 10% kaolin ore while 330 g of ground quartz was mixed with 220 g of kaolin to prepare 40% kaolin ore. Table 1 shows the information about all the samples used in this work. It is very important to note that $CaCl_2$ was added in different samples to investigate its influence on grinding performance.

Table 1. Ore mineralogy and water consumptions for all the samples.

Samples	Solid %	Kaolin %	Quartz (g)	Kaolin (g)	Water (g)	$CaCl_2$ (g)
1	70	10	900	100	428	0
2	70	10	900	100	428	3
3	70	40	600	400	428	0
4	70	40	600	400	428	1.5
5	70	40	600	400	428	3
6	70	40	600	400	428	4.5
7	40	10	495	55	820	0
8	40	10	495	55	820	3
9	40	40	330	220	820	0
10	40	40	330	220	820	3
11	40	40	330	220	820	3
12	40	40	330	220	820	3

The particle size of the ground quartz was less than 6.38 mm. The kaolin had P_{80} of 10 µm as seen in Figure 1. The purity of the quartz was 99.5% whereas the kaolin had 87% kaolinite and 13% quartz as found by XRD as seen in Figure 2.

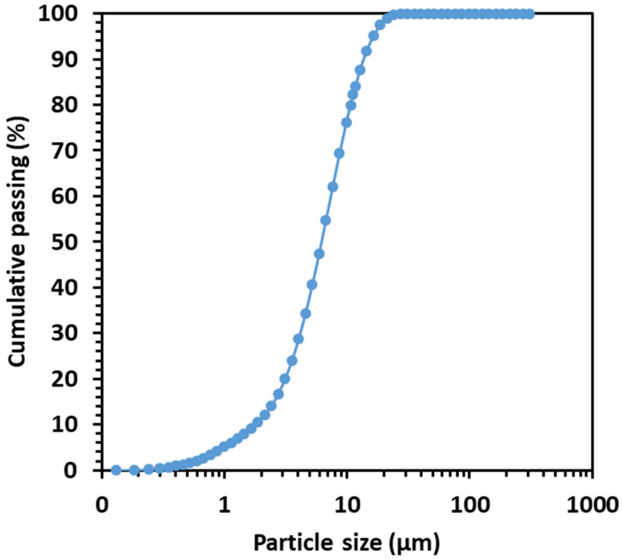

Figure 1. Particle size distributions of kaolin (Basnayaka, 2018).

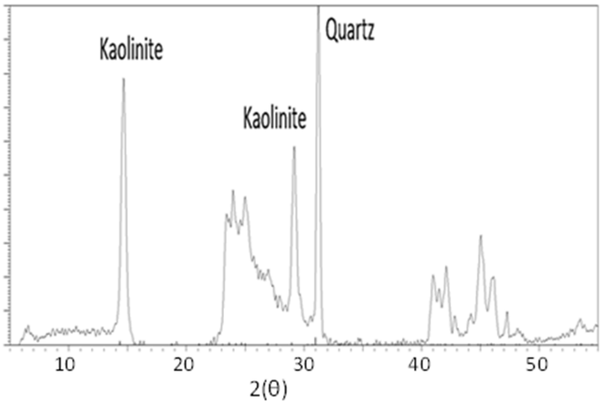

Figure 2. XRD analysis of kaolin (Basnayaka et al, 2017).

2.2. Grinding

All the slurries were prepared by mixing 428 g of the tap water or 820 g of the tap water with the synthetic ores to obtain 70% and 40% solid percentage, respectively. After that, grinding took place for 45 min in the laboratory rod mill (Labtech Essa Pty Ltd, Australia). The experiments were performed in the absence and the presence of different dosages of $CaCl_2$; the purity of $CaCl_2$ was 99% (Thermo Fisher Scientific, US). The charge filling of the mill (10690 g of the rods and 1428 g of the slurry) and the rotational speed of the mill of 1370 rpm were maintained constant. In all experiments, 15 griniding rods were used and each rod had 24.5 cm in length and 2.2 cm in diameter. The slurry pH was also constant in all experiments i.e., pH = 7.5 ± 0.2.

The full factorial design was used with three variables: kaolin concentrations (10 or 40%), solid percentage (40 or 70%) and $CaCl_2$ dosage (0 or 3000 g/ton, ionic strength 0 or 0.0811M respectively). The grinding experiments were also conducted to study the effect of different $CaCl_2$ dosages on the grinding performances. It is important to note that the tap water had 59 mg/L of $CaCO_3$ and 110mg/L of Na^+ (Drinking Water Quality Annual Report Data, 2021).

2.3. Particle size distributions

Malvern Mastersizer was used for obtaining particle size distributions of the slurries generated after grinding the ore. The particle size distributions (PSD) for the slurries in the absence and the presence of $CaCl_2$ at the investigated clay concentrations were presented in Figure 3; the standard deviation of the three repeats was 2%. It is important to note that agglomeration of particles did not occur during these measurements. The reason is that the particle size distributions remained the same in the presence and absence of ultrasound. Additionally, these measurements were also performed in the presence of dispersant (sodium oleate, 400 g/ton) and the results showed that the addition of dispersant did not affect the particle size distributions.

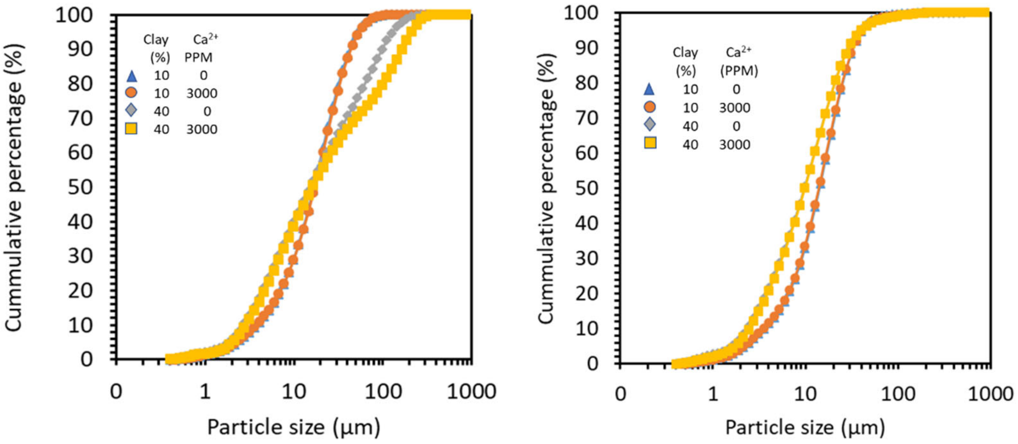

Figure 3. Particle size distributions for the mixture of quartz and kaolin (a) 70% solid percentage (b) 40% solid percentage.

2.4. Rheological measurements

The rheological measurements were carried out with DV1 MLV viscometer (Brookfield, USA); 16 ml sample was used for the UL adapter whereas 600 ml sample was used for the LV01 standard spindle arrangement. It should be noted that in the case of the UL adapter smaller amount of samples were used considering that the UL adapter can by filled with the sample volume of 16 ml; however, in the case of the LV01 spindle arrangement, the measurements were conducted using the Griffin beaker in which the minimum sample volume was 600 ml. The rheograms (shear stress vs shear rate) were generated for the investigated systems. All rheological measurements were conducted at room temperature (20 ± 5 °C).

2.5. Zeta potential measurements

Zeta potential measurements were conducted using the zetasizer (Malvern Nano Z, UK). The mixture of 0.05 g of kaolin and 50 ml of water was used to perform the zeta potential measurements at different pH levels (i.e. 4, 6, 7, 9 and 11). Each test was repeated three times and an average of three readings was used for further investigation.

2.6. Settling experiments

The settling experiments were conducted using the 100 ml graduated cylinders. In these experiments, 5% and 10% kaolin clay slurries were used. Each test was performed at room temperature (20 ± 5 °C) at a pH of 7.5 ± 0.2. The experiments were carried out in the presence of different $CaCl_2$ dosages (0, 1500, 3000 and 4500 g/ton (ionic strength 0, 0.0405, 0.811 and 0.1216M respectively)). The slurries were mixed strongly and then allowed to settle in the cylinders. Settling behaviour was recorded for 30 mins by observing the solid-liquid interface every minute.

3. Results and discussions

3.1. Grinding experiments

The grinding experiments were performed to investigate the effect of kaolin on grinding operations by varying three independent variables: clay concentration, solid percentage and $CaCl_2$ concentration as seen in Table 2. The dependant variable is P_{80}.

Table 2. Grinding performance at different levels of three variables

Clay conc. (%)	Ca^{2+} (g/t)	Solid percentage (%)	P_{80}
10	0	70	32
10	0	40	25
10	3000	70	32
10	3000	40	25
40	0	70	63
40	0	40	21
40	3000	70	100
40	3000	40	21

The analysis of variance (ANOVA) for the grinding experiments is shown in Table 3. The solid percentage was observed to be the most significant variable while Ca^{2+} concentration was the least significant variable; the significance of variables was described based on the p-value (i.e. the higher the p-value of the variable, the variable is less significant).

Table 3. ANOVA results for kaolin.

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Clay Conc.	1	1008.8	1008.8	5.95	0.248
Ca^{2+}	1	188.1	188.1	1.11	0.483
Solid percentage	1	2320.7	2320.7	13.70	0.047
Clay Conc. * Ca^{2+}	1	175.8	175.8	1.04	0.494
Clay Conc. * Solid percentage	1	1443.0	1443.0	8.52	0.210
Ca^{2+} * Solid percentage	1	192.1	192.1	1.13	0.480
Error	1	169.4	169.4		
Total	7	5498.1			

Although ANOVA shows significant variables, Tukey analysis (see Table 4) demonstrate the effect of the investigated variables on the grinding performance i.e. P_{80}. As seen in Table 4, the higher the solid percentage, the higher the values of P_{80}. This observation may be explained by the fact that a high solid percentage led to a higher collision efficiency between particles, resulting in a higher shear force between particles (see Figure 7).

Table 4. Tukey results for kaolin.

Variables	Number of experiments	Mean P_{80}
Clay Cons., 40 %	4	51.20
Clay Cons., 10 %	4	28.74
Ca^{2+}, 3000 g/t	4	44.82
Ca^{2+}, 0 g/t	4	35.12
Solid percentage, 70 %	4	57.01
Solid percentage, 40 %	4	22.94

Table 4 shows that the increase in clay concentration led to an increase in P_{80}. However, there is a strong relationship between the clay concentration, the solid percentage and P_{80}. For example, at a low solid percentage (i.e., 40%), no significant change in P_{80} was observed by increasing the clay concentration. On the contrary, at a high solid percentage (i.e., 70%), P_{80} increased up to 3.1 times with increasing the clay concentration, demonstrating a significant effect of clay concentration. The reason could be that the shear forces at the low solid percentage between particles are much less significant than those at the high solid percentage (see Figure 7), resulting in the decreased grinding performance at the high solid percentage.

Table 4 also shows that the increase in Ca^{2+} concentrations led to a higher P_{80}. This is true when there is a high solid percentage (i.e., 70%) and a high clay concentration (i.e., 40%) as seen in Figure 4. However, when a solid percentage is low (i.e., 40%) or/and a clay concentration is low (i.e., 10%), no change of P_{80} was observed with increasing Ca^{2+} concentrations.

The reason for the increase in P_{80} with an increase in Ca^{2+} concentrations at a high solid percentage and a high clay concentration could be explained due to the agglomeration of clay particles. The agglomeration occurred probably because the zeta potential of kaolin (see Figure 5) was significantly reduced in the presence of Ca^{2+} considering that kaolin particles have negative zeta potential; kaolin particles in the presence of Ca^{2+} have very low zeta potentials, reducing repulsion forces between kaolin particles and thus leading to agglomeration of these particles.

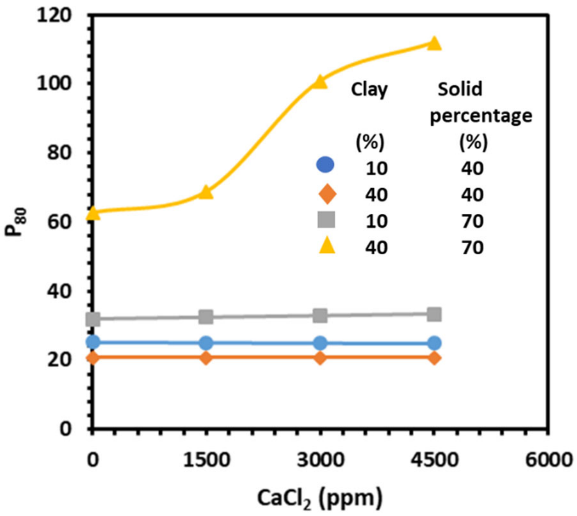

Figure 4. Influence of Ca^{2+} dosage on P_{80}.

3.2. Zeta potential measurements and settling tests

Figure 5 shows that in the case of pure kaolin, the increase in pH resulted in the lower zeta potentials probably due to the adsorption of OH^- ions on kaolin surfaces. The increase in Ca^{2+} dosage led to the lower zeta potential; the reason is due to the adsorption of different calcium ions (Ca^{2+} for all pH-s and $Ca(OH)^+$ for pH-s higher than 9.5, modifying the double layer around kaolinite particles (Abdi and Wild, 1993; Wild et al., 1993).

For a given Ca^{2+} dosage, the increase in pH did not significantly affect the zeta potentials up to pH 7. However, after pH 7, the zeta potential changed substantially due to the presence of $Ca(OH)^+$ ions at pH higher than 9 as well as Ca^{2+} ions (Wang et al., 2018). Further research is required for a better understanding of Ca^{2+} adsorption on kaolin surfaces as a function of pulp pH.

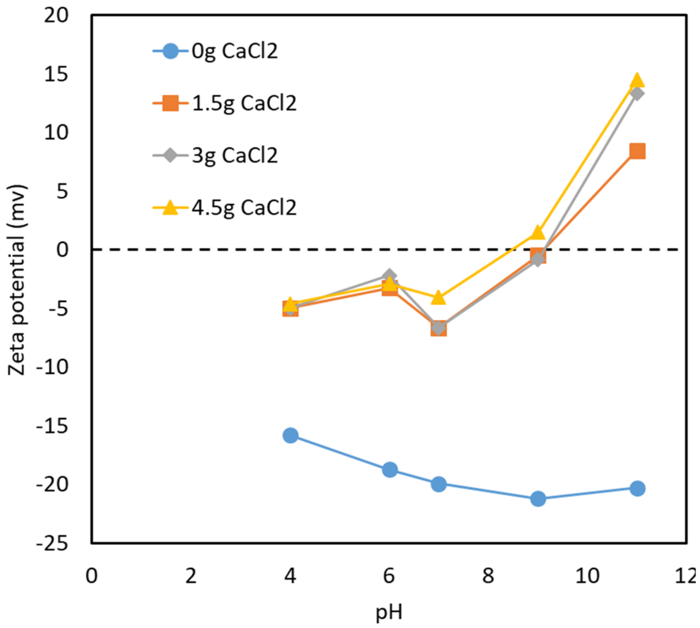

Figure 5. Zeta potential of kaolin as a function of solution pH at selected concentrations of $CaCl_2$ (Ca^{2+}).

Apart from zeta potentials, the settling tests (see Figure 6) were also conducted to investigate the effect of different dosages of Ca^{2+} ions on the settling behaviour of two selected kaolin percentages (5% and 10%). As seen in Figure 6, the addition of Ca^{2+} ions negatively affected the settling behaviour of kaolin. The reason is probably the agglomeration of kaolin particles due to the reduced repulsion forces between kaolin particles in the presence of Ca^{2+}; the reduced repulsion forces between particles were observed based on zeta potential measurements (see Figure 5). The experimental evidence of kaolin particle agglomerations was found by the Cryo-SEM method (Cruz et al., 2013). There are three types of kaolinite agglomerations, resulting in the formation of the following bonds between kaolinite platelets: face to face, edge to face and edge to edge bonds (Basnayaka et al., 2017; Jeldres et al., 2017a, 2017b, 2017c). Cruz et al., 2015; Zhang and Peng, 2015, Chen and Peng, 2018). Another potential reason could be that the addition of Ca^{2+} led to a higher slurry viscosity (see Figure 7), which agrees well with the results obtained by other authors (Abdi and Wild, 1993; Wild et al., 1993). It is also worth mentioning that the intercrystalline swelling of kaolinite (Kruglitskii et. Al, 1985; Heidug and Wong, 1996) under the experimental conditions in this work even though kaolinite is classified as a non-swelling clay. It should be noted that the negative effect of Ca^{2+} was more dominant in the case of 10% of kaolin than that in the case of 5% of kaolin probably because the higher percentage of kaolin particles may have led to the formation of more kaolinite aggregates.

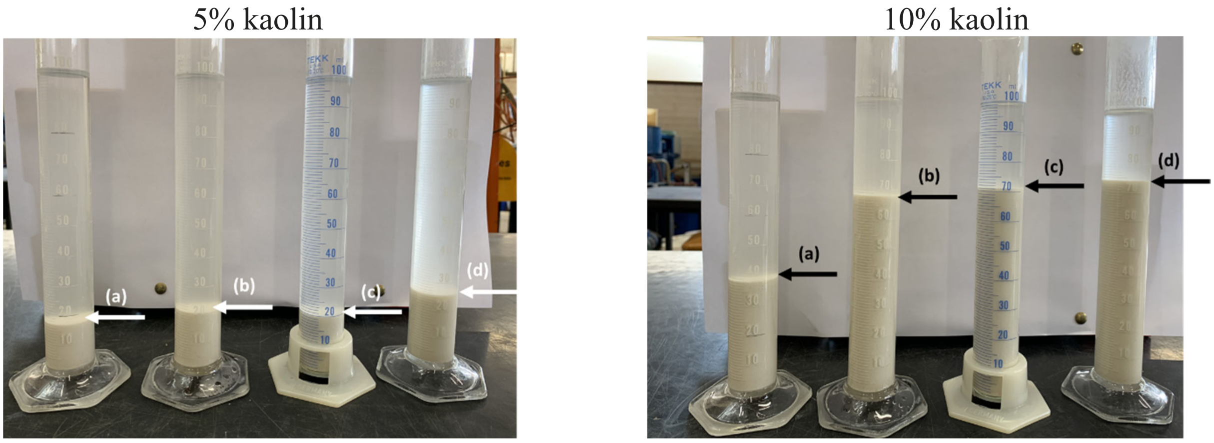

Figure 6. Settling tests results after 30 min for 5% kaolin and 10% kaolin at different $CaCl_2$ concentration (a) 0 ppm, (b) 1500 ppm (c) 3000 ppm (d) 4500ppm. Arrows indicate the level of settled solids.

3.3. Slurry rheology

Figure 7 shows the effect of kaolin percentage and Ca^{2+} dosage on the rheological behaviour. As seen in Figure 7, the increase in Ca^{2+} dosage slightly increased the shear stress of the slurry probably due to the formation of kaolin aggregates formed due to the reduced zeta potential. This trend was observed at different kaolin percentages. The increased viscosity in the presence of Ca^{2+} could be a possible explanation for reduced settling behaviour and eventually affecting the grinding performance negatively.

Similar relationships between grinding performance, kaolin percentage and solid percentage may occur in the presence of different ions other than Ca^{2+}. However, a significant amount of further work is required.

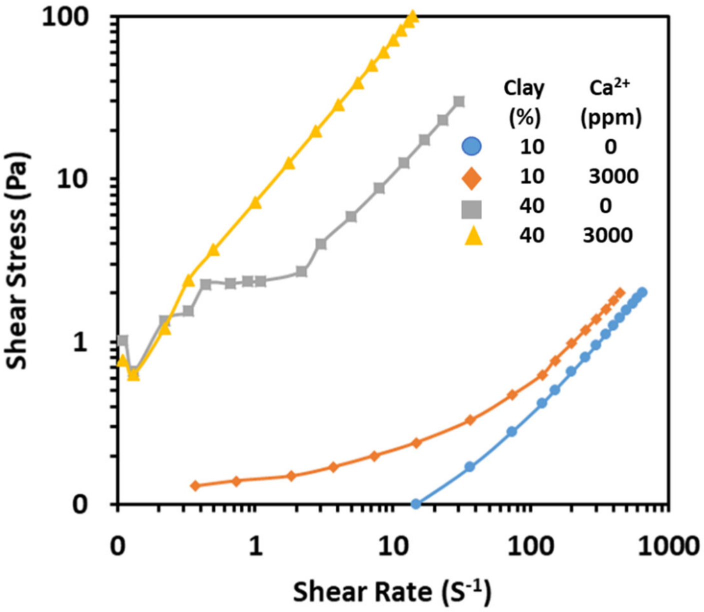

Figure 7. Rheograms of the slurries with 10 and 40% solid percentages.

4. Conclusions

The paper investigates the influence of Ca^{2+} ions on the grinding performance of the kaolin-containing ores by determining grinding efficiency, particle size distributions, rheology, zeta potentials and settling behaviour. The results of this paper showed that the addition of Ca^{2+} ions had adverse effects on the grinding performance of the kaolin-containing ores when there was a high clay percentage (40%) and a high solid percentage (70%). It was observed that the addition of Ca^{2+} ions reduced the zeta potentials because of the reduced repulsion forces between kaolin particles. The settling test showed that the addition of Ca^{2+} ions affected the settling rate negatively possibly due to the agglomeration of kaolin particles caused by the reduced repulsion forces between these particles. The rheological studies of the kaolin containing slurries obtained after grinding showed that the shear stress increased in the presence of Ca^{2+} ions at a high clay percentage (40%). The negative effect of Ca^{2+} ions on grinding performance may be mitigated by adding sulfate ions, resulting in the formation of $CaSO_4$ which has similar solubility product as $Ca(OH)_2$; it should be noted that $CaSO_4$ does not affect pH of a solution while the opposite is true in the case of $Ca(OH)_2$. This work demonstrated the importance of optimizing Ca^{2+} concentrations in plant water for kaolin-containing ores. A significant amount of further work should be conducted to investigate the influence of different ions on the grinding performance of kaolin-containing ores.

References

Aabdi, M. R., Wild, S., 1993. Sulphate expansion of lime-stabilized kaolinite: I. Physical cahractristics. Clay Minerals 28, 555-567.

Basnayaka, L., Albijanic, B., Subasinghe, N., 2020. Performance evaluation of processing clay-containing ore in Knelson concentrator. Minerals Engineering 152, 106372.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2017. Influence of clays on the slurry rheology and flotation of a pyritic gold ore. Appl. Clay Sci. 136, 230–238.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2018. Influence of clays on fine particle filtration. Appl. Clay Sci. 156, 45–52.

Basnayaka, L., 2018. Influence of clay on mineral processing techniques, PhD thesis, Curtin University.

Benna, M., Ariguib, N.K., Clinard, C., Bergaya, F., 2001. Static filtration of purified sodium bentoite clay suspensions. Effect of clay content. Appl. Clay Sci. 19, 103–120.

Besra, L., Sengupta, D.K., Roy, S.K., 1999. Particle characteristics and their influence on dewatering of kaolin, calcite and quartz suspensions. Int. J. Miner. Process. 59, 89–112.

Brigatti, M. F., Galán, E., and Theng, B. K. G., 2013, Chapter 2 – structure and mineralogy of clay minerals, In Developments in Clay Science, (B. Faïza and L. Gerhard, Ed.), Amsterdam, Netherlands: Elsevier, Vol. 5, pp. 21–81.

Celik, M.S., Elma, I., Hancer, M., Miller, J.D., 1998. Effect of insitu ultrasonic treatment on the floatability of slime coated colemanite. In: Proceedings of the International Mineral Processing 7th Symposium.

Cruz, N., 2016, “Interactions of clay minerals and their effects on copper gold flotation.” PhD Thesis, The University of Queensland.

Cruz, N., Peng, Y., Farrokhpay, S., Bradshaw, D., 2013. Interactions of clay minerals in copper-gold flotation: part 1 - rheological properties of clay mineral suspensions in the presence of flotation reagents. Miner. Eng. 50–51, 30–37. https://doi.org/10. 1016/j.mineng.2013.06.003.

Cruz, N., Yongjun, P., Wightman, E., Xu, N., 2015. The interaction of clay minerals with gypsum and its effects on copper–gold flotation. Min. Eng. 77, 121–130.

de Kretser, R.G., Scales, P.J., Boger, D.V., 1998. Surface chemistry–rheology interrelationships

Du, J., Morris, G., Pushkarova, R.A., Smart, R.S., 2010. Effect of surface structure of kaolinite on aggregation, settling rate, and bed density. Langmuir 26 (16), 13227–13235.

Drinking Water Quality Annual Report Data. https://pw-cdn.watercorporation.com.au/-/media/WaterCorp/Documents/About-us/Our-performance/Drinking-Water Quality/Dwq-annual-report-goldfields-and-ag-aesthetic-tables.pdf (accessed 22nd September 2021).

Grim, R. E., Clay Minerology, 2nd ed., McGraw-Hill, NY, 1968, pp. 596.

Heidug, W. K. and Wong, S. W. (1996): Hydration swelling of water-absorbing rocks: A constitutive model, Int. J. Num. Anal. Meth. Geomech., 20, 403-430

Jeldres, R.I., Arancibia-Bravo, M.P., Reyes, A., Aguirre, C.E., Cortes, L., Cisternas, L.A., 2017a. The impact of seawater with calcium and magnesium removal for the flotation of copper-molybdenum sulphide ores. Miner. Eng. 109, 10–13. https://doi.org/ 10.1016/j.mineng.2017.02.003.

Jeldres, R.I., Calisaya, D., Cisternas, L.A., 2017b. An improved flotation test method and pyrite depression by an organic reagent during flotation in seawater. J. South. African Inst. Min. Metall. 117, 499–504. https://doi.org/10.17159/2411-9717/2017/ v117n5a12.

Jeldres, R.I., Piceros, E.C., Leiva, W.H., Toledo, P.G., Herrera, N., 2017c. Viscoelasticity and yielding properties of flocculated kaolinite sediments in saline water. Colloids Surf. A Physicochem. Eng. Asp. 529, 1009–1015. https://doi.org/10.1016/j.colsurfa. 2017.07.006.

Kruglitskii, N. N., Lomtadze, O. G., Kruglitskaya, V. Y. and Pakhovchishin, S. V. (1985): Study of lyophilic properties of clinoptilolite, Colloid J. USSR (English translation of Russian, Kolloidnyi Zhurnal), 47, 589-593

Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite suspensions. Adv. Colloid Interf. Sci. 82 (1–3), 43–92.

Ndlovu, B., Forbes, E., Farrokhpay, S., Becker, M., Bradshaw, D., Deglon, D., 2014. A preliminary rheological classification of phyllosilicate group minerals. Miner. Eng. 55, 190–200.

Nelson, A. S., 2014. Weathering & Clay Minerals. Mineralogy Tulane University. This document last updated on 19-Nov-2014

Oats, W.J., Ozdemir, O., Nguyen, A.V., 2010. Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation. Miner. Eng. 23 (5), 413–419.

Quast, K., Ding, L., Fornasiero, D., Ralston, J., 2008. Effect of slime clay particles on coal flotation. In: Proceedings of Chemeca 2008, Newcastle, September 28– October 1, Australia.

Rand, B., Pekenc´ , E., Goodwin, J.W., Smith, R.W., 1980. Investigation into the existence of edge—face coagulated structures in Na-montmorillonite suspensions. J. Chem. Soc., Faraday Trans. 1: Phys. Chem. Condens. Phases 76, 225–235.

Ricardo I. Jeldres, Lina Uribe, Luis A. Cisternas, Leopoldo Gutierrez, Williams H. Leiva, Julio Valenzuela, The effect of clay minerals on the process of flotation of copper ores - A critical review. Applied Clay Science Volume 170, 15 March 2019, Pages 57-69.

Theng, B.K.G., 2012. Chapter 1 - The Clay Minerals, in: Theng, B.K.G. (Ed.), Developments in Clay Science. Elsevier, pp. 3-45.

Wang, B., Peng, Y., 2014. The interaction of clay minerals and saline water in coarse coal flotation. Fuel 134, 326–332.

Wang, X.; Liu, W.; Duan, H.; Wang, B.; Han, C.; Wei, D. The adsorption mechanism of calcium ion on quartz (101) surface: A DFT study. Powder Technol. 2018, 329, 158–166, doi:10.1016/j.powtec.2018.01.086.

Wild, S., Aabdi, M. R., Leng,-Ward, G. 1993. Sulphate expansion of lime-stabilized kaolinite: II. Reaction products and expansion. Clay Minerals (1993) 28, 569-583.

Chen, X., Peng, Y. (2018): Managing clay minerals in froth flotation—A critical review, Mineral Processing and Extractive Metallurgy Review, DOI: 10.1080/08827508.2018.1433175

Yu, Y., Cheng, G., Ma, L., Huang, G., Wu, L., Xu, H., 2017a. Effect of agitation on the interaction of coal and kaolinite in flotation. Powder Technol. 313, 122–128. https://doi.org/10.1016/j.powtec.2017.03.002.

Yu, Y., Ma, L., Wu, L., Ye, G., Sun, X., 2017b. The role of surface cleaning in high intensity conditioning. Powder Technol. 319, 26–33.

Zhang, M., 2016, "The effect of clay minerals on copper and gold flotation." PhD Thesis, The University of Queensland.

Zhang, M., Peng, Y., 2015. Effect of clay minerals on pulp rheology and the flotation of copper and gold minerals. Miner. Eng. 70, 8–13.

Chapter IV

Grinding of highly viscous bentonite containing slurries

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Abstract

The influence of bentonite on the grinding efficiencies of ores has not been investigated. In this work, the relationships between the properties of bentonite-containing slurries (such as rheology and settling behaviour) and grinding efficiency are examined. The results demonstrated that the presence of bentonite in the ore negatively affected the grinding performance of the ore, and the negative effect of bentonite was mitigated by adding Ca^{2+} ions. The additions of Ca^{2+} ions reduced the repulsive forces between bentonite particles as confirmed using the zeta potential measurements as well as the water-swelling capacity of bentonite as found using the settling tests. Therefore, the ore-bentonite slurries in the presence of Ca^{2+} ions had reduced shear forces between particles, leading to improved settling rates and grinding performance. This is particularly true when the solid percentage of the bentonite-containing slurries was 62% or higher than that even at a lower bentonite concentration (i.e. 5%). This paper demonstrated that the changes in pulp chemistry or solid percentage can significantly improve the grinding performance of bentonite-containing ores.

Keywords: Bentonite; grinding; rheology; settling

3. Introduction

The existence of clay minerals in ore deposits as gangue is challenging for the mining industry due to its deleterious effects on mining operations such as grinding and flotation as well as on the operational units involved in mining operations. The gradual depletion of high-grade ore deposits has prompted global attention towards exploring the possibilities of processing clay-bearing ores. As a result, the research on the action mechanism and effects of clay minerals on different mineral processing operations has become of more scientific interest than ever before. It is essential to investigate the cost-effective strategies to mitigate the detrimental effect of clay minerals to meet the increasing necessity of utilising clay-bearing minerals. Studies on different ores to understand and minimise the undesirable effects (Chen and Peng, 2018; Jeldres et al., 2019; Basnayaka et al., 2017; Basnayaka et al., 2018) have shown that different types of clays react differently under the same operational conditions.

Bentonite is the most problematic clay mineral due to the particle size less than 2 µm and high absorbent water-swelling characteristics (Basnayaka et al., 2017); bentonite volumes can increase up to 8 times in water solutions. The particles of bentonite clay present in the slurry swell and form a gel-like structure that increases the slurry viscosity significantly even at the clay concentration lower than 5% (Goh et al., 2011). Shakeel et al (2021) studied rheology of bentonite suspensions and observed that bentonite-containing slurries exhibited a single-step yielding behaviour at all investigated concentrations (3-20 wt%) considering strong electrostatic repulsive forces between bentonite particles while ionic strength was low. The challenging rheological behaviour of such slurries causes complexity in all downstream processes; i.e beneficiation (wet-grinding, classification, flotation), de-watering, thickening, management of tailings and transportation. Slurry dilution cannot be a viable option because it will increase the operating and capital costs to process larger volumes while maintaining the valuable mineral production levels (Cruz et al, 2019).

During flotation of bentonite-containing slurries, collisions between bubbles and particles are reduced due to the poor mobilisation of particles and inferior dispersion of bubbles, leading to a lower flotation recovery (Bakker et al., 2009; Shabalala et al., 2011). Additionally, bentonite slime coating was also a key factor for the flotation depression of chalcocite (Peng and Zhao, 2011)). The negative effect of bentonite was also observed during filtration (Basnayaka et al., 2018; Besra et al., 2000) and dewatering (Kretser et al., 1997).

It was found that the addition of Ca^{2+} ions reduced the water-swelling properties of bentonite (Assemi et al., 2015; Cruz et al., 2015), leading to a lower slurry viscosity and thus a higher flotation recovery (Basnayaka et al., 2017) and higher filtration rate (Basnayaka et al., 2018). The possible reason is the replacement of interlayer monovalent Na^{+} ions with Ca^{2+} ions considering that Ca^{2+} ions have higher binding energy with oxygen atom in montmorillonite than that of the Na^{+} ions (i.e., Ca^{2+} ions have two missing valence electrons while Na^{+} ion have one missing valence electron) (Assemi et al., 2015; Cruz et al., 2015, Basnayaka et al., 2017; Basnayaka et al., 2018).

In contrast, the performance of the Knelson concentrator was found to be unaffected by the presence of bentonite clay particles. No significant influence of the presence of any type of clay was observed by Basnayaka et al. (2020). A possible reason can be that the clay particles did not enter the concentrated bed inside the concentrate bowl but were rejected to the tailings instead.

Although the influence of bentonite was studied for filtration, flotation, and Knelson concentration, there is no study investigating the influence of bentonite on grinding performance. Moreover, different studies using laboratory mills (Klimpel, 1982, 1983, 1984; Clarke and Kitchener, 1968; Tucker, 1982; Fuerstenau et al., 1990; Gao and Forssberg, 1993) and industrial mills (Shi and Napier-Munn 2002) showed that the viscosity and rheological properties of fine-containing slurries affect the grinding performance, but no clay-specific research has been conducted. Chipakwe et al (2020) discussed a number of additives that are used as grinding aids in wet or dry grinding to reduce the viscosity of slurries with excessive fines. Grinding aids can be organic or inorganic chemicals that may reduce the viscosity by altering the surface properties of the valuable mineral or the flow properties of the slurry or the arrangement of particles in the slurry (i.e. agglomeration, dispersion, flocculation) (Chipakwe et al., 2020). Considering that there is no study investigating grinding performance in the presence of bentonite, the main objective of this work was to quantify the influence of bentonite on grinding efficiency in the presence and absence of Ca^{2+} ions. Ca^{2+} ions were selected due to their positive effect on flotation and filtration efficiencies in bentonite containing ores (Basnayaka et al., 2017; Basnayaka et al., 2018).

4. Materials and Methods

4.1. Synthetic ore

The synthetic ores were prepared by mixing ground quartz (99.5% purity) and bentonite (montmorillonite and 17.1% quartz). The ores had either 5% or 10% of bentonite. The bentonite had the P_{80} of 10 μm while the crushed quartz had less than 6.38 mm. The mixtures, used in this work, are shown in the supplementary material. It should be noted that $CaCl_2$ was added in different mixtures to investigate its influence on grinding performance.

4.2. Grinding

All the ores were mixed with the tap water to prepare various ore solid percentages (40, 55, 62, and 70%), and then grinding lasted for 45 min in the laboratory rod mill (Labtech Essa Pty Australia). The ionic strength of tap water was 0.006 mol/l and that of filtered process water was in the range between 0.02 and 0.06 mol/l.

The experiments were conducted in the presence and absence of $CaCl_2$ (99% purity, Thermo Fisher Scientific, US). The mill charge (10690 g of the rods and 1428 g of the slurry) and the mill rotational speed (1370 rpm) were kept constant. The pH of all the slurries (7.5±0.2) was adjusted using NaOH (98% grade, Alpha Chemicals, Australia) and HCl (32% grade and distilled water, Alpha Chemicals, Australia). The grinding experiments were conducted using the full factorial design with three variables and two levels: bentonite concentrations (5 or 10%), solid percentage (62 and 70%), and $CaCl_2$ dosage (0 and 3000 g/ ton (ionic strength 0 and 0.0811M respectively)). Apart from these experiments, additional experiments were also performed to investigate the relationships between grinding performance and rheology.

4.3. Particle size distributions

Malvern Mastersizer was used for determining particle size distributions of the slurries obtained after grinding the ore. The particle size distributions (PSD) for the slurries with and without $CaCl_2$ at the selected clay concentrations were given in the supplementary material. The standard deviation of the three repeats was less than 3%.

4.4. Rheological measurements

The rheological measurements were performed with the DV1 MLV viscometer (Brookfield USA). The rheological experiments were conducted using shear-rate ramp-up experiments. The couette rheometer was used in this work. The rheograms (shear stress vs shear rate) were obtained for the studied systems. These experiments were carried out at 20 ± 5 °C.

4.5. Zeta potential measurements

Zeta potential measurements were performed using the zetasizer (Malvern Nano Z, UK). The mixture of 0.05 g of bentonite and 50 ml of water was used to perform the zeta potential measurements at different pH levels. Each test was repeated three times and an average value was used for further investigation.

5. Results and discussions

3.1. Grinding experiments

The grinding experiments were conducted in the absence of bentonite and the results showed that the values for P_{80} were 25 µm (40% solids), 29 µm (55% solids), 37 µm (62% solids) and 39 µm (70% solids). The grinding experiments were also conducted in the presence of bentonite by changing three factors: solid percentage, concentration of clay and dosage of $CaCl_2$ as shown in Table 1. P_{80} was the dependent variable. The supplementary material includes the statistical analysis using ANOVA (analysis of variance) and Tukey. ANOVA results showed that the significance level α was higher than 0.05, indicating that all these variables were not statistically significant. However, the significance of the variables decreased in the following order: Ca^{2+} > clay concentration > solid percentage, demonstrating that the most significant variable was Ca^{2+} dosage (p-value was the lowest) while the least significant variable was the solid percentage (p-value was the highest). Tukey analysis showed that the increase in solid percentage led to a higher P_{80} probably due to the higher concentration of bigger particles in the suspensions, leading to higher shear forces between particles (see Figure 3).

Table 1. Grinding experimental results

Clay Conc. (%)	Ca^{2+} (g/t)	Solid percentage (%)	P_{80} (μm)
5	0	70	110.8
5	0	62	63.65
5	3000	70	37.1
5	3000	62	40.9
10	0	70	169.6
10	0	62	173.2
10	3000	70	71.29
10	3000	62	59.04

Table 1 and Fig. 1 show that the higher the calcium dosage the lower the values of P_{80} due to the decrease in the water-swelling capacity of bentonite in the presence of Ca^{2+} (Bradshaw et al., 2013; Basnayaka et al., 2017). Ca^{2+} ions replaced Na^+ ions in the interlayers of bentonite, holding these layers strongly and thus significantly reducing the water- swelling capacity of bentonite clay (Basnayaka et al., 2017). Therefore, the increase in Ca^{2+} ions reduced the shear forces between particles (see Figure 3), making the addition of these ions highly beneficial for the grinding of bentonite-containing ores. It should be noted that the ionic radii of Ca^{2+} (114 pm) are slightly smaller than that of Na^+ (116 pm), demonstrating that the smaller Ca^{2+} ions can penetrate through the interlayers of bentonite replacing Na^+ ions; Ca^{2+} ions form stronger bonds with oxygen atoms in montmorillonite crystal than Na^+ ions because Ca^{2+} have two missing valence electrons while Na^+ ion have one missing valence electron. Although the addition of Ca^{2+} ions was beneficial for grinding of bentonite-containing ores, the opposite was true for the grinding of kaolin-containing ore (Kashif et al., 2021).

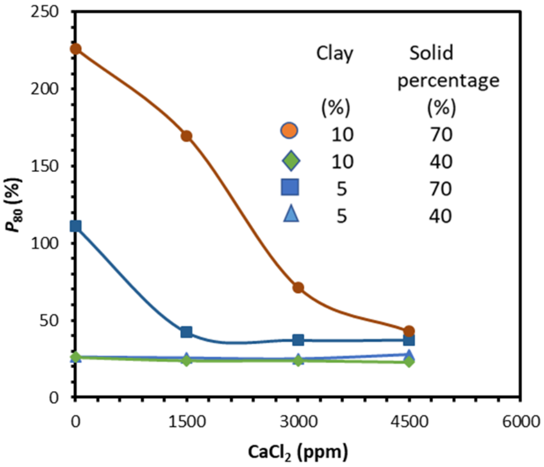


Figure 1. Effect of Ca^{2+} dosage on P_{80}.

Table 1 and Figure 2 also show that the increase in solid percentage led to a higher P_{80}. However, as seen in Figure 2, this effect was observed when the solid percentage was higher than the critical solid percentage i.e., 62%. It appears that the shear forces at the high solid percentage between particles were more dominant than those at the low solid percentage (see Figure 3), leading to the reduced grinding performance at the high solid percentage.

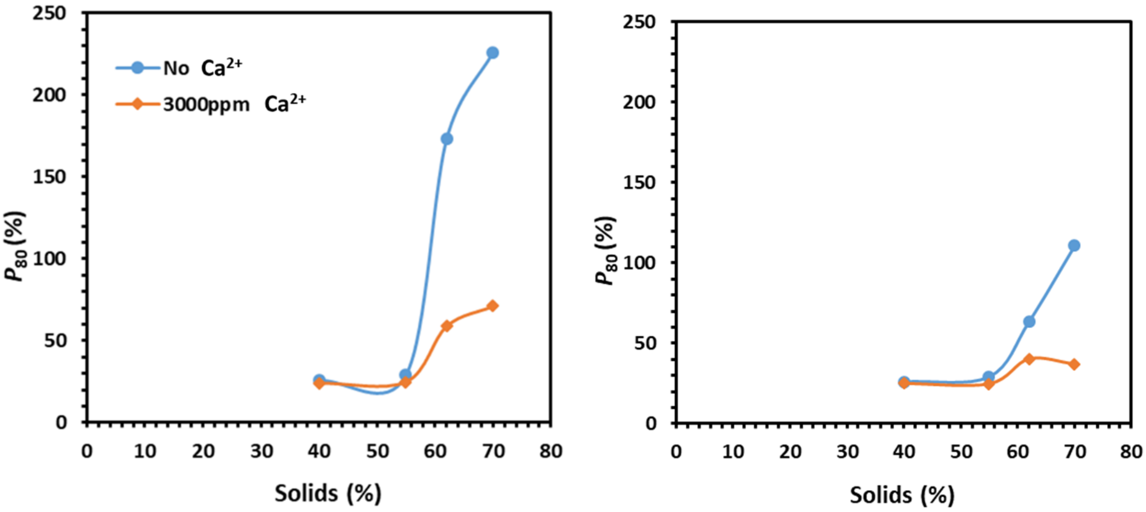

a) b)

Figure 2. Influence of solid percentage and Ca^{2+} dosage on grinding performance for a) 5% bentonite and b) 10% bentonite.

3.2. Rheology and settling behaviour of slurries

Figure 3 shows that the increase in Ca^{2+} dosage led to a reduced shear stress of the slurry due to the reduced water swelling capacity of bentonite. This trend was observed at different clay concentrations. The increase in clay concentration also resulted in higher shear stress for different Ca^{2+} dosages probably due to the increase in shear force. It is true that at 40% solid, the increase in Ca^{2+} dosages led to a reduced slurry viscosity during rheological experiments but the increase in Ca^{2+} dosages did not affect the grinding performance; the reason is that during grinding the impact forces were significantly stronger than the viscous forces. It means that the results in Figure 3 cannot explain the results given in Figure 1. Due to the limitations of the rheological measurements, it was not possible to determine the slurry viscosity when in the case of 70% solids.

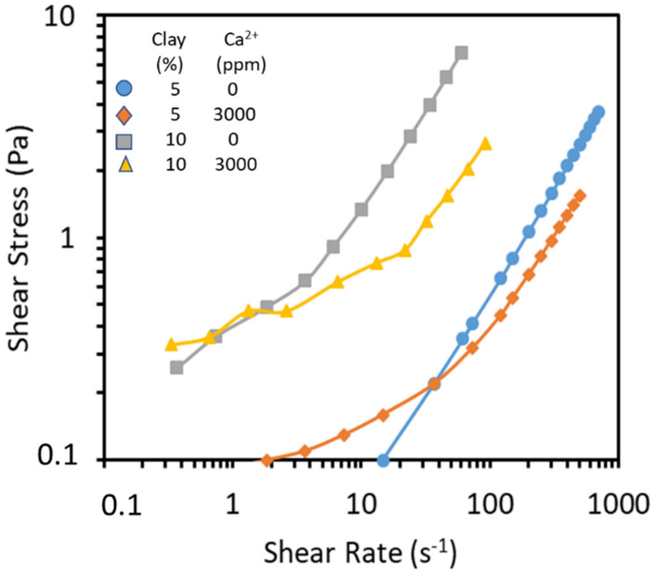
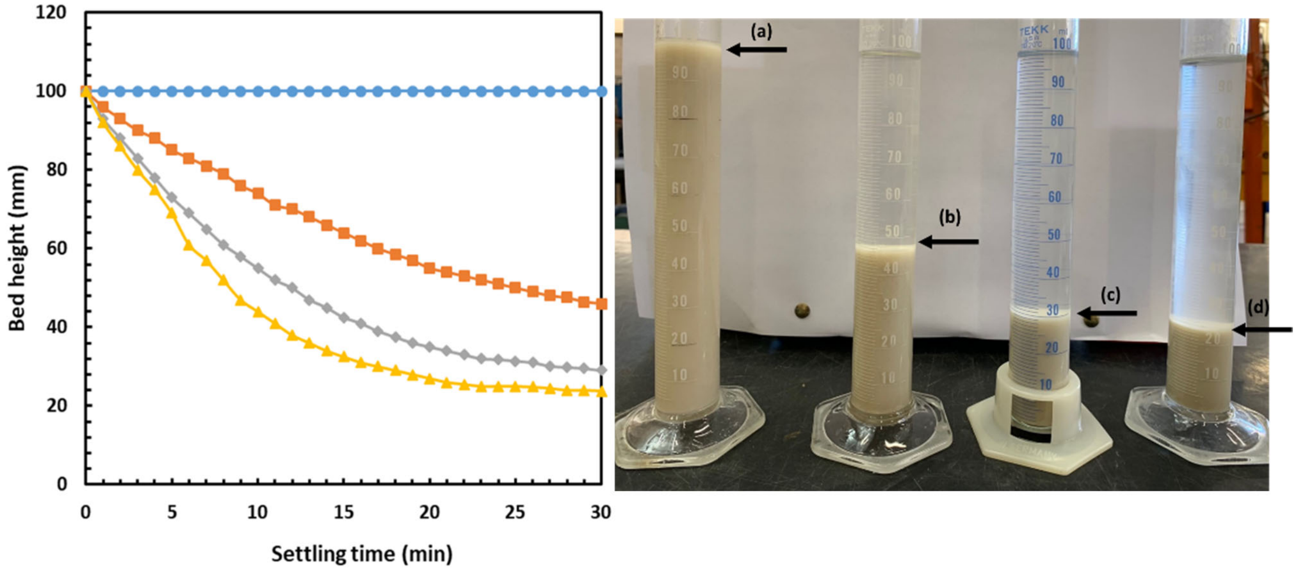


Figure 3. Rheograms of slurry with 40% solid percentage (shear stress vs shear rate)

Figure 4 shows the influence of concentrations of clay and Ca^{2+} ions on settling behaviour. The experiments were conducted using 5% and 10% clay-water mixtures at four selected concentrations of Ca^{2+} (i.e. 0, 1500, 3000 and 4500 ppm) at the same pulp pH as that during grinding. As seen in Figure 4, the presence of Ca^{2+} reduced the water-swelling capacity of bentonite, resulting in an improved settling rate of bentonite particles due to the reduced shear forces between these particles (see Figure 5). This agrees with the results of other studies (Assemi et al., 2015; Cruz et al., 2015). The effect of Ca^{2+} ions on the settling behaviour was much more significant in the case of 5% bentonite-water mixtures than that in the 10% bentonite-water mixtures. The reason is that in the case of 5% bentonite-water mixtures, there were probably sufficient concentrations of Ca^{2+} to significantly reduce the water-swelling capacity of bentonite particles. Another reason could be that the presence of Ca^{2+} also reduced the zeta potential of bentonite at pH 7.5; therefore, the repulsion forces between bentonite particles decreased, leading to improved settling behaviour. It is true that at 40% solid, during the grinding experiments, the viscous forces and gravitational forces were less significant than the impact forces, meaning that the grinding performance was not affected by the increase in bentonite concentration. However, during the settling tests, the viscous forces were higher than the gravitational forces, leading to a reduced setting rate of bentonite particles. Thus, the addition of Ca^{2+} ions were beneficial to reduce the viscous forces during settling tests. However, this effect was not observed in the case of grinding because viscous forces were significantly smaller than the impact force.

5% bentonite



10% bentonite

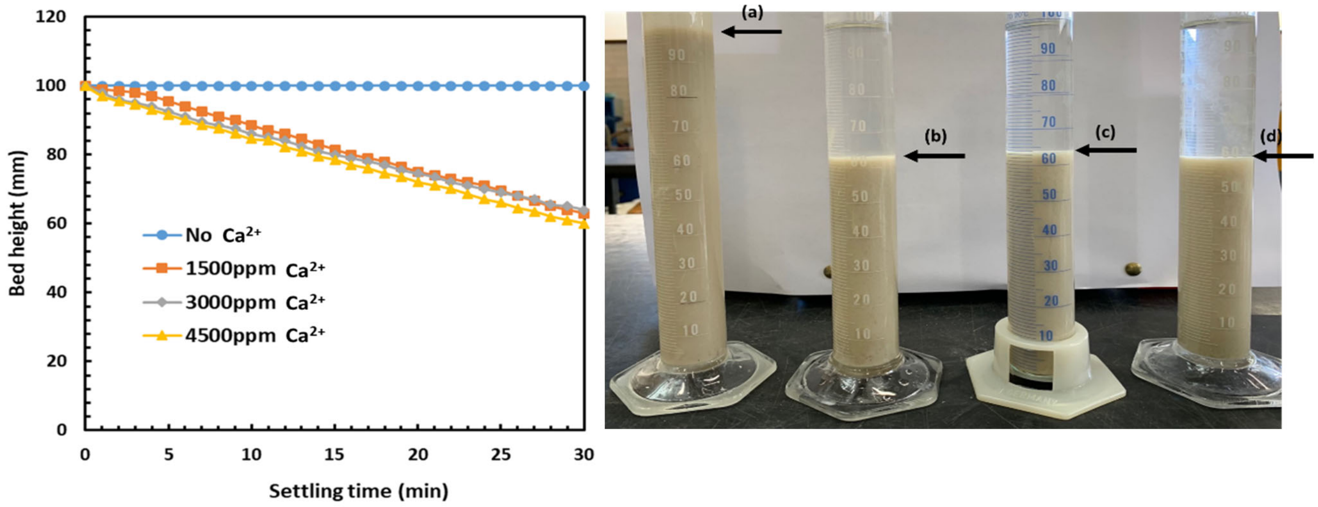


Figure 4. Settling behaviour after 30 min for 5 and 10% bentonite when $CaCl_2$ concentration is (a) 0 ppm, (b) 1500 ppm (c) 3000 ppm, or (d) 4500ppm. The arrows show the level of the settled solids.

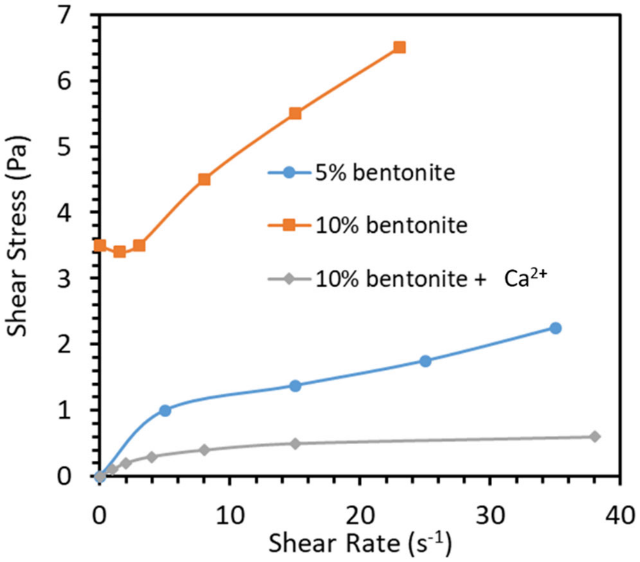


Figure 5. Rheograms of the slurry containing 5 and 10% bentonite in the absence and presence of 1500 ppm $CaCl_2$.

3.3. Zeta potential experiments

The zeta potential measurements of pure bentonite in the presence of selected concentrations of $CaCl_2$ (Ca^{2+}) as a function of pH solutions are shown in Table 2. In the case of pure bentonite, the increase in pulp pH resulted in a lower zeta potential probably due to the adsorption of OH^- ions on bentonite surfaces. However, in the presence of Ca^{2+}, the increase in pH did not affect significantly the zeta potential of bentonite up to pH 8; the reason is possibly that Ca^{2+} ions replaced Na^+ ions in the interlayers of bentonite and thus there were not sufficient concentration of Ca^{2+} ions available to be adsorbed on bentonite surface. However, when pH was higher than 8, the increase in pH resulted in the higher zeta potentials of bentonite. There are two possible explanations for this behaviour. The adsorption capacity of bentonite was significantly reduced at a higher pH and hence Ca^{2+} ions were adsorbed on bentonite surfaces; the decrease in adsorption capacity of bentonite with increasing in pH was also found by Lin et al. (2018). Another potential explanation could be that the increase in pH resulted in a significant increase in $Ca(OH)^+$ ions but it did not affect the concentration of Ca^{2+} ions (Wang et al, 2018). It means that the increase in $Ca(OH)^+$ ions at higher pH might be the reason for the increase in the zeta potential of bentonite. Further research would be required to better understand the influence of pH on Ca^{2+} adsorption capacity of bentonite. The increase in Ca^{2+} concentration at the constant pH resulted in a higher zeta potential probably due to higher adsorption of different calcium species (Ca^{2+}, $Ca(OH)^{+}$) on bentonite surfaces.

Table 2. Zeta potential of bentonite in the presence and absence of $CaCl_2$

pH	**$CaCl_2$ (g/l)**			
	0	1.5	3	4.5
4	-10.37	-5.08	-4.01	-4.46
6	-13.73	-8.17	-5.98	-3.40
7	-18.00	-6.80	-4.92	-3.24
9	-18.57	-7.59	-4.07	2.15
11	-20.40	7.96	12.00	11.70

All these results showed that the presence of Ca^{2+} ions reduced the water-swelling capacity of bentonite, leading to an improved settling behaviour of bentonite, a decrease in shear forces between particles and thus an improved grinding performance i.e. reduced P_{80}.

6. Conclusions

This work showed that the presence of bentonite had adverse effects on the grinding performance mainly due to the high swelling capacity of bentonite. When the solid percentage of the bentonite-containing slurries was higher than 62%, the grinding performance was significantly reduced. However, the addition of Ca^{2+} ions significantly improved the grinding performance by reducing the swelling capacity of bentonite as confirmed by rheological measurements. It was observed that the higher the solid percentage, the lower the grinding performance. The Ca^{2+} dosage was the most significant variable, influencing the grinding performance. This work showed that grinding performance for bentonite-containing ores can be optimized by controlling solid percentage or Ca^{2+} dosage; certainly, it is not possible to control bentonite concentration in any ore. The findings of this research would be useful to develop more effective methods to alleviate the detrimental effects of the presence of bentonite by manipulating the process variables involved in industrial grinding processes.

References

Assemi, S., Sharma, S., Tadjiki, S., Prisbrey, K., Ranville, J., Miller, J.D., 2015. Effect of surface charge and elemental composition on the swelling and delamination of montmorillonite nanoclays using sedimentation field-flow fractionation and mass spectroscopy. Clay Clay Miner. 63 (6), 457–468.

Bakker, C.W., Meyer, C.J., Deglon, D.A., 2009. Numerical modelling of non Newtonian slurry in a mechanical flotation cell. Miner. Eng. 22 (11), 944–950.

Basnayaka, L., Albijanic, B., Subasinghe, N., 2020. Performance evaluation of processing clay-containing ore in Knelson concentrator. Minerals Engineering 152, 106372.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2017. Influence of clays on the slurry rheology and flotation of a pyritic gold ore. Appl. Clay Sci. 136, 230–238.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2018. Influence of clays on fine particle filtration. Appl. Clay Sci. 156, 45–52.

Besra, L., Sengupta, D.K., Roy, S.K., 2000. Particle characteristics and their influence on dewatering of kaolin, calcite and quartz suspensions. Int. J. Miner. Process. 59, 89–112.

Bradshaw, S.L., Benson, C.H., Scalia, J., 2013. Hydration and cation exchange during subgrade hydration and effect on hydraulic conductivity of geosynthetic clay liners. J. Geotech. Geoenviron. Eng. 139 (4), 526–538.

Chen, X., Peng, Y., 2018. Managing clay minerals in froth flotation—A critical review, Mineral Processing and Extractive Metallurgy Review, 39(5), 289-307. DOI: 10.1080/08827508.2018.1433175

Chipakwe, V., Semsari, P., Karlkvist, T., Rosenkranz, J., Chehreh Chelgani, S., 2020. A critical review on the mechanisms of chemical additives used in grinding and their effects on the downstream processes, Journal of Materials Research and Technology, Volume 9, Issue 4, Pages 8148-8162, ISSN 2238-7854,

Clarke, B., Kitchener, J.A., 1968. The influence of pulp viscosity on fine grinding in a ball mill. Br. Chem. Eng. 13, 991 – 995

Cruz, N., Yongjun, P., Wightman, E., Xu, N., 2015. The interaction of clay minerals with gypsum and its effects on copper–gold flotation. Min. Eng. 77, 121–130.

Cruz, N., Forster, J., Bobicki, E.R., 2019. Slurry rheology in mineral processing unit operations: A critical review. Can. J. Chem. Eng., 97: 2102-2120. https://doi.org/10.1002/cjce.23476

Fuerstenau, D.W., Kapur, P.C., Velamakanni, B.V., 1990. A multi-torque model for the effects of dispersants and slurry viscosity on ball milling. Int. J. Miner. Process. 28, 81 – 98.

Gao, M.W., Forssberg, E., 1993. The influence of slurry rheology on ultra-fine grinding in a stirred ball mill. Proceedings XVIII Int. Min. Process. Cong., Sydney. The Australasian Institute of Mining and Metallurgy (AusIMM), Melbourne, pp. 237 – 244.

Goh, R., Leong, Y.K., Lehane, B., 2011. Bentonite slurries-zeta potential, yield stress, adsorbed additive and time-dependent behaviour. Rheol. Acta 50 (1), 29–38.

Jeldres, R. I., Uribe, L., Cisternas, L.A., Gutierrez, L., Leiva, W.H., Valenzuela, J., 2019. The effect of clay minerals on the process of flotation of copper ores - A critical review. Applied Clay Science (170), 57-69.

Kashif, N., Albijanic, B., Xu J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M. K., 2021. Detrimental effect of calcium on grinding performance of a kaolin-containing ore. Applied Clay Science 215, 106307.

Klimpel, R.R., 1982. Slurry rheology influence on the performance of mineral/coal grinding circuit. Part 1, Min. Eng. 34 (12), 1665 – 1668.

Klimpel, R.R., 1983. Slurry rheology influence on the performance of mineral/coal grinding circuit. Part 2, Min. Eng. 35 (1), 21 – 26.

Klimpel, R.R., 1984. Influence of material breakage properties and associated slurry rheology on breakage rates in wet grinding of coal/ores in tumbling media mills. In: Jones, M.J., Oblatt, R. (Eds.), Reagents in the Mineral Industry. I.M.M., London, pp. 265 – 270.

Kretser, R. D., Scales, P. J., Boger, D. V., 1997. Improving clay-based tailings disposal: case study on coal tailings. AICHE J., 43, 1894-1903, 10.1002/aic.690430724

Lin, B. Jiang, Y. Zhan, 2018. Effect of pre-treatment of bentonite with sodium and calcium ions on phosphate adsorption onto zirconium-modified bentonite, J.Environ. Manage. 217 183–195.

Peng, Y., Zhao, S., 2011. The effect of surface oxidation of copper sulfide minerals on clay slime coating in flotation. Miner. Eng. 24 (15), 1687–1693.

Shabalala, N.Z.P., Harris, M., Filho, L.S.L., Deglon, D.A., 2011. Effect of slurry rheology on gas dispersion in a pilot-scale mechanical flotation cell. Miner. Eng. 2 (13), 1448–1453.

Shakeel, A., Kirichek, A., Chassagne, C., 2021. Rheology and yielding transitions in mixed kaolinite/bentonite suspensions. Applied Clay Science, Volume 211, 106206.

Shi, F. N., T.J Napier-Munn, T. J., 2002. Effects of slurry rheology on industrial grinding performance, International Journal of Mineral Processing, Volume 65, Issues 3–4, 2002, Pages 125-140,

Tucker, P., 1982. The role of viscosity in the wet-grinding of ores, with special reference to grinding aids. Warren Spring Laboratory Report, LR 421 (MP), May

Wang, X., Liu, W., Duan, H., Wang, B., Han, C., Wei, D., 2018. The adsorption mechanism of calcium ion on quartz (101) surface: A DFT study. Powder Technol. 329, 158–166, doi:10.1016/j.powtec.2018.01.086.

Supplementary material

Table 1S. Ore mineralogy and water consumptions for all the samples.

Mixtures	Solid %	Clay %	Quartz (g)	Bentonite (g)	Water (g)	$CaCl_2$ (g)
1	70	5	950	50	428	0
2	70	10	900	100	428	0
3	70	5	950	50	428	1.5
4	70	10	900	100	428	1.5
5	70	5	950	50	428	3
6	70	5	950	50	428	3
7	70	5	950	50	428	3
8	70	10	900	100	428	3
9	70	5	950	50	428	4.5
10	70	10	900	100	428	4.5
11	40	5	522.5	27.5	820	0
12	40	10	495	55	820	0
13	40	5	522.5	27.5	820	3
14	40	10	495	55	820	3
15	55	5	731.5	38.5	630	0
16	55	5	731.5	38.5	630	3
17	55	10	693	77	630	0
18	55	10	693	77	630	3
19	62	5	807.5	47.5	520	0
20	62	5	807.5	47.5	520	3
21	62	10	765	85	520	0
22	62	10	765	85	520	3

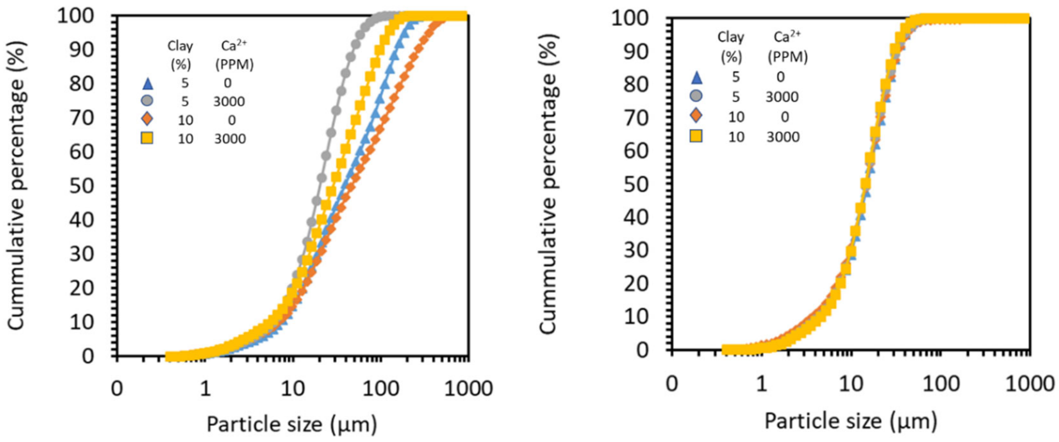


Figure 1S. Particle size distributions of the ore (a) 70% solid percentage (b) 40% solid percentage.

Table 2S. ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Clay Conc. (%)	1	6089.7	6089.7	10.90	0.187
Ca^{2+} (g/t)	1	11932.0	11932.0	21.37	0.136
Solid percentage (%)	1	337.5	337.5	0.60	0.579
Clay Conc.(%) * Ca^{2+} (g/t)	1	1683.7	1683.7	3.02	0.333
Clay Conc.(%) * Solid percentage (%)	1	150.9	150.9	0.27	0.695
Ca^{2+}(g/t) * Solid percentage (%)	1	153.7	153.7	0.28	0.692
Error	1	558.4	558.4		
Total	7	20905.9			

Table 3S. Tukey results

Variables	Number of experiments	Mean P_{80}
Clay Cons., 10 %	4	118.292
Clay Cons., 5 %	4	63.112
Ca^{2+}, 0 g/t	4	129.322
Ca^{2+}, 3000 g/t	4	52.082
Solid percentage, 70 %	4	97.1975
Solid percentage, 62 %	4	84.2075

Chapter V

Investigating the drying behaviour of clay-containing slurries

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Abstract

Managing clay-containing slurries during drying process remains a persistent challenge in various industries. Despite challenges of drying clay-containing-slurries, limited information is available. The aim of this study is to explore the drying performance of slurries containing kaolin and bentonite and gain insights into the underlying drying mechanisms. The research presented integrates drying experiments, rheology measurements, settling experiments, zeta potential measurements, FTIR, TGA/DTA, and SEM analysis. Bentonite-containing slurries retained more moisture due to their high-water adsorption capacity, with higher bentonite percentages extending drying times. The addition of Ca^{2+} ions reduced moisture content by replacing Na^+ ions with smaller Ca^{2+} ions, making the slurries less viscous. The addition of Ca^{2+} disrupted the gel-like structure of bentonite as confirmed by SEM and FTIR. In contrast, kaolin-containing slurries maintain lower moisture levels owing to the non-swelling structure of kaolinite. SEM showed the formation of agglomerates for kaolin when Ca^{2+} was added The addition of Ca^{2+} ions had a subtle impact on drying rates, despite a slight increase in slurry viscosity probably due to the agglomeration of kaolinite particles. Both slurries exhibited three drying phases: rapid drying due to high moisture, a moderate phase with reduced rates, and a final phase of slowed drying as tightly bound moisture was harder to remove. This paper demonstrated the significance of understanding the drying processes of clay-containing slurries to enhance the overall drying efficiency.

Keywords: Bentonite, Kaolin, Drying, Rheology, Zeta potential

1. Introduction

Clay minerals are distributed throughout the Earth's crust, often accompanying valuable mineral deposits. Clay minerals are the result of chemical or physical weathering processes that transform primary silicate minerals, originally formed during the cooling and crystallization of magma in the Earth's crust, into clay minerals (Wimpenny, 2018). The prevalence of clay minerals can be attributed to their exceptionally fine particle size (typically less than 2μm) and the presence of relatively insoluble aluminium compounds, such as aluminium oxide (Appelo and Postma, 2005; Wimpenny, 2018).

While all clay minerals share a common structural foundation consisting of layers of silica tetrahedra (T) and alumina octahedra (O), it is their unique layer arrangements and the binding forces between these layers that classify them into three distinct groups, each possessing specific characteristics (Brigatti et al., 2013). These groups are referred to as kaolinite/kaolin, montmorillonite/bentonite, and mica/muscovite/illite, with ratios of 1:1 (TO), 2:1 (TOT), and 2:1 (TOT), respectively.

An alternate classification of clay minerals is based on their capacity to absorb water, categorizing them as either swelling or non-swelling clays, as proposed by Jeldres et al. (2019). Kaolin group clay minerals, characterized by van der Waals attractive forces and strong hydrogen bonds, and illite group clay minerals, which have potassium ions between their layers, exhibit impermeability to water penetration, classified as non-swelling clays (Zhang, 2016; Chen and Peng, 2018). Conversely, bentonite group clay minerals rely primarily on van der Waals forces between atoms (Anandarajah and Chen, 1997) due to the absence of exposed hydroxyl groups on their surface for strong hydrogen bonding. Consequently, when bentonite clay interacts with water, it readily allows water penetration through its layers, classifying it as a swelling clay (Luckham and Rossi, 1999; Zhang, 2016).

All these groups of clays have a negative charge on their faces while the edges can be negatively or positively charged depending on the pH of the solution (Lagaly, 1989; Tombácz and Szekeres, 2006). Clays are colloidal materials but in real suspensions they tend to form single layers or aggregates (i.e. face-face, edge-face or edge-edge) depending on the chemistry and rheology of the suspension and the properties of clay mineral (Luckham and Rossi, 1999). E-F and E-E aggregation results in an increased viscosity of montmorillonite clay minerals (Zhang and Peng, 2015; Rand and Melton, 1977).

The increased viscosity of clay-containing slurries due to a high-water adsorbing capacity of bentonite-containing ores (Bakker et al. 2010; Chen and Peng, 2018; Farrokhpay 2011; Ndlovu et al. 2011; Patra et al. 2012; Shabalala et al. 2011), slime coating of valuable mineral particles (Chen and Peng, 2018; Forbes et al. 2014; Gaudin et al. 1960; Kashif et al., 2023; Peng and Zhao, 2011; Xu et al. 2003; Zhao and Peng 2012;) and mechanical entrainment of fine clay particles (Bisshop and White 1976; Chen and Peng, 2018; Gaudin 1957; Wang and Peng 2013; Wang et al. 2014a) have been observed. Therefore, the presence of clay together with valuable minerals poses a range of challenges at various stages of ore processing. These challenges manifest in the form of fines generated during crushing, reduced grinding performance (Kashif et al., 2021 & 2023), reduced ore grades and recovery rates in flotation (Basnayaka et al., 2017;

Chen and Peng, 2018; Seaman et al. 2012; Wang and Peng 2013; Zhang 2016), decreased filtration (Basnayaka et al., 2018) and dewatering process rates (Chryss, 2017; McFarlene, 2005), reduced drying of suspensions (Basnayaka et al., 2018; Gualtieri et al., 2016) as well as the problems during tailing dam management (Chryss, 2017; Liu et al., 2017).

Clays can be removed using hydrocyclones (Oats et al., 2010). Additionally, the presence of Ca^{2+} ions in slurries also significantly reduced swelling properties of bentonite containing ores, reducing a slurry viscosity (Basnayaka et al., 2017, Kashif et al, 2023). The addition of Ca^{2+} ions significantly reduced the swelling of bentonite in water. The reason is that the ionic radius of Ca^{2+} (114 pm) is slightly smaller than that of Na^{+} (116 pm) in a montmorillonite structure, allowing smaller Ca^{2+} ions to replace Na^{+} ions in the interlayers of bentonite (Kashif et al., 2023). Moreover, Ca^{2+} ions form stronger bonds with oxygen atoms in the montmorillonite crystal than Na^{+} ions, as Ca^{2+} ions have two missing valence electrons while Na^{+} ions have only one missing valence electron (Kashif et al., 2023). Using Ca^{2+} ions for bentonite-containing slurries offer the advantage of being both cost-effective and environmentally friendly, as only a small amount of this chemical is required (Basnayaka et al., 2017). However, in the case of kaolinite ores, the presence of Ca^{2+} led to agglomeration of kaolinite particles, resulting in increased slurry viscosities (Kashif et al, 2021). The disadvantage of Ca^{2+} ions on kaolin ores can be solved using different techniques for removal of Ca^{2+} from water such as ultrafiltration or nanofiltration (Guerra et al., 2023).

Dewatering and disposal of the clay containing tailings is also a great challenge for mine operators due to swelling and gelation properties of bentonite (Kretser et al, 1997; Clement and Bonjer, 1975; Vick, 1983). Sedimentation under gravity is the main mechanism involved in many cases when tailings are pumped into tailing dams as a final stage of disposal system. But exceptionally poor sedimentation due to diverse shear rheological characteristics and significantly poor dewatering ability of clay containing tailings make these tailing dams less stable (Chryss, 2017; Liu et al., 2017).

Apart from sedimentation, drying is also used to further remove water from ores. Most authors investigated the drying of clay-containing minerals in coatings (Nechita, 2021), ceramics (Khalfi and Blanchart, 1999; Oummadi, 2019; Zaccaron et al., 2022;) or desiccation crack formation in different engineering fields (Mohammad et al., 2020) like geotechnical (Li et al. 2009), agricultural (Bronswijk, 1991), and environmental geotechnics (Daniel and Brown

1987; Peron et al., 2009). However, drying of clay-containing slurries in the presence and absence of Ca^{2+} ions have not been yet investigated. Ca^{2+} ions were used considering that these ions were found to mitigate the detrimental effects of different clays by improving rheological properties of clay-containing slurries during flotation (Basnayaka et al., 2017) and fine particle filtration (Basnayaka et al., 2018). The grinding performance of bentonite-containing ores was also improved in the presence of Ca^{2+} ions (Kashif et al, 2023). Hence, this paper aims to investigate how the presence of Ca^{2+} ions affects the drying performance of bentonite and kaolin-containing ores. Therefore, the main objective of this research is to study the influence of Ca^{2+} ions on the drying performance of bentonite and kaolin-containing ores in the presence and absence of Ca^{2+} ions. This study is very important for practical applications considering that efficient drying is essential for reducing the handling cost of the final products.

2. Materials and methods

2.1. Synthetic ore samples

The synthetic ore with 40% solids was used for all experiments. The synthetic ores were prepared by mixing 23.4 g of ground quartz and 2.6 g of clay (i.e. to achieve an ore with 10% clay) while 15.6 g of ground quartz and 10.4 g of clay (i.e. to achieve an ore with 40% clay). Table 1 shows the ore mineralogy for all the samples used in this work. It should be noted that the influence of $CaCl_2$ on drying performance was investigated by the addition of $CaCl_2$ in different samples.

Table 1. Ore mineralogy and water consumptions for all the samples.

Clay type	Temp ˚C	Clay %	Quartz (g)	Clay (g)
Kaolin	150	10	23.4	2.6
Kaolin	150	10	23.4	2.6
Kaolin	100	10	23.4	2.6
Kaolin	100	10	23.4	2.6
Kaolin	150	40	15.6	10.4
Kaolin	150	40	15.6	10.4
Kaolin	100	40	15.6	10.4
Kaolin	100	40	15.6	10.4
Bentonite	150	10	23.4	2.6
Bentonite	150	10	23.4	2.6
Bentonite	100	10	23.4	2.6
Bentonite	100	10	23.4	2.6
Bentonite	150	40	15.6	10.4
Bentonite	150	40	15.6	10.4
Bentonite	100	40	15.6	10.4
Bentonite	100	40	15.6	10.4

The ground quartz had a particle size less than 75 µm. The bentonite and kaolin had P_{80} of 10 µm (Basnayaka et al., 2018). Particle size distributions were determined using Malvern Mastersizer. The XRD shows that the kaolin had 87% kaolinite and 13% quartz whereas the bentonite had 82.9% montmorillonite and 17.1% quartz (Basnayaka et al., 2017). The XRF results showed that the quartz sample had91 % SiO_2, 6.6% Al_2O_3 and other impurities such as 1.16% Fe_2O_3 and 0.6% Cr_2O_3. The XRF results showed that the main components of the bentonite sample were 63% SiO_2, 24% Al_2O_3, 6.4% Fe_2O_3, 3.8% MgO, 1.5% K_2O, and other impurities such as 0.08% CaO and 0.8% TiO_2. The XRF results showed that the main components of the kaolin sample were 52% SiO_2, 43% Al_2O_3, and other impurities such as 1.4% TiO_2 and 1.6% Fe_2O_3, etc.

2.2. Drying experiments

All the synthetic ores were mixed with 39 g of the tap water to achieve 40% solid percentage slurries and then drying was carried out at 100˚C and 150˚C in the laboratory oven. The moisture content was recorded as a function of time for all the samples. The drying was conducted until the moisture content was zero. The experiments were conducted in the presence and absence of different concentrations of $CaCl_2$ (99% purity, Thermo Fisher Scientific, US). The pH of all the slurries (7.5±0.2) was kept constant using HCl (99% grade, Sigma Aldrich, US) and NaOH (99% grade, Sigma Aldrich, US). The drying experiments were performed using the full factorial design with four variables: clay type (kaolin or bentonite), clay concentration (10 or 40%), temperature (100 or 150˚C) and $CaCl_2$ dosage (0 or 4500ppm (ionic strength 0 or 0.1216M respectively)).

The drying experiments were analysed using ANOVA and Tukey analysis for three separate drying regions. ANOVA is a statistical method of analysing the differences among group means in a dataset and stands for Analysis of Variance (Minitab, 2023). In the ANOVA analysis, the following parameters are used: df, Adj SS, Adj MS, p values and F values. The degree of freedom (df) represents the amount of information in the data. The adjusted sums of squares (Adj SS) represent the measures of variation attributed to various components within the model. The adjusted mean (Adj MS) squares quantify the amount of variation explained by a model, under the assumption that all other terms are included in the model. The F-value serves as the test statistic for assessing whether the term is linked with the response. The p-value represents the probability for the evidence against the null hypothesis. In other words, the lower the p-value, the stronger the evidence against the null hypothesis. Additionally, Tukey method (Minitab, 2023) is used to establish confidence intervals for all pairwise differences among factor level means while controlling the family error rate. Apart from ANOVA and Tukey method, the Bingham model as well as the models available in the LabFit software (Minitab, 2023) were used to describe the experimental drying data.

The Lewis model (Ertekin and Firat, 2017), based on an analogy to Newton's law of cooling, was used to determine the drying rate constant:

$$k = \frac{dM}{dt}\frac{1}{M_e - M} \tag{1}$$

Where k represents the drying rate constant (s^{-1}), M_e is the equilibrium moisture content, M is the actual moisture content, and dM/dt is the drying rate.

2.3. Settling experiments

The settling experiments were carried out using the 100 ml graduated cylinders. For this purpose, 5% and 10% kaolin clay slurries, and 5% and 10% bentonite clay slurries were used. Each experiment was carried out at 20 ± 5°C and a slurry pH of 7.5. The experiments were conducted as a function of $CaCl_2$ dosage (0, 1500, 3000 and 4500 ppm (ionic strength 0, 0.0405, 0.0811 and 0.1216M respectively)). The slurries were mixed vigorously and then allowed to settle in the graduated cylinders. Settling behaviour for each slurry was observed for 30 min by recording the changes in the solid-liquid interface.

2.4. Rheological measurements

The rheological measurements were performed with the DV1 MLV viscometer (Brookfield USA). These experiments were carried out at 20 ± 5°C. The rheograms (shear stress vs shear rate) were obtained for the studied systems. For bentonite containing slurries, the rheological experiments were conducted using shear-rate ramp-up experiments. The couette rheometer was used in this work. For kaolin containing slurries, 16 ml sample was used for the UL adapter whereas 600 ml sample was used for the LV01 standard spindle arrangement.

The Bingham model (King, 2002) was used to describe the rheological measurements:

$$\tau=\tau_X+\mu_{PL}\gamma \qquad (2)$$

Where τ represents the shear stress, γ is the shear rate, τ_X is the yield stress, and μ_{PL} is the plastic viscosity. The yield stress represents the minimum stress required to initiate flow. The plastic viscosity measures a fluid resistance to flow after surpassing its yield stress, in the context of shear-thinning behaviour observed in Bingham plastics.

2.5. Zeta potential measurements

Zetasizer (Malvern Nano Z, UK) was used to conduct the zeta potential measurements. The measurements were carried out at different pH levels (i.e. 4, 6, 7, 9 and 11) for the mixture of

0.05 g of bentonite or kaolin and 50 ml of water. Each test was repeated three times and an average value was used for further investigation.

2.6. FTIR experiments

A Nicolet iS50 (Thermo Fisher Scientific Inc., US) Fourier-transform infrared spectroscopy (FTIR) was used to determine the surface functional groups on the clay samples (kaolin or bentonite) after drying them in a laboratory oven at 100 ºC for 24 h to ensure complete water removal. More precisely, the samples were prepared by mixing 10% (w/w) bentonite or kaolin clay with deionised water in the presence and absence of Ca^{2+} ions.

2.7. SEM experiments

A Zeiss Neon 40EsB Cross-beam (Zeiss, Germany) Scanning Electron Microscope (SEM) was utilized to examine the microstructure of the dried samples. The SEM analysis was performed on the clay samples (kaolin or bentonite) after drying the samples in a laboratory oven at 100 ºC for 24 h to completely remove water. The samples were prepared by mixing 10% (w/w) bentonite or kaolin clay with deionised water in the presence and absence of Ca^{2+} ions. The scanned images of the samples were magnified 10000 times.

2.8. TGA-DTA experiments

A SDT Q600 (TA Instruments , US) TGA (Thermogravimetric Analysis) was employed to validate the changes in the sample mass over a specified duration, with temperature constantly increasing from room temperature to 1000°C at a constant rate of 10ºC/min under a nitrogen atmosphere flowing at 100 ml/min. The homogenized samples were placed into a 110 µL platinum crucible equipped with a pinhole lid. A corresponding empty crucible served as a reference. The samples were prepared by mixing 10% (w/w) bentonite or kaolin clay with deionised water in the presence and absence of Ca^{2+} ions (4500 ppm (ionic strength 0.1216M).

3. Results and discussions

3.1. Bentonite containing ores

3.1.1. Drying results

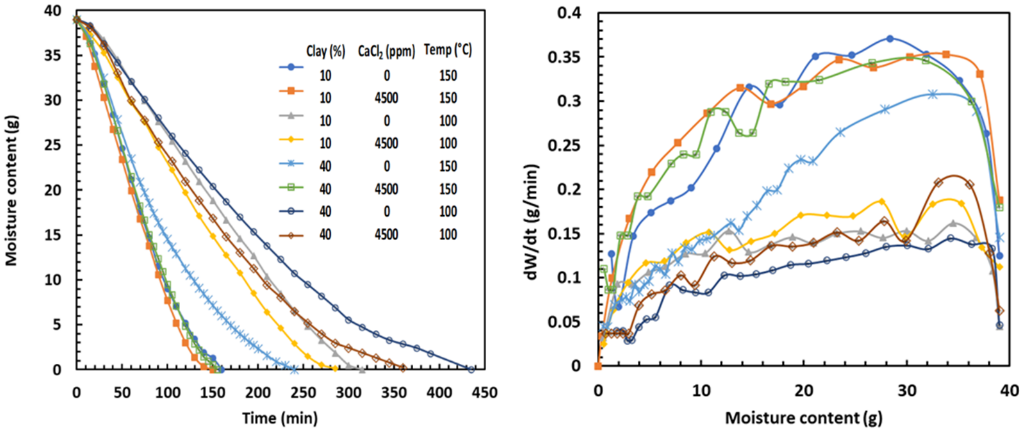
Figure 1a show the moisture content as a function of time. As seen in Figure 1a, the increase in bentonite percentage resulted in a higher retained moisture content because of the higher water adsorbing capacity of bentonite (Basnayaka et al., 2017; Kashif et al., 2023). For example, the sample containing 10% bentonite in the absence of $CaCl_2$ was dried after 150 min while the sample containing 40% bentonite in the absence of $CaCl_2$ was dried after 240 min. The addition of $CaCl_2$ significantly reduced the moisture content because Ca^{2+} ions replaced Na+ ions in the interlayers of montmorillonite (Kashif et al., 2023). The increase in temperature lead to faster evaporation of moisture and the drying was completed faster. It should be noted that some authors (Loh and Wijeyesekera, 2009; Pier et al., 1993) found that the moisture content decreased slower in the case of drying of pure bentonite than that obtained in our work considering that these authors conducted drying at a significantly lower temperature.

Bentonite is a montmorillonite clay that can absorb and contain moisture in various forms such as free water, capillary water, adsorbed water, interlayer water, and hydroxyl water (Bergaya et al., 2006; Lang et al., 2017; Velde, 1992). Free and capillary water exist in macropores such as inter-aggregate and inter-particle pores and can be easily removed under normal environmental conditions (Lang et al., 2017). Bentonite particles have charged surfaces that generate an electrostatic field. When these particles are in contact with water, the electrostatic field causes positively charged ions to attract and polar water molecules to be adsorbed, forming a diffused double-layer and creating a water film. Water that enters the interlayer spaces in a clay-water system is known as interlayer water, and its presence is influenced by interlayer cation hydration, interactions between clay surfaces and water molecules, as well as water activity and interlayer cations. Hydroxyl water, also called crystalline water, is present as OH units within the clay's structure. During the dehydroxylation reaction (i.e., above 400°C), the OH units undergo oxidation, resulting in the formation of H_2O.

The drying rates were determined by measuring changes in moisture content over time, and the relationship between moisture content and drying rate was shown in Figure 1b. As illustrated in the Figure 1b, three distinct drying regions can be identified based on the change in slope of the drying curves. In the first region, the drying rate shows a clear trend of increasing as the moisture content decreases, up to 37 g. During the first region heat removed the water molecules, loosely held in the surface of the sample, at a faster rate. The drying rate increases rapidly because the moisture content of the sample is relatively high, and there is a large driving force for moisture to evaporate from the sample surface; the driving force for drying is the difference in vapor pressure between the surface of the sample and the surrounding air. At this point, the heat provided to the sample is mainly used to evaporate moisture, so the drying rate is primarily controlled by the rate of heat transfer to the surface of the sample. Free water and capillary water are removed because those two types of water are held in macropores like inter-aggregate, inter-particle pores and can be easily removed under ambient conditions (Lang et al., 2017). To some extent, adsorbed water can also be removed in this region. It is because, the adsorbed water was transported to the surface of montmorillonite particles and can be removed when the sample was heated at a temperature of 80–90°C (Lang et al., 2017).

In the second region, the drying rate decreases slightly as the moisture content decreases (see Figure 1b). This is due to the presence of water in the interlayers, making it challenging to remove moisture effectively. Interlayer water can be removed at temperatures between 100-250°C, depending on the interlayer cations. Factors such as diffusion limitation and the layered structure of bentonite clay contribute to the reduced drying rate in this region. In other words, after the removal of the loosely held water molecules from the sample surface in the first region, the removal of water molecules became difficult because the remaining moisture was penetrated through the layered structure of bentonite (i.e. 2:1 layered structure of silicate tetrahedral "T" and alumina octahedral "O" that is responsible for the swelling capacity of bentonite clay). Moreover, as the free moisture content on the surface decreases, the internal resistance and transporting through the capillaries for water molecules to reach the surface becomes difficult, leading to a reduced drying rate. Another factor that becomes active as the moisture content on the surface of the sample decreases, is the development of a moisture and concentration gradient within the sample. A concentration variation is established between the surface and the interior of the sample that opposes the flow of moisture towards the surface, leading to a decreased drying rate in this region. Additionally, the material properties are altered as the surface of the sample undergoes a physical change. A dried hard surface of the sample offers a barrier for the moisture removal from the sample resulting in a reduced drying rate.

In the third region, a notable decline in the drying rate is observed, reaching an equilibrium moisture content (see Figure 1b). The drying rate experiences a significant reduction because the majority of the loosely bound surface and subsurface moisture has already been eliminated during the initial two regions. The remaining water is bound more tightly within the structure of bentonite-containing ore, making its removal more challenging. It is possible that the removal of the remaining interlayer water and hydroxyl water contributes to this sharp reduction in the drying rate. When heated to a temperature in the excess of 125°C, the interlayer distance is reduced by approximately 3 Å as a result of the removal of one layer of interlayer water (Ferrage et al, 2005 & 2007; Gadikota et al 2017; Gadikota et al, 2019).



(a) (b)

Figure 1. Drying performance of bentonite containing slurries.

The drying experiments were analyzed using ANOVA and Tukey analysis for three separate drying regions. The results for ANOVA and Tukey analysis are presented in Tables 2, 3, and 4 for region one, two and three, respectively.

In the first region, the ANOVA (see Table 1S-a in the supplementary material) indicated that temperature had the highest significance (i.e., p-value of 0.032) followed by $CaCl_2$. The clay percentage was found to be the least significant variable with a p-value higher than 0.05. The Tukey analysis for region one (see Table 1S-b in the supplementary material) supported these findings, showing that increasing temperature and $CaCl_2$ concentration led to higher drying rates, while clay concentration did not have a significant effect. It means that in region one, temperature and $CaCl_2$ concentration are more significant variables compared to clay concentration.

In the second region (see Table 2S-a in the supplementary material), none of the variables showed statistical significance according to the ANOVA results. However, it was observed that the drying rate was most significantly affected by the changes in temperature, while the impact of $CaCl_2$ concentration was found to be the least pronounced. The Tukey analysis for region two (see Table 2S-b in the supplementary material) revealed that only temperature had a significant effect on the drying rate, while clay concentration and $CaCl_2$ concentration did not show a significant effect.

In the third region (see Table 3S-a in the supplementary material), the ANOVA indicated no significant variables. The Tukey analysis for region three (see Table 3S-b in the supplementary material) confirmed that temperature had a substantial effect on the drying rate while clay concentration and $CaCl_2$ concentration did not show any effect on drying. In summary, the analysis reveals the varying significance of variables in different drying regions. Temperature consistently appears as the most significant variable, while the significance of clay concentration and $CaCl_2$ concentration varies across the regions. The correlations for drying kinetics in all three regions are shown in Table 4S in the supplementary material. All these correlations successfully predicted the rate constants (R2 higher than 0.92).

3.1.2. TGA-DTA measurements for bentonite

Figure 2 presents the TGA-DTA curves of the mass changes for the bentonite samples heated from 25 ˚C to 1000 ˚C. As seen in Figure 2, the mass loss of the bentonite sample in absence of Ca^{2+} ions was higher than that in the presence of Ca^{2+} ions. The reason could be probably because the amount of water adsorbed on bentonite in the presence of Ca^{2+} ions was lower than that in the absence of Ca^{2+} ions. Figure 2 also shows that 50% of water was removed at 101.3°C in the presence of Ca^{2+}, whereas the same percentage of water was removed at 94.2°C in the absence of Ca^{2+}. It indicates that Ca^{2+} improves the drying rate.

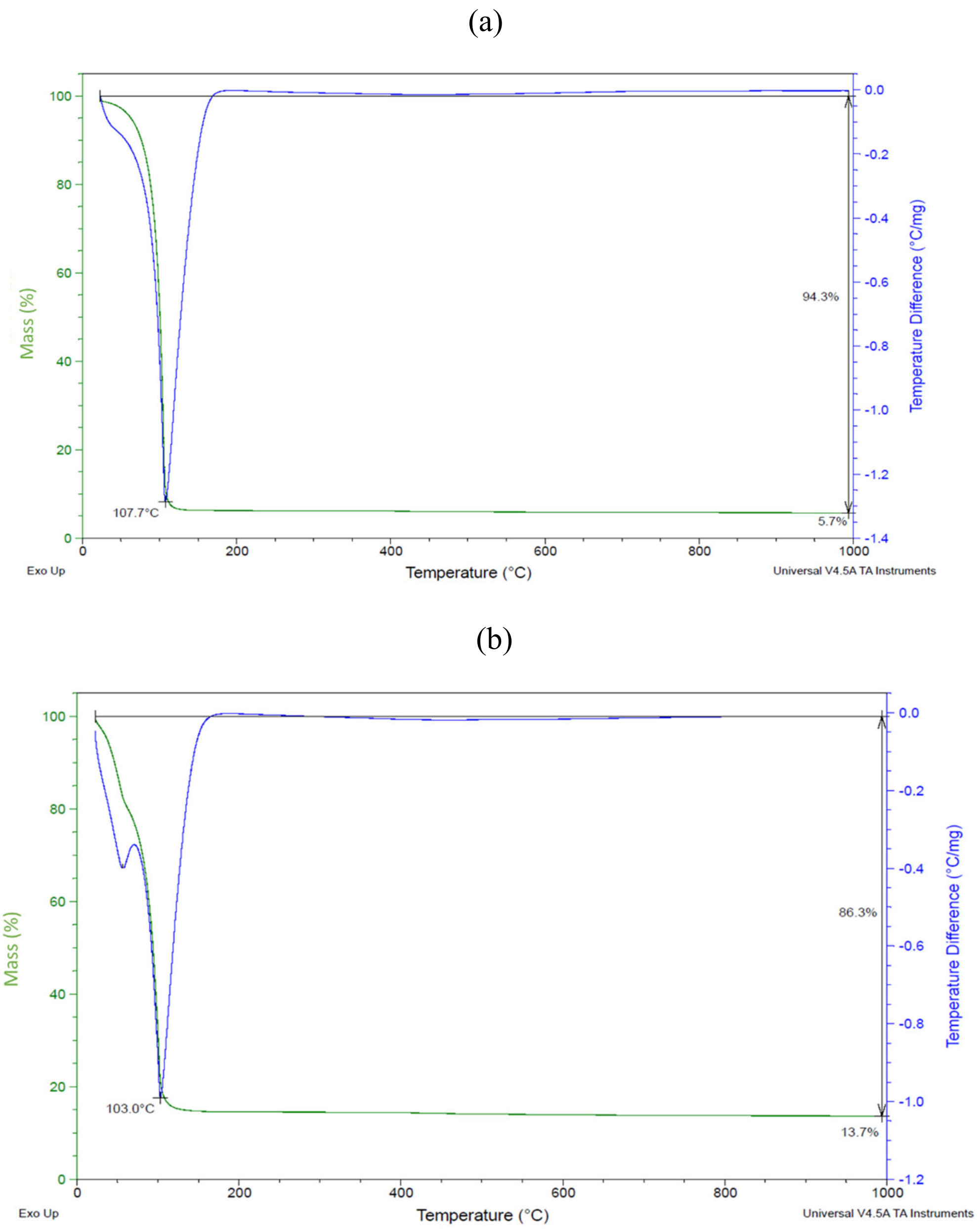
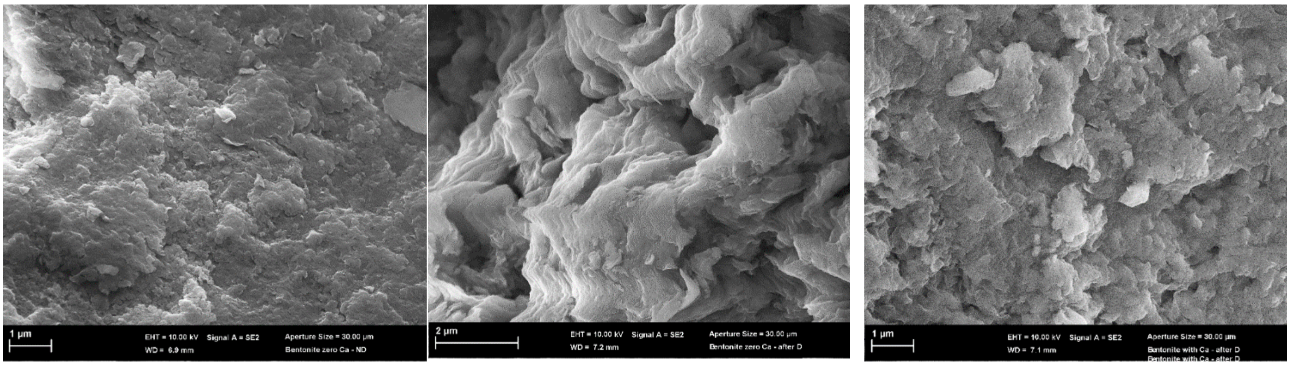


Figure 2. TGA-DTA curves for bentonite a) in the absence of Ca^{2+} and b) in the presence of Ca^{2+}.

3.1.3. SEM analysis for bentonite

SEM analysis was employed to investigate the drying behaviour of bentonite-containing slurries, focusing on morphological changes occurring during the drying process. Figure 3 shows the SEM images of bentonite before and after drying. As seen in Figure 3a, the SEM micrograph illustrates the densely packed structure of bentonite prior to drying. After mixing 10% bentonite with deionized water and subsequent drying at 100°C, the SEM micrograph of the dried sample (see Figure 3b) reveals the formation of a gel-like or honeycomb network structure by the bentonite particles. This observation aligns with the previous literature, which indicated that bentonite particles tend to form edge-edge or edge-face configurations in water suspensions, resulting in increased viscosity and volume of the bentonite clay (Güngör, 2000; Johnston, 2001, Hong et. Al., 2017).

Figure 3c presents the SEM image of 10% bentonite mixed with water in the presence of Ca^{2+} ions. As depicted in Figure 3c, the addition of Ca^{2+} ions induced a change in morphology by altering the network structure formed by the bentonite particles. The addition of Ca^{2+} ions led to the disruption of the gel-like structure formed by bentonite particles in the slurry, thereby reducing the formation of edge-edge and edge-face networks and subsequently decreasing the viscosity and swelling capacity of bentonite. Consequently, more water molecules became available for free movement, thereby enhancing the drying rate.



(a) (b) (c)

Figure 3. SEM images of a) bentonite before drying, b) dried mixture of 10% (w/w) bentonite and deionised water in the absence of Ca^{2+} ions, c) dried mixture of 10% (w/w) bentonite and deionised water 10% (w/w) in the presence of Ca^{2+} ions.

3.1.4. Rheology of bentonite containing ores

The rheology measurements are shown in the supplementary material (see Figure 1S). As seen in Figure 1S in the supplementary material, the addition of Ca^{2+} led to a reduced shear stress of the slurry and thus viscosity that may be attributed to the reduced water swelling capacity of bentonite. Understanding slurry viscosity is very important considering that the increase in slurry viscosity led to a lower dewatering rate (Sofra and Boger, 2011) and consequently the lower drying rate. In the case of bentonite containing slurries, the edge-edge or face-edge network formation significantly reduce the water molecules from free movement, resulting in a higher slurry viscosity and thus decreased drying rate. Additionally, the slurries with high viscosity tend to form a thicker crust when the surface of the slurry dries, thus further preventing the evaporation of moisture from the slurry. This is particularly important for drying region three in which the drying rate of the bentonite-containing slurries is very slow. The Bingham model for 10% bentonite is $\tau=333.5\gamma-18.4$ while that for 10% bentonite is $\tau=243.6\gamma-37.6$.

3.1.5. Zeta potential of bentonite suspensions

The zeta potential measurements of pure bentonite in the presence of different concentrations of Ca^{2+} as a function of pH solutions are shown in the supplementary material (see Figure 2S). For pure bentonite suspension, the increase in pulp pH resulted in a lower zeta potential, may be due to the adsorption of OH^- ions on bentonite surfaces. However, a slight increase in zeta potential up to pH 8 and a significant increase after pH 8 was observed as the concentration of calcium ions increased in bentonite-containing suspensions. This increase in zeta potential resulted in increased repulsive forces between the suspended particles. Consequently, these stronger repulsive forces contributed to the formation of a stable and well-dispersed suspension, effectively increasing the available surface area for drying. As a result, the drying rate was improved in the presence of Ca^{2+} (see Figure 1a).

3.1.6. FTIR results for bentonite

Figure 4 shows the FTIR results in which a single very sharp band is observed at 3625 cm^{-1} followed by a broad band at 3380 cm^{-1}. These two bands are assigned to OH^- stretching of structural hydroxyl groups and water present in montmorillonite (Herzberg, 1962; Hunt and Salisbury, 1970). This indicates the possibility of the hydroxyl linkage between octahedral and tetrahedral layers. A very sharp and intense band observed at 1625 cm^{-1} due to the asymmetric OH stretch (deformation mode) of water and is a structural part of montmorillonite (Famer and Russel,1964; Rotenberg, 2014). This indicates that the bands at 3625 cm^{-1}, 3380 cm^{-1}, and 1625 cm^{-1} correspond to the presence of water in montmorillonite. Furthermore, the area under these bands was found to be smaller in the presence of Ca^{2+} compared to its absence. These findings validate the hypothesis that Ca2+ ions diminish the amount of water adsorbed by bentonite. The band in the lower region of FTIR spectrum occurs due to the vibrational modes of SiO_4 tetrahedron (i.e., bands below 2000 cm^{-1}). The maximum absorption sharp band appears at around 1000 cm^{-1} and is assigned to the triply degenerate Si-O stretching (in-plane) vibration which is a characteristic of layered silicate montmorillonite. These results agree with the reported values of bentonites obtained by Ravindra et al. (2017).

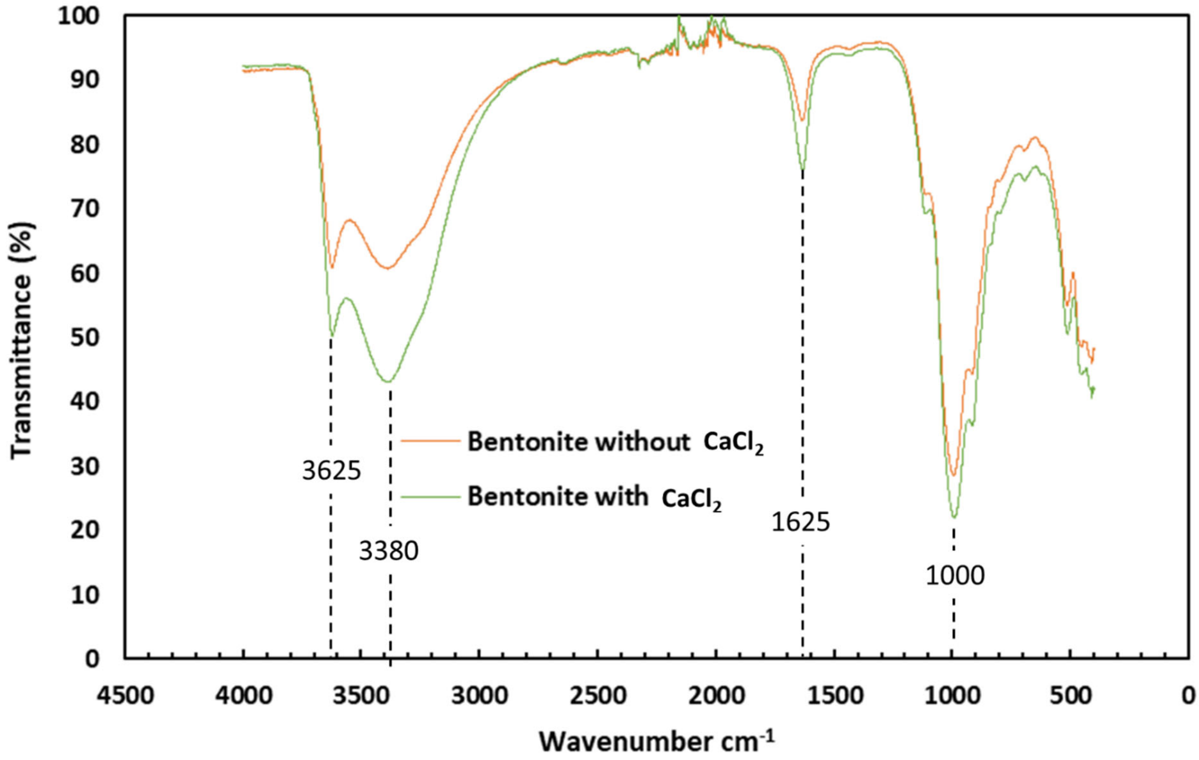


Figure 4. FTIR spectra of bentonite in the presence and absence of Ca^{2+}.

3.1.7. Settling behaviour of bentonite containing-slurries.

The settling behaviour of bentonite containing slurries is shown in the supplementary material (see Figure 3S). High viscosity and water swelling capacity of bentonite led to reduced settling rate in the absence of Ca^{2+} considering that viscous forces were higher than the gravitational forces. The addition of $CaCl_2$ reduced the viscosity and swelling capacity of bentonite thus increasing the settling rate and breaking the gel like structure formed by bentonite particle in slurry. As a result, more water molecules are available for free movement, hence improving the drying rate (see Figure 1a).

3.2. Kaolin containing-ore

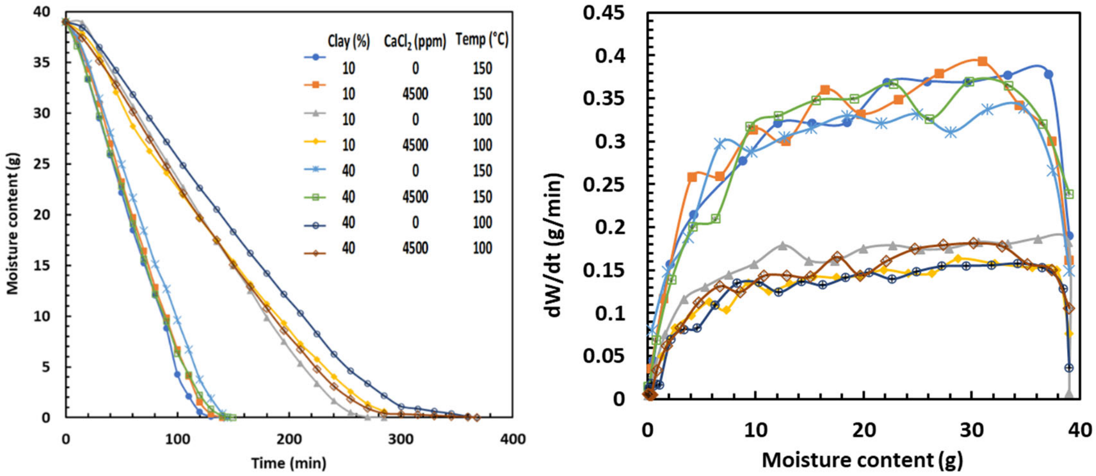
3.2.1. Drying results

Figure 5a shows the moisture content as a function of time. As seen in Figure 5a, the increase in kaolin percentage led to a slightly higher retained moisture content (Nesse, 2000). This phenomenon can be explained due to the non-swelling properties of kaolinite attributed to its crystal structure. Specifically, the arrangement of silica tetrahedral (T) sheets and alumina octahedral (O) sheets in a 1:1 ratio characterizes the structure of the kaolin group of clays. This structure has two significant bonding forces (i.e., van der Waals forces and strong hydrogen bonds), preventing water molecules to penetrate between interlayers. More precisely, the hydrogen atoms from the octahedral sheet in one layer establish a strong hydrogen bond with the oxygen atoms in the tetrahedral sheet of the adjacent layer (Chen and Peng, 2018; Zhang, 2016). It should be noted that Ketelaars et al (1995) found that the decrease in moisture content was slower in the case of drying of pure kaolin than that obtained in our work considering that these authors conducted drying at a significantly lower temperature. Sander et al. (2003) observed that the drying rate of pure kaolin was comparable to that achieved in our study, despite conducting the drying process at a lower temperature than that in our study. However, it is worth noting that their initial moisture content was also lower compared to that in our study.

The addition of $CaCl_2$ slightly increased the drying rate, especially when the clay concentration was 40%. This observation may be attributed to the fact that the addition of Ca^{2+} acted as a flocculant for kaolin, causing kaolin particles to form flocs (Kashif et al., 2021; Lee et al, 2010). Larger flocs can help in reducing the water content in the ore slurry, making it easier to separate water from the solid material. It is also worth mentioning that kaolinite possesses high chemical stability and low cation exchange capacity (Assarson et al., 1974; Mustapha et al., 2019; Shareef, 2016; Uddin, 2016).

However, the increase in the temperature resulted in accelerated moisture evaporation, leading to a faster drying process. When kaolinite is heated from room temperature to 150 °C, it experiences the elimination of both loosely attached water and confined interlayer water on a nanoscale. This process does not result in any significant changes in the interlayer basal distance in kaolinite structure. In other words, although heating it to temperatures of up to 150 °C leads to the removal of this loosely bound or confined interlayer water, the interlayer basal distance in kaolinite remains stable at 7.2 A even when heated to 650 °C (Gadikota et al, 2019). It can be explained since kaolinite is a non-swelling clay and water molecules, that may present in interlayer pore spaces at room temperatures, are not sufficient to alter the distance between the interlayers of kaolinite. This water is removed by heating kaolinite above 100°C (Gadikota et al, 2019).

Kaolin clay interacts with water through four types of hydroxyl groups (Ledoux et al. 1964; Han et al, 2020). The first two hydroxyl groups are found on the outer surfaces of kaolinite, one at the broken edge site and the other on the upper surface of the kaolinite crystal structure. The remaining two hydroxyl groups are located on the inner surfaces: one on the surface of the octahedral sheets opposite the tetrahedral oxygen, and the other within the kaolinite structure as inner hydroxyl groups. Each hydroxyl group has different bonding energy with water. The moisture loss at 75 °C could be attributed to the evaporation of free adsorbed water while moisture loss at 150°C could be due to the predehydration process where intercalated water is removed (Han et al, 2020).



(a) (b)

Figure 5. Drying performance of kaolin containing slurries.

Drying rates were determined by determining moisture changes over time as shown in Figure 5b. Three distinct drying regions are evident in Figure 5b. In the first region, the drying rate increases notably as moisture content drops until 37 g. Heat effectively removes loosely held surface water, driven by the high moisture content. It should be noted that kaolinite surfaces have hydroxyl groups that can form hydrogen bonds with water molecules. The rapid drying is due to a substantial moisture gradient between the sample surface and the surrounding air. Heat mainly evaporates moisture, making heat transfer to the surface the primary drying rate control. Capillary water within macropores is also easily evaporated in this region (Han et al, 2020).

In the second region, the drying rate slightly decreases with decreasing moisture content (see Figure 5b). Reduced surface moisture increases internal resistance, hindering water movement through capillaries to the surface and thus reducing drying rates (Hammouda, 2014; Kiennemann, 2005). Water molecules form bridges between the kaolinite layers, and these bridges are maintained by capillary forces. As surface moisture lessens, a moisture and concentration gradient forms (Gualtieri et al., 2016) within the sample, hindering moisture flow towards the surface, thus decreasing drying rates Hammouda, 2014; Kiennemann, 2005). Additionally, material properties shift as the surface undergoes physical changes.

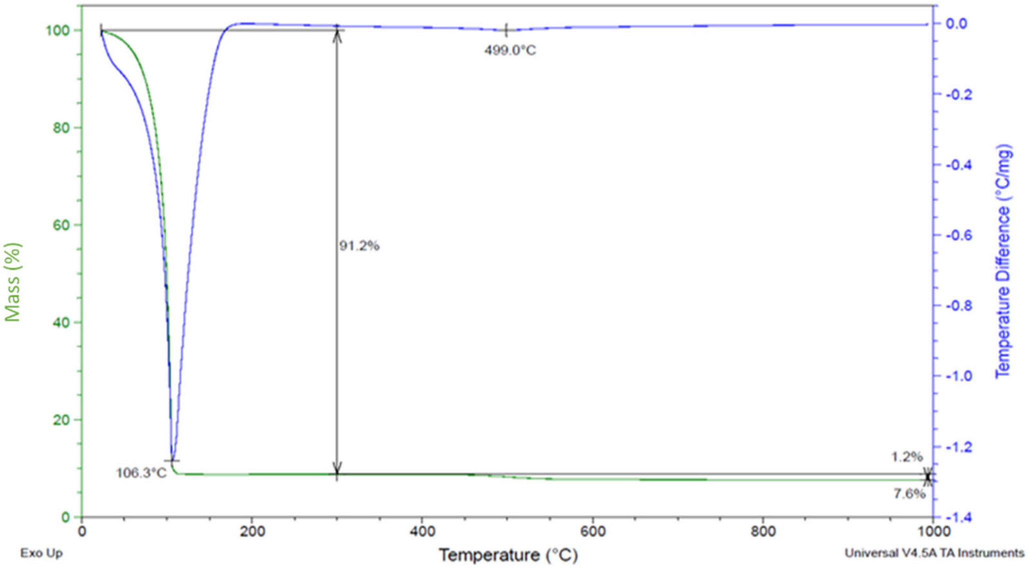
In the third region, there is a noticeable decrease in the drying rate, eventually completely removing water from kaolinite as shown in Figure 5b. This reduction in drying rate occurs primarily because most of the loosely attached moisture on the surface and in capillaries were removed in the initial two regions. The water that remains is held strongly within narrow pores, making it harder to evaporate (Han et al, 2020). The decrease in drying rate is linked to the elimination of the remaining water in pores.

The ANOVA and Tukey analysis for three different drying regions of kaolin-containing ores are provided in the supplementary material (see Tables 5S, 6S and 7S). In the first region, the ANOVA results demonstrated that temperature had the greatest significance, followed by kaolin percentage. The concentration of Ca^{2+}, on the other hand, displayed the least influential factor. These conclusions were corroborated by the Tukey analysis conducted for the first region, which validated that elevated temperatures and higher kaolin percentages correlated with accelerated drying rates. In contrast, the increase in Ca^{2+} concentration did not have a noteworthy impact. Similar trends were also observed for the second and third regions of kaolin-contain ores, indicating that the drying rate was most significantly affected by the changes in temperature, while the impact of $CaCl_2$ concentration was found to be the least pronounced. The correlations for drying kinetics in all three regions are shown in the supplementary material (see Table 8S). All these correlations successfully predicted the rate constants (R^2 higher than 0.92).

3.2.2. TGA-DTA measurements for kaolin

Figure 6 presents the TGA-DTA curves of the mass changes for the kaolin samples heated from 25 ˚C to 1000 ˚C. Figure 6 shows that 50% of water was removed at 101°C in the presence of Ca^{2+} as well as in the absence of Ca^{2+}. It indicates that Ca^{2+} did not affect the drying rate in this temperature range.

(a)



(b)

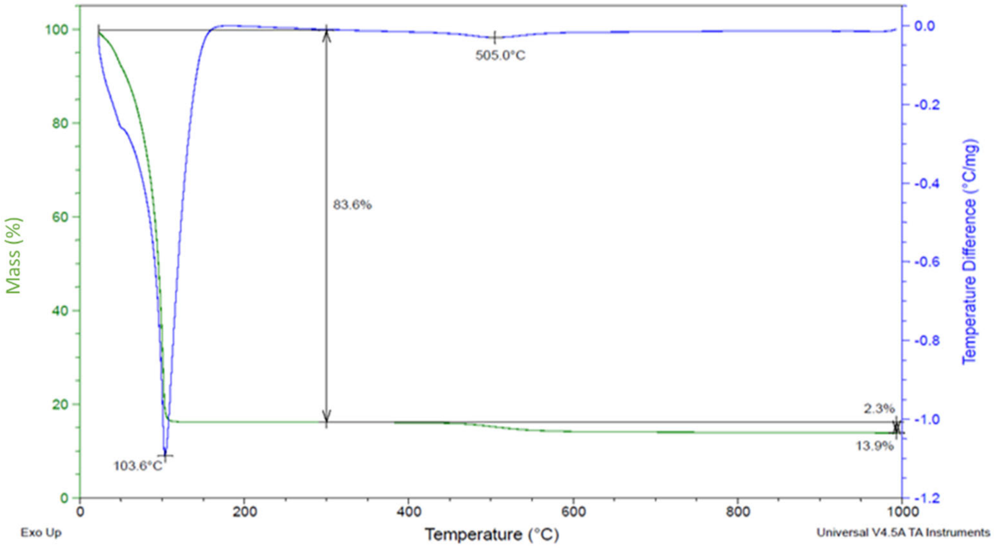
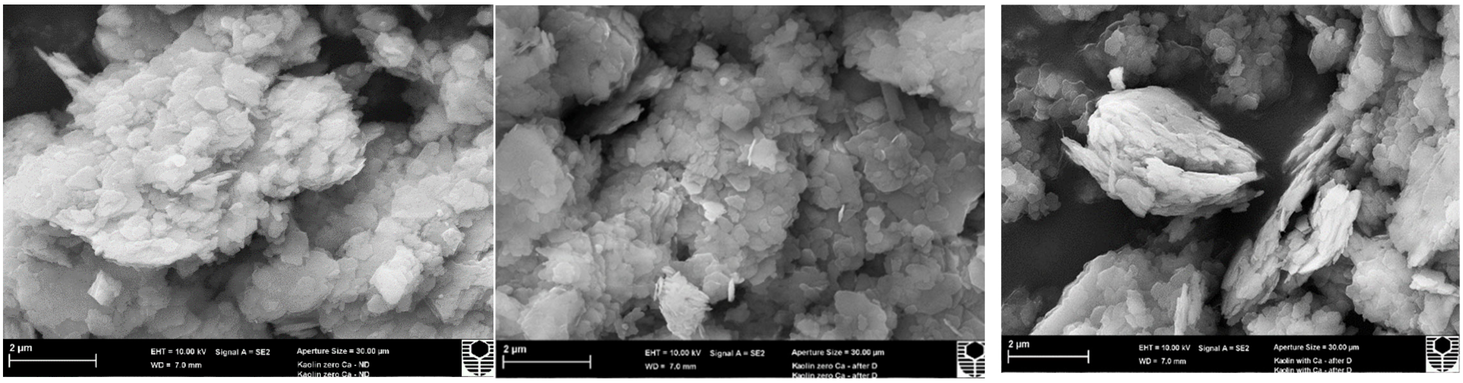


Figure 6. TGA-DTA curves for kaolin a) in the absence of Ca^{2+} and b) in the presence of Ca^{2+}.

3.2.3. SEM analysis for kaolin

SEM analysis was employed to investigate the drying behaviour of kaolin-containing slurries. Figure 7 shows the SEM images of kaolin before and after drying. As seen in Figure 7a, the SEM micrograph illustrates the typical plate-like structure of kaolin prior to drying, attributed to the prevalent face-face network configuration (Mitrovic and Zdujic, 2014; Muhmed and Wanatowski, 2013). After mixing 10% kaolin with deionized water and subsequent drying at 100°C, the SEM micrograph of the dried sample (see Figure 7b) revealed that the morphology remains largely unchanged, with kaolin particles still arranged in face-face network configuration. This observation is consistent with prior literature (Elgamouz et. al., 2019, Stanislas et. al., 2022), suggesting that kaolin particles tend to maintain face-face configurations in water suspensions, with minimal impact on viscosity.

Figure 7c presents the SEM image of 10% kaolin mixed with water in the presence of Ca^{2+} ions. As depicted in Figure 7c, the presence of Ca^{2+} ions resulted in a modification of morphology by altering the network structure formed by the kaolin particles. The addition of Ca^{2+} ions led to the agglomeration of kaolin particles, by forming edge-face network configuration, as reported in previous studies (Liu et al., 2017; Teh et al., 2009). Consequently, more water molecules are trapped between the edge-face structures, slightly inhibiting the evaporation, and thereby slowing down the drying process.



(a) (b) (c)

Figure 7. SEM images of a) kaolin before drying, b) dried mixture of 10% (w/w) kaolin and deionised water in the absence of Ca^{2+} ions, c) dried mixture of 10% (w/w) kaolin and deionised water 10% (w/w) in the presence of Ca^{2+} ions.

3.2.4. Rheology of kaolin-containing ores

The rheology measurements for a kaolin-containing slurry are given in the supplementary material (see Figure 4S). The addition of Ca^{2+} resulted in an increased shear stress of the slurry and, consequently, viscosity. This can be attributed to the formation of kaolin agglomerates in the presence of Ca^{2+} (Cruz et al., 2013; Kashif et al., 2021;). Consequently, a negligible increase in the drying rate was observed when Ca^{2+} was present. The addition of Ca^{2+} potentially influenced the formation of the double layer around kaolin particles by substituting existing monovalent ions with bivalent Ca^{2+}. Bivalent cations are known to create a thinner electrical double layer compared to monovalent cations (Pavel, 2002). This thinner electrical double-layer brings particles closer together, initiating agglomeration processes. As a result, voluminous agglomerates form, retaining significant amounts of water (Pavel, 2002), thereby reducing the layers of water between the particles, and leading to higher slurry viscosity (Barbato et al., 2008).

The Brownian motion of agglomerated particles is less effective compared to well-dispersed slurries containing colloidal particles due to the larger size of agglomerated particles. Furthermore, water molecules held within the internal structures of agglomerated particles do not contribute to the particle flow. Consequently, the solid-to-liquid ratio in the slurry increases, resulting in higher viscosity compared to dispersed suspensions (Ortega et al., 1997), hence slightly affecting the drying rate of kaolin containing ores in presence of Ca^{2+}. The Bingham model for 10% kaolin is $\tau=9.2\gamma-2.37$ while that for 10% kaolin in the presence of Ca^{2+} is $\tau=40.3\gamma-15.9$.

3.2.5. Zeta potential of kaolin suspensions

The zeta potential measurements are given in the supplementary material (see Figure 5S), demonstrating that for pure kaolin, increasing pH resulted in lower zeta potentials, attributed to the adsorption of OH^- ions on kaolin surfaces. Similarly, addition of Ca^{2+} led to lower zeta potentials, possibly by altering the double layer around kaolinite particles because calcium ions (Ca^{2+} and $Ca(OH)^+$) are adsorbed on kaolin surfaces (Aabdi and Wild, 1993; Wild et al., 1993). Kaolinite layers being amphoteric i.e., kaolinite crystals carry permanent negative charge on the crystal planes or surface and a positive or negative charge on the edges depending on the pH of the system. The resultant electrostatic forces of attraction or repulsion and the attractive van der Waals forces between the particles give rise to the formation of edge-edge (E-E), edge-face (E-F) configurations in the suspension leading to dispersion or agglomeration of the kaolin clay particles (Barbato et al., 2008). The effect of Ca^{2+} was also observed by Liu et al (2017) where increasing Ca^{2+} caused the electrical double layer compression, leading to slightly negative surfaces charges. Low zeta potentials of kaolinite particles resulted in stronger bridging interactions between these particles giving rise to higher agglomeration. However, agglomerated kaolin showed a negligible increase in drying rate probably because the addition of Ca^{2+} induced the formation of low-density edge-face network structures (Liu et al, 2017; Teh et al, 2009). Therefore, more water molecules are trapped between the edge-face structure impeding the evaporation, reducing the drying process.

3.2.6. FTIR results for kaolin

The FTIR results shows a single sharp band at 3680 cm^{-1}, 3610 cm^{-1} and 1640 cm^{-1} (see Figure 8). Additionally, the band at 3400 cm^{-1} was observed in the presence of Ca^{2+} only. These bands are assigned to OH^- stretching vibrations and water adsorption on kaolin (Mustapha, et al., 2019; Tironi, et al., 2012). In the presence of Ca^{2+}, the area under these bands was observed to be smaller compared to when Ca^{2+} was absent. The results may show that the presence of Ca^{2+} ions lead to a reduction in the amount of water adsorbed by kaolin. The bands at 1000cm^{-1}, 1120cm^{-1} and 905 are present due to Si–O–Si group of the tetrahedral sheet, Si–O stretching vibration and Al–OH, respectively. These results agree with the reported values of kaolin obtained by other authors (Mustapha, et al., 2019; Tironi, et al., 2012).

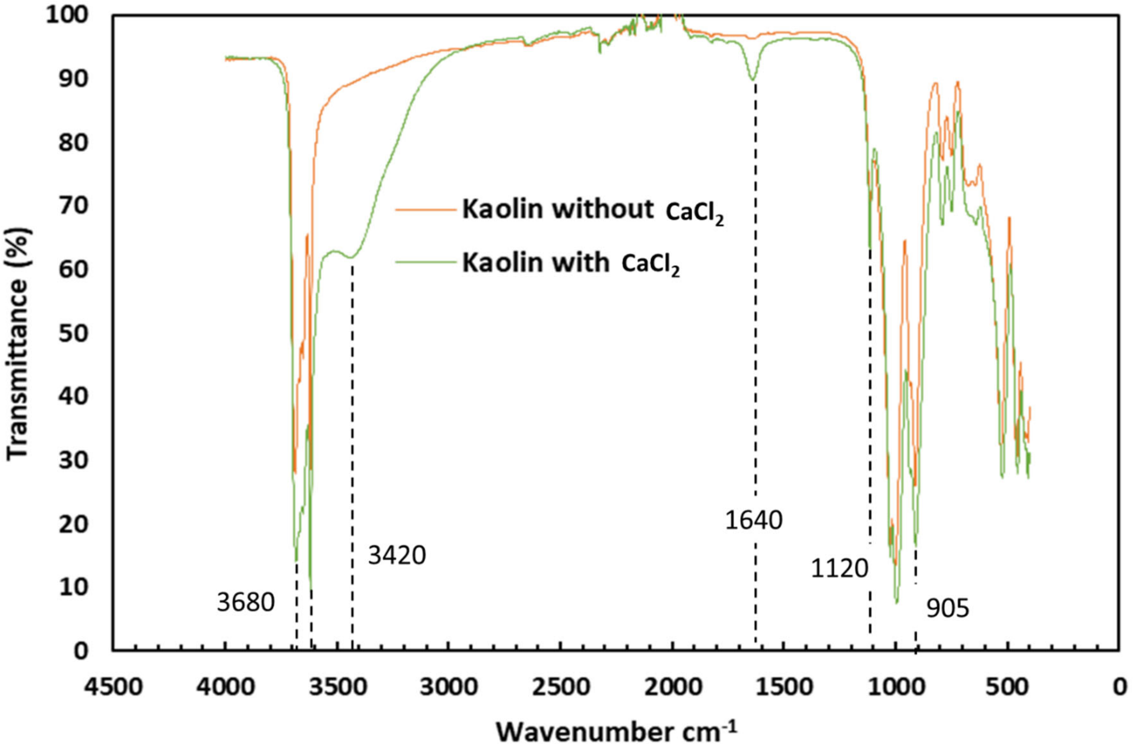


Figure 8. FTIR spectra of kaolin in the presence and absence of Ca^{2+}.

3.2.7. Settling behaviour of kaolin-containing slurries

The settling behaviour of kaolin containing slurries is shown in the supplementary material (see Figure 6S). It has been observed from rheology and zeta potential results that the addition of Ca^{2+} increased the viscosity and lowered the zeta potentials of kaolin containing slurries. As a result, the settling rates were also affected by addition of Ca^{2+}. The addition of Ca^{2+} reduced the settling rates of kaolin containing slurries. The presence of less dense edge-face network structures of kaolinite particles could be a possible reason of negligible improvement in the drying rate of these slurries (Liu et al, 2017). The cryo-SEM tests also showed the prevalence of edge-face network structure in the presence of high salinity water while compact face-face and loose edge-face network structures co-existed (Liu et al, 2017). This configuration has a higher tendency to retain water, leading to increased viscosity and buoyancy force, slower settling rate, and consequently slightly hindering the drying rate.

3.3. Comparing the drying performance of bentonite-containing ores with that of kaolin-containing ores

Kaolin-containing ore and bentonite-containing ore exhibit contrasting drying behaviours. Firstly, bentonite-containing ore has higher moisture retention capacity due to high water adsorption capacity of bentonite. As the percentage of bentonite increases, the drying time was longer, with the sample containing 40% bentonite requiring more time to dry than the sample with 10% bentonite. The addition of $CaCl_2$ effectively reduces the moisture content by replacing Na+ ions with smaller Ca^{2+} ions in the bentonite interlayers. This ore shows three distinctive drying regions: a rapid drying phase attributed to high moisture content, a moderate drying phase marked by reduced drying rates due to interlayer water, and a final phase with a sharp decline in drying rate as tightly bound moisture becomes challenging to remove.

Kaolin-containing ore maintains a slightly lower moisture content compared to bentonite-containing ore due to the non-swelling nature of kaolinite crystal structure. The addition of $CaCl_2$ has a mild impact on the drying rate and moisture content. Similar to bentonite-containing ore, kaolin ore exhibits three drying regions characterized by variations in drying rates. The first region experiences a notable increase in drying rate driven by high moisture content, followed by a region with a slight drying rate decrease due to internal resistance and moisture gradients. Finally, the third region had a significant reduction in drying rate as most loosely bound moisture was removed.

It is very important to understand the relationship between the rheology performance and the drying performance of the investigated systems. Figure 9 shows the relationship between the plastic viscosity and the drying rates for all three drying regions. As seen in Figure 9, in the case of the region 1, the increase in plastic viscosity resulted in a lower drying rate likely due to the highest water content observed during the initial stages of drying. However, the amount of water was significantly less in the regions 2 and 3 and thus the increase in plastic viscosity did not significantly affect the drying rate.

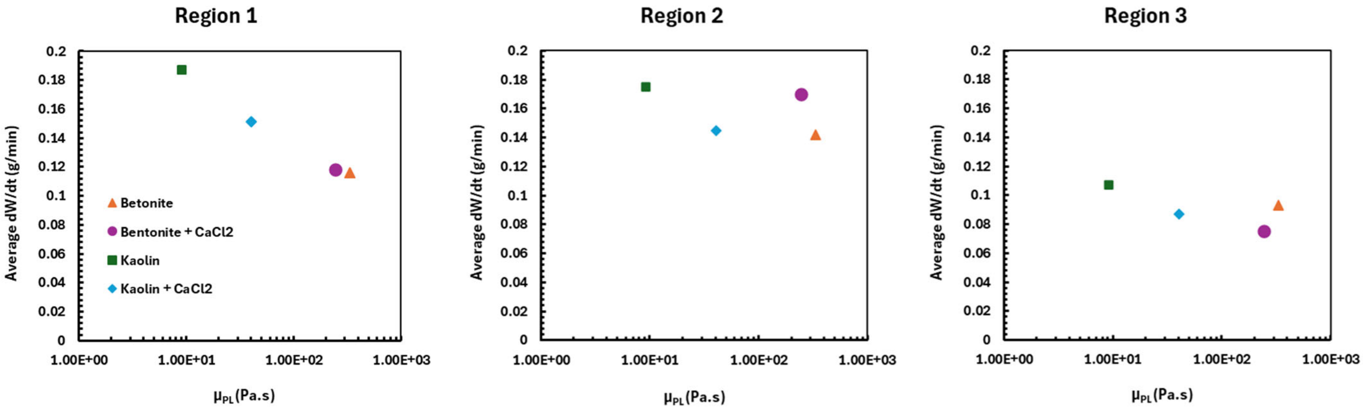


Figure 9. The relationships between the plastic viscosity and the average drying rate.

4. Conclusions

This paper aims to investigate the drying performance of kaolin and bentonite-containing slurries by integrating drying experiments, rheology measurements, settling experiments, zeta potential measurements, SEM, FTIR and TGA/DTA to reveal the underlying drying mechanisms. The addition of Ca^{2+} ions proved advantageous for enhancing the drying performance of bentonite-containing slurries. This improvement was observed through lowered slurry viscosity, attributed to the decreased water swelling capacity of bentonite since larger Na^+ ions in bentonite interlayers were replaced by smaller Ca^{2+} ions. Ca^{2+} ions induced stronger repulsive forces between bentonite particles by modifying the zeta potential of bentonite clay particles, resulting in a stable and well-dispersed suspension. Moreover, FTIR and DTA-TGA analysis revealed that the presence of Ca^{2+} resulted in a lower amount of adsorbed water compared to its absence, indicating a significant reduction in the swelling properties of bentonite due to the presence of Ca^{2+}. The gel-like structure of bentonite was disrupted after adding Ca2+, as evidenced by SEM analysis. As a result, settling rates and available surface area for drying increased, leading to an enhanced drying rate for bentonite-containing slurries.

In contrast, the addition of Ca^{2+} ions had a slight impact on the drying performance of kaolin-containing slurries. This was evident since the addition of Ca^{2+} ions lowered the zeta potential of kaolin slurries, causing agglomeration of kaolinite particles due to the formation of edge to face network structure among crystals. FTIR and DTA-TGA analysis showed that the presence of Ca^{2+} resulted in a slightly lower amount of adsorbed water compared to its absence. The agglomeration of kaolin particles in the presence of Ca^{2+} ions was observed using SEM.

However, the drying rates did not exhibit significant improvements in the case of kaolin-containing slurries.

Three different drying regions were observed for both kaolin and bentonite-containing slurries. Correlations for drying kinetics were established for all three regions. The statistical analysis revealed that temperature was the predominant factor across all three drying regions for both kaolin and bentonite-containing slurries. In the case of bentonite-containing slurries, the presence of Ca^{2+} had a positive impact on drying rates in regions one and three, and no effect in region two. In the case of kaolin-containing slurries, an increase in kaolin percentage marginally reduced drying rates in regions one and three, with no noticeable effect on region two. The results of this study could be valuable for mitigating the adverse effects associated with bentonite and kaolin containing slurries in industrial drying processes, reducing the handling cost of the final products.

References

Aabdi, M. R., Wild, S., 1993. Sulphate expansion of lime-stabilized kaolinite: I. Physical cahractristics. Clay Minerals 28, 555-567.

Anandarajah, A., Chen, J., 1997. Van Der Waals Attractive Force Between Clay Particles in Water and Contaminants, Soils and Foundations, 37(2), 27-37.

Appelo, C.A.J., Postma, D., 2005 Geochemistry, groundwater and pollution. CRC Press, Leiden

Assarson, K., Broms, B., Granholm, S., and Paus, K., 1974. Deep Stabilization of Soft Cohesive soil, Linder Alimark, Sweden.

Bakker, C. W., Meyer, C. J., Deglon, D. A., 2010. The development of a cavern model for mechanical flotation cells. Minerals Engineering, 23(11–13), 968–972.

Barbato, C.N., Nele, M., Pinto, J.C., Silvia, C. A. F., 2008. Studies of kaolin rheology. X Jornadas Argentinas de Tratamiento de Minerales. San Juan, Argentina. 1-10.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2017. Influence of clays on the slurry rheology and flotation of a pyritic gold ore. Appl. Clay Sci. 136, 230–238.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2018. Influence of clays on fine particle filtration. Appl. Clay Sci. 156, 45–52.

Bergaya, F., Theng, B.K.G., Lagaly, G., 2006 Handbook of clay science, Elsevier Science, Burlington, 2006.

Bisshop, J. P., White, M. E., 1976. Study of particle entrainment in flotation froth. Transactions Institute Min Metall, C85. pp. C191– C194.

Brigatti, M.F., Gal´an, E., Theng, B.K.G., 2013. Chapter 2 – structure and mineralogy of clay minerals. In: Faïza, B., Gerhard, L. (Eds.), Developments in Clay Science, 5. Elsevier, Amsterdam, Netherlands, pp. 21–81.

Chen, X., Peng, Y., 2018. Managing clay minerals in froth flotation—a critical review. Miner. Process. Extr. Metall. Rev. 39(5), 289-307.

Chryss, A., 2017. Effects of Clay in Tailings Handling and Storage. https://doi.org/10.1017/9781316661888.011 Published online by Cambridge University Press

Clement, M., J. Bonjer, 1975. Investigation on Mineral Surfaces for Improving the De-watering of Slimes with Polymer Flocculants. Mineral Process. Congr., Caligari, Italy, 271.

Cruz, N., Peng, Y., Farrokhpay, S., Bradshaw, D., 2013. Interactions of clay minerals in copper-gold flotation: part 1 - rheological properties of clay mineral suspensions in the presence of flotation reagents. Miner. Eng. 50–51, 30–37.

Elgamouz, A., Tijani, N., Shehadi, I., Hasan, K., Qawam, M. 2019. Characterization of the firing behaviour of an illite-kaolinite clay mineral and its potential use as membrane support. Heliyon. 5. e02281. 10.1016/j.heliyon.2019.e02281.

Ertekin C, Firat M. Z. 2017. A comprehensive review of thin-layer drying models used in agricultural products. Crit Rev Food Sci Nutr, 57(4):701-717. doi: 10.1080/10408398.2014.910493. PMID: 25751069.

Famer, V. C., Russel, J. D.1964. “The Infrared Spectra of Layered Silicates.” Spectrochimica Acta. Spectro Chim Acta 20: 1149-1173.

Farrokhpay, S., 2011. The significance of froth stability in mineral flotation – a review. Adv. Colloid Interface Sci. 166 (1–2), 1–7.

Ferrage, E., Kirk, C.A., Cressey, G., Cuadros, J., 2007. Dehydration of Ca-montmorillonite at the crystal scale. Part I structure evolution. Am. Mineral. 92 (7), 994–1006.

Ferrage, E., Lanson, B., Malikova, N., Plançon, A., Sakharov, B.A., Drits, V.A., 2005. New Insights on the Distribution of Interlayer Water in Bi-Hydrated Bentonite from X-Ray Diffraction Profile Modeling of 00l Reflections. Chem. Mater. 17, 3499– 3512.

Forbes, E., Davey, K. J., Smith, L., 2014. Decoupling rheology and slime coatings effect on the natural flotability of chalcopyrite in a clayrich flotation pulp. Minerals Engineering, 56, 136–144.

Gadikota, G., Zhang, F., Allen, A., 2019, In-Situ Angstrom-to-Micrometer Characterization of the Structural and Microstructural Changes in Kaolinite on Heating using Ultra-Small-Angle, Small-Angle, and Wide-Angle X-ray Scattering (USAXS/SAXS/WAXS), Ind Eng Chem Res. 56: 10.1021/acs.iecr.7b02810.doi : 10.1021/acs.iecr.7b02810

Gadikota, G., Zhang, F., Allen, A.J., 2017. Towards Understanding the Microstructural and Structural Changes in Natural Hierarchical Materials for Energy Recovery: In-Operando Multi-Scale X-Ray Scattering Characterization of Na- and Ca- Montmorillonite on Heating to 1150°C. Fuel. 196, 195–209. [PMC free article] [PubMed] [Google Scholar]

Gaudin, A. M., 1957. Flotation, New York: McGraw-Hill.

Gaudin, A. M., Fuerstenau, D. W., Miaw, H. L., 1960. Slime-coatings in galena flotation. CIM Bulletin, 53, 3.

Gualtieri, A.F., Ricchi, A., Lassinantti Gualtieri, M., Maretti, S., Tamburini, M., 2016. Kinetic study of the drying process of clay bricks, J Therm Anal Calorim. 123, 153–167.

Guerra, H., Tadesse, B., Albijanic, B., Dyer, L. 2023. Nanofiltration for treatment of Wesern Australian bore water for mineral processing operations: A pilot scale study, Journal of Water Process Engineering, Volume 52, 103484, ISSN 2214-7144, https://doi.org/10.1016/j.jwpe.2023.103484.

Güngör, N. 2000. "Effect of the adsorption of surfactants on the rheology of Na-bentonite slurries." Journal of Applied Polymer Science no. 75 (1):107-110.

Hammouda, I., Mihoubi, D., 2014. Comparative numerical study of kaolin clay with three drying methods: Convective, convective–microwave and convective infrared modes, Energy Conversion and Management 87, 832–839

Han, Y., Yan, Z., Jin, L., Liao, J., Feng, G., 2020. In situ study on interactions between hydroxyl groups in kaolinite and re-adsorption water; RSC Adv. 10(29), 16949–16958.

Herzberg, G. 1962. “Molecular Spectra and Molecular Structure.” Van No strand, New York, 2: 167.

Hong, E., Yeneneh, A. M., Sen, T. K., Shah, J. 2017. “Study on rheological properties of kaolin and bentonite slurry solutions.” Clay Minerals: Properties, Occurrence and Uses; Nova Science: New York, NY, USA.

Hunt, G. R., Salisbury, J. W.1970. “Visible and Near-Infrared Spectra of Minerals and Rocks—I.” Silicate Minerals. Modern Geology 1: 283.

Jeldres, R. I., Uribe, L., Cisternas, L. A., Gutierrez, L., Leiva, W. H., Valenzuela, J., 2019. The effect of clay minerals on the process of flotation of copper ores - A critical review. Applied Clay Science 170, 57-69.

Johnston, Cliff T, and Gnanasiri S Premachandra. 2001. "Polarized ATR-FTIR study of smectite inaqueous suspension." Langmuir no. 17 (12):3712-3718.

Kashif, N., Albijanic, B., Xu, J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M.K., 2021. Detrimental effect of calcium on grinding performance of a kaolin-containing ore. Appl. Clay Sci. 215, 106307.

Kashif, N., Albijanic, B., Xu, J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M.K., 2023. Grinding of highly viscous bentonite containing slurries. Applied Clay Science 232, 106794.

Ketelaars, A. A. J., Pel, U., Coumans, W. J., Kerkhof, P. J. A. M. 1995. Drying kinetics: A Comparison of diffusion coefficients from moisture concentration profiles and drying curves. Chemical Engineering Science, Vol. 50, No. 7, pp. 1187-1191.

Khalfi, A., Blanchart, P., 1999. Desorption of water during the drying of clay minerals. Enthalpy and entropy variation. Ceramics International 25, 409-414.

Kiennemann, J., Chartier, T., Pagnoux, C., Baumard, J.F., Huger, M., Lamerant J.M., 2005. Drying mechanisms and stress development in aqueous alumina tape-casting. J Eur Ceram Soc., 25, 1551–64.

King, R.P., 2002. Introduction to Practical Fluid Flow. first ed. Butterworth-Heinemann, Oxford.

Kretser, R. D., Scales, P. J., Boger, D. V., 1997. Improving clay-based tailings disposal: case study on coal tailings. AICHE J., 43, 1894-1903.

Lang, L. Z., Xiang, W., Huang, W., Cui, D. S., Schanz, T., 2017. An experimental study on oven-drying methods for laboratory determination of water content of a calcium-rich bentonite, Applied Clay Science, 150, 153-162.

Ledoux, R. L., White, J. L., 1964. Infrared study of the OH groups in expanded kaolinite. Science, 143(3603), 244-246.

Lee, K. L., Teng, T. T., Morad, N., Poh, B. T., Hong, Y. F., 2010, Flocculation of kaolin in water using novel calcium chloride-polyacrylamide($CaCl_2$-PAM) hybrid polymer, Separation and Purification Technology 75, 346–351

Liu, D., Edraki, M., Berry, L., 2017. Investigating the settling behaviour of saline tailing suspensions using kaolinite, bentonite, and illite clay minerals, Powder Technology, doi:10.1016/j.powtec.2017.11.070

Loh, E.W.K., Wijeyesekera, D.C. 2009. Drying Kinetic of Prehydrated and Extruded Clay Mat' Proceedings of the AC&T, pp. 95-101. Link to published version:http://www.uel.ac.uk/act/proceedings/documents/FinalProceedings.pdf

Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite suspensions. Adv. Colloid Interf. Sci. 82 (1–3), 43–92.

McFarlene, A.J., Bremmell, K.E., Addai-Mensah, J., 2005. Optimising the dewatering behaviour of clay tailings through interfacial chemistry, orthokinetic flocculation and controlled shear. Powder Technol. 160, 27–34.

Minitab, LLC. Minitab. Version 21.4.2 (64-bit). Computer software. State College, PA: Minitab, LLC, 2023.

Mitrovic, A., Zdujic, M. 2014. Preparation of pozzolanic addition by mechanical treatment of kaolin clay. International Journal of Mineral Processing. 132. 10.1016/j.minpro.2014.09.004.

Mohammad, N., Meng, W., Zhang, Y., Liu, M., El-Zein, A., Gan, Y., 2020. Desiccation Crack Formation and Prevention in Thin Bentonite Layers. Environmental Geotechnics. 9. 1-14. 10.1680/jenge.19.00112.

Muhmed, A., Wanatowski, D. 2013. Effect of Lime Stabilisation on the Strength and Microstructure of Clay. IOSR Journal of Mechanical and Civil Engineering. 6. 87-94. 10.9790/1684-638794.

Mustapha, S., Ndamitso, M.M., Abdulkareem, A.S., J.O. Tijani, J.O., A.K. Mohammed, A.K., Shuaib, D.T., 2019. Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater. Heliyon, Volume 5, Issue 11, e02923, ISSN 2405-8440, https://doi.org/10.1016/j.heliyon.2019.e02923.

Ndlovu, B., Becker, M., Forbes, E., Deglon, D., Franzidis, J. P., 2011. The influence of phyllosilicate mineralogy on the the reology of mineral slurries. Minerals Engineering, 24(12), 1314–1322.

Nechita, P., 2021. The Influence of Drying Conditions of Clay-Based Polymer Coatings on Coated Paper Properties. Coatings, 11, 12. https://doi.org/10.3390/coatings11010012

Nesse, W. D., 2000, Introduction to mineralogy. New York: Oxford University Press, 254–255.

Oats, W. J., Ozdemir, O., Nguyen, V. A., 2010. Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation, Minerals Engineering, Volume 23, Issue 5, Pages 413-419, ISSN 0892-6875, https://doi.org/10.1016/j.mineng.2009.12.002.

Ortega, F.S.. Pandolfelli, V.C.. Rodrigues, J.A., Souza, D. P. F., 1997. Aspects of rheology and stabilization of ceramic suspensions. Part I: Fundamentals. Cerâmica, 43, 5-10.

Oummadi, S., 2019. Drying behaviour of ceramic green bodies: experimental characterization and numerical modelling. Institut de Recherche sur les Céramiques (IRCer)

Patra, P., Bhambhani, T., Nagaraj, D. R., Somasundaran, P., 2012. Impact of pulp rheological behavior on selective separation of Ni minerals from fibrous serpentine ores. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 411. 24–26.

Pavel, V., Zdeněk, C., Jiří, K., 2002. Thinning of kaolin slurry, Národní konference s mezinárodní úcastí Inženýrská Mechanika 2002 13. – 16. 5., Svratka, Ceská republika

Peng, Y., Zhao, S., 2011. The effect of surface oxidation of copper sulfide minerals on clay slime coating in flotation. Minerals Engineering, 24(15), 1687–1693.

Pierre, A.C., Zou, J., Barker, C. 1993. Structure reorganization in montmorillonite gels during drying. J Mater Sci 28, 5193–5198. https://doi.org/10.1007/BF00570063

Rand, B., Melton, I.E., 1977. Particle interactions in aqueous kaolinite suspensions: I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions. J. Colloid Interface Sci. 60 (2), 308–320.

Ravindra R. T., Kaneko S., Endo T., Lakshmi R. S. 2017. Spectroscopic Characterization of Bentonite. J Laser Opt Photonics 4: 171. doi: 10.4172/2469-410X.1000171

Rotenberg, B. 2014. Water in clay nanopores. MRS Bulletin 39: 1074-1081

Sander, A., Skansi, D., Bolf, N. 2003. Heat and mass transfer models in convection drying of clay slabs. Ceramics International, Volume 29, Issue 6, Pages 641-653, ISSN 0272-8842, https://doi.org/10.1016/S0272-8842(02)00212-2.

Seaman, D., Lauten, R. A., Kluck, G., and Stoitis, N., 2012. Usage of anionic dispersants to reduce the impact of clay particles in flotation of copper and gold at the Telfer Mine. 11th AusIMM Mill Operators' Conference, Melbourne, The Australasian Institute of Mining and Metallurgy.

Shabalala, N. Z. P., Harris, M., Filho, L. S. L., Deglon, D. A., 2011. Effect of slurry rheology on gas dispersion in a pilot-scale mechanical flotation cell. Minerals Engineering, 24(13), 1448–1453.

Shareef, A. H., 2017, Investigation of Cement with Lime as a Stabilized Materials for Soft Soils Thesis · September 2016 DOI: 10.13140/RG.2.2.30646.40003

Sofrà, F., Boger, D.V., 2011. Rheology for thickened tailings and paste — history, state-of-the-art and future directions, in R Jewell & AB Fourie (eds). Paste 2011: Proceedings of the 14th International Seminar on Paste and Thickened Tailings, Australian Centre for Geomechanics, Perth, 131-133, https://doi.org/10.36487/ACG_rep/1104_12_Sofra

Stanislas, V., Mazel, I., Mozalin, F., Raunel, L., Flora, D., Joseph-Marie, M. 2022. Study of the Curing Temperature of 600°C, 700°C and 800°C of Mouyondzi Clay on the Mechanical, Physical and Microstructural Properties of Geopolymer Obtained. Journal of Minerals and Materials Characterization and Engineering, 10, 185-197. doi: 10.4236/jmmce.2022.102015.

Teh, E-J., Leong, Y-K., Liu, Y., Fourie, A., Fahey, M., 2009. Differences in the rheology and surface chemistry of kaolin clay slurries: The source of the variations. Chemical Engineering Science, 64(17), 3817-3825. https://doi.org/10.1016/j.ces.2009.05.015

Tironi, A., Trezza, M., Irassar, E., Scian, A.N. 2012. Thermal Treatment of Kaolin: Effect on the Pozzolanic Activity. Procedia Materials Science. 1. 343–350. 10.1016/j.mspro.2012.06.046.

Tombácz, E., Szekeres, M., 2006. Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. Applied Clay Science, 34, 105-124.

Uddin, M.K., 2016. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem. Eng. J. 308, 438–462.

Velde, B., 1992. Introduction to clay minerals. Chemistry, origins, uses and environmental significance, Chapman & Hall, 164-175.

Vick, S. G., 1983. Planning, Design and Analysis of Tailings Dams, Wiley, New York.

Wang, B., Peng, Y., 2013, The behaviour of mineral matter in fine coal flotation using saline water. Fuel, 109, 309–315.

Wang, B., Peng, Y., Vink, S., 2014a. Effect of saline water on the flotation of fine and coarse coal particles in the presence of clay minerals. Minerals Engineering, 66–68, 145–151.

Wild, S., Aabdi, M. R., Leng,-Ward, G. 1993. Sulphate expansion of lime-stabilized kaolinite: II. Reaction products and expansion. Clay Minerals (1993) 28, 569-583.

Wimpenny, J., 2018. Clay Minerals. In: White, W.M. (eds) Encyclopedia of Geochemistry. Encyclopedia of Earth Sciences Series. Springer, Cham. https://doi.org/10.1007/978-3-319-39312-4_51

Xu, Z., Liu, J., Choung, J. W., Zhou, Z., 2003. Electrokinetic study of clay interactions with coal in flotation. International Journal of Mineral Processing, 68(1–4), 183–196.

Zaccaron, A., de Souza Nandi, V., Dal Bó, M., 2022. The behaviour of different clays subjected to a fast-drying cycle for traditional ceramic manufacturing. Journal of King Saud University – Engineering Sciences, https://doi.org/10.1016/j.jksues.05.003

Zhang, M., 2016. The Effect of Clay Minerals on Copper and Gold Flotation. PhD Thesis. The University of Queensland.

Zhang, M., Peng, Y., 2015. Effect of clay minerals on pulp rheology and the flotation of copper and gold minerals. Miner. Eng. 70, 8–13.

Zhao, S., and Peng, Y., 2012. The oxidation of copper sulfide minerals during grinding and their interactions with clay particles. Powder Technology, 230, 112–117.

Supplementary material

1. Bentonite containing slurries

1.1. Statistical analysis of drying performance for all tree drying regions

Table 1S. Region 1 during drying of the bentonite-containing slurry

a) ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Temp	1	0.003121	0.003121	390.06	0.032
Clay %	1	0.000800	0.000800	100.00	0.063
$CaCl_2$ (ppm)	1	0.001200	0.001200	150.06	0.052
Temp* Clay %	1	0.001300	0.001300	162.56	0.050
Temp* $CaCl_2$ (ppm)	1	0.002450	0.002450	306.25	0.036
Clay %*$CaCl_2$ (ppm)	1	0.000061	0.000061	7.56	0.222
Error	1	0.000008	0.000008		
Total	7	0.008940			

b) Tukey results

Variables	Number of experiments	Mean Drying rate
Temp, 150 °C	4	0.101
Temp, 100 °C	4	0.061
Clay Conc., 40 %	4	0.071
Clay Conc., 10 %	4	0.091
$CaCl_2$, 4500 (ppm)	4	0.093
$CaCl_2$, 0 (ppm)	4	0.069

Table 2S. Region 2 during drying of the bentonite-containing slurry

a) ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Temp	1	0.0514	0.0514	33.35	0.109
Clay %	1	0.0029	0.0030	1.90	0.400
$CaCl_2$ (ppm)	1	0.0020	0.0020	1.27	0.462
Temp* Clay %	1	0.0002	0.0002	0.11	0.795
Temp* $CaCl_2$ (ppm)	1	0.0001	0.0001	0.05	0.859
Clay %*$CaCl_2$ (ppm)	1	0.0012	0.0012	0.80	0.536
Error	1	0.0015	0.0015		
Total	7	0.0593			

b) Tukey results

Variables	Number of experiments	Mean Drying rate
Temp, 150 °C	4	0.302
Temp, 100 °C	4	0.142
Clay Cons., 40 %	4	0.203
Clay Cons., 10 %	4	0.241
$CaCl_2$ 4500 (ppm)	4	0.237
$CaCl_2$ 0 (ppm)	4	0.206

Table 3S. Region 3 during drying of the bentonite-containing slurry

a) ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Temp	1	0.0499	0.0499	81.52	0.070
Clay %	1	0.0001	0.0001	0.18	0.742
$CaCl_2$ (ppm)	1	0.0006	0.0006	0.94	0.509
Temp* Clay %	1	0.0001	0.0001	0.18	0.742
Temp* $CaCl_2$ (ppm)	1	0.0005	0.0005	0.84	0.528
Clay %*$CaCl_2$ (ppm)	1	0.0004	0.0004	0.69	0.560
Error	4	0.0006	0.0006		
Total	7	0.0523			

b) Tukey results

Variables	Number of experiments	Mean Drying rate
Temp, 150 °C	4	0.283
Temp, 100 °C	4	0.125
Clay Cons., 40 %	4	0.200
Clay Cons., 10 %	4	0.207
$CaCl_2$ 4500 (ppm)	4	0.195
$CaCl_2$ 0 (ppm)	4	0.212

1.2. Correlations for drying kinetics for all three drying regions

Table 4S. Correlations for drying kinetics in all three regions

Region 1	**Region 2**	**Region 3**
$k = 0.135 \times e^{-0.118t+0.467t^{0.5}}$	$k = A \times t \times e^{B\times t}$	$k = \frac{1}{A \times t + B}$
	$A = 1.1710^{-8} \times {Con_{Clay}}^{-0.52} \times (1 + Con_{Ca^{2+}})^{-0.075} \times T^{3.1}$	$A = 2.22 \times {Con_{Clay}}^{0.124} \times (1 + Con_{Ca^{2+}})^{-0.027} \times T^{-0.182}$
	$B = \frac{A}{(0.48 + 369.1A^2)}$	$B = 6160.5A^3 + 29913A^2 - 47804A + 24904$

t-time; *k*-drying rate constant; Con_{Clay} – clay concentrations, A and B – drying parameters.

1.3. Rheology of bentonite containing ores

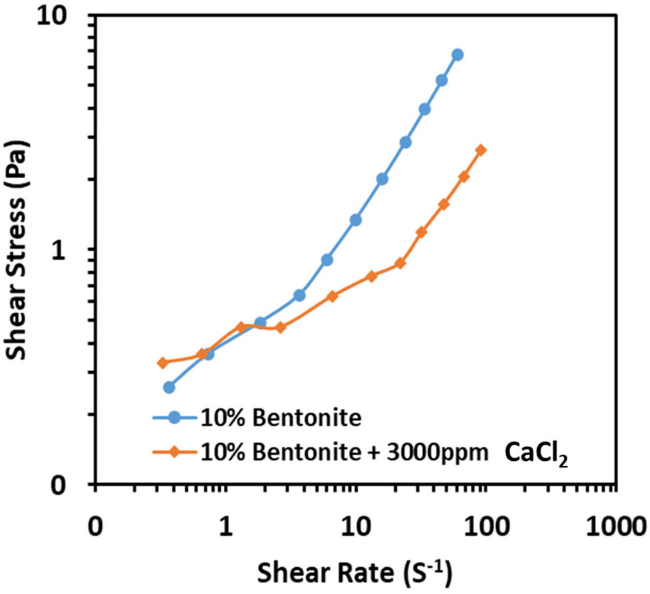


Figure 1S. Rheograms of 10% bentonite-containing slurries (Kashif et al., 2023).

1.4. Zeta potential of bentonite containing ores

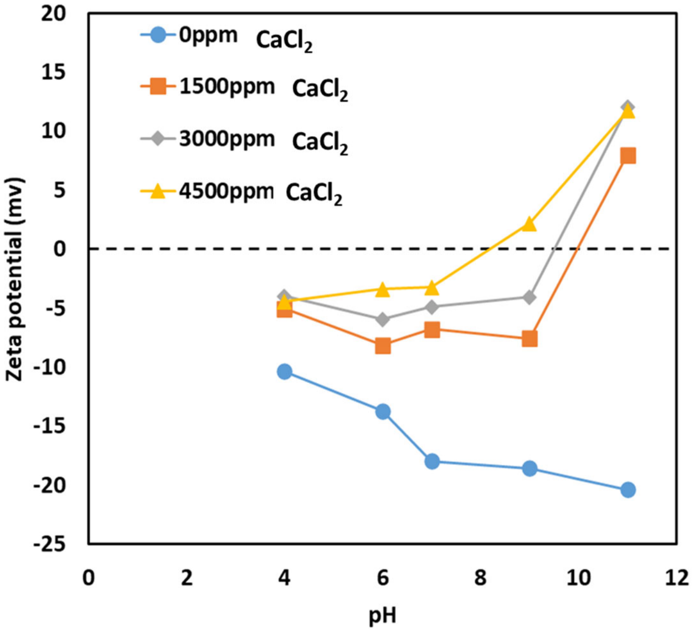


Figure 2S. Zeta potential measurements versus pH for solutions of bentonite at different $CaCl_2$ concentrations Kashif et al. (2023).

1.5. Settling behaviour of bentonite containing ores

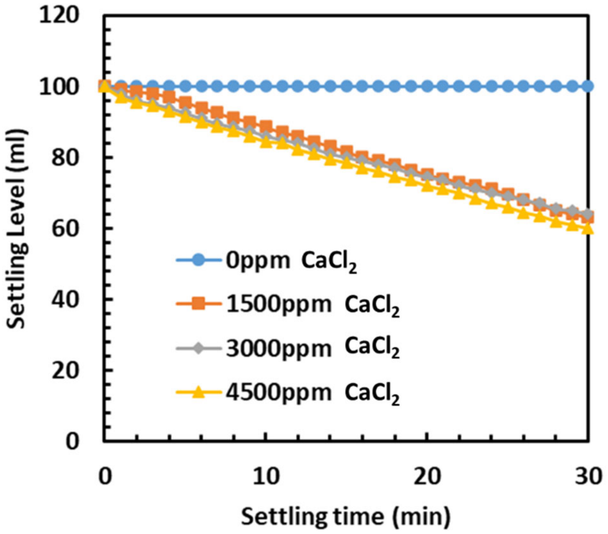


Figure 3S. Settling behaviour after 30 min for 10% bentonite at different $CaCl_2$ concentrations (Kashif et al., 2023).

2. Kaolin containing slurries

2.1. Statistical analysis of drying performance for all tree drying regions

Table 5S. Region 1 during drying of the kaolin-containing slurry

a) ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Temp	1	0.016110	0.016110	49.55	0.090
Clay %	1	0.000741	0.000741	2.28	0.372
$CaCl_2$ (ppm)	1	0.000006	0.000006	0.02	0.913
Temp* Clay %	1	0.000010	0.000010	0.03	0.889
Temp* $CaCl_2$ (ppm)	1	0.000078	0.000078	0.24	0.710
Clay %*$CaCl_2$ (ppm)	1	0.000001	0.000001	0.00	0.963
Error	1	0.000325	0.000325		
Total	7	0.017272			

b) Tukey results

Variables	Number of experiments	Mean Drying rate
Temp, 150 °C	4	0.17825
Temp, 100 °C	4	0.08850
Clay Cons., 10 %	4	0.14300
Clay Cons., 40 %	4	0.12375
$CaCl_2$ 4500 (ppm)	4	0.13250
$CaCl_2$ 0 (ppm)	4	0.13425

Table 6S. Region 2 during drying of the kaolin-containing slurry

a) ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Temp	1	0.069006	0.069006	22081.96	0.004
Clay %	1	0.000066	0.000066	21.16	0.136
$CaCl_2$ (ppm)	1	0.000010	0.000010	3.24	0.323
Temp* Clay %	1	0.000153	0.000153	49.00	0.090
Temp* $CaCl_2$ (ppm)	1	0.000300	0.000300	96.04	0.065
Clay %*$CaCl_2$ (ppm)	1	0.000561	0.000561	179.56	0.047
Error	1	0.000003	0.000003		
Total	7	0.070100			

b) Tukey results

Variables	Number of experiments	Mean Drying rate
Temp, 150 °C	4	0.33850
Temp, 100 °C	4	0.15275
Clay Cons., 10 %	4	0.24850
Clay Cons., 40 %	4	0.24275
$CaCl_2$ 4500 (ppm)	4	0.24450
$CaCl_2$ 0 (ppm)	4	0.24675

Table 7S. Region 3 during drying of the kaolin-containing slurry

a) ANOVA results

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Temp	1	0.051040	0.051040	96.64	0.065
Clay %	1	0.002145	0.002145	4.06	0.293
$CaCl_2$ (ppm)	1	0.000666	0.000666	1.26	0.463
Temp* Clay %	1	0.000325	0.000325	0.62	0.576
Temp* $CaCl_2$ (ppm)	1	0.000010	0.000010	0.02	0.912
Clay %*$CaCl_2$ (ppm)	1	0.002628	0.002628	4.98	0.268
Error	4	0.000528	0.000528		
Total	7	0.057343			

b) Tukey results

Variables	Number of experiments	Mean Drying rate
Temp, 150 °C	4	0.31875
Temp, 100 °C	4	0.15900
Clay Cons., 10 %	4	0.25525
Clay Cons., 40 %	4	0.22250
$CaCl_2$ 4500 (ppm)	4	0.22975
$CaCl_2$ 0 (ppm)	4	0.24800

2.2. Correlations for drying kinetics for all three drying regions

Table 8S. Correlations for drying kinetics in all three regions

Region 1	Region 2	Region 3
$k = 0.05 \times t \times e^{-0.1055 \times t}$	$k = 0.573 \times 0.949^{t}$	$k = A \times t^{-B \times X}$ $A = 1.74 \times 10^{5} \times Con_{Clay}{}^{-1.1} \times Con_{Ca^{2+}}{}^{-0.177} \times T^{-2.4}$ $B = -0.13 \times 10^{-2} \times ln(A + 0.15 \times 10^{5})$

t-time; *k*-drying rate constant; Con_{Clay} – clay concentrations, Con_{Ca2+} – clay concentrations; A and B – drying parameters.

2.3. Rheology of kaolin containing ores

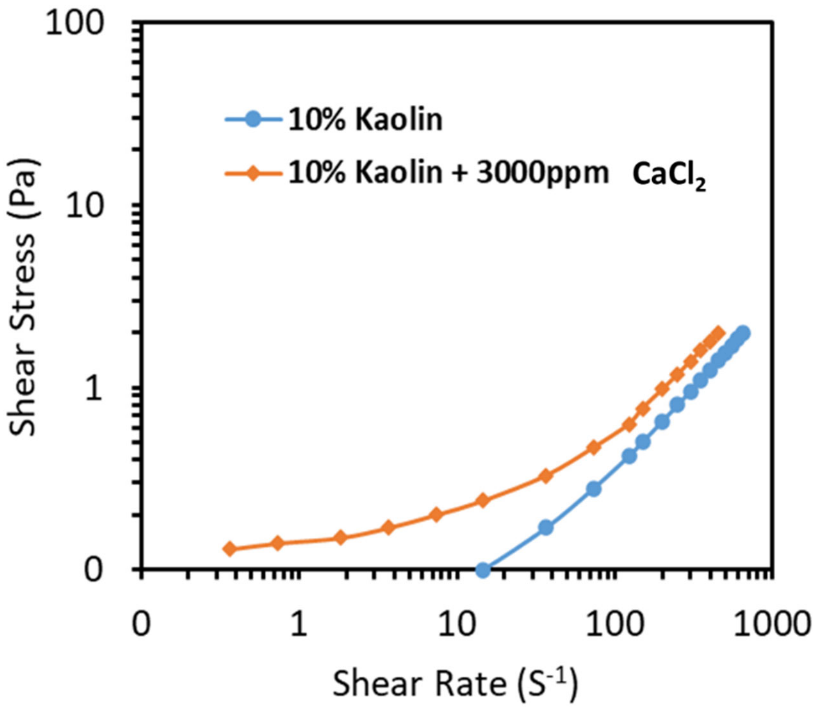


Figure 4S. Rheograms of 10% kaolin-containing slurries (Kashif et al., 2021).

2.4. Zeta potential of kaolin containing ores

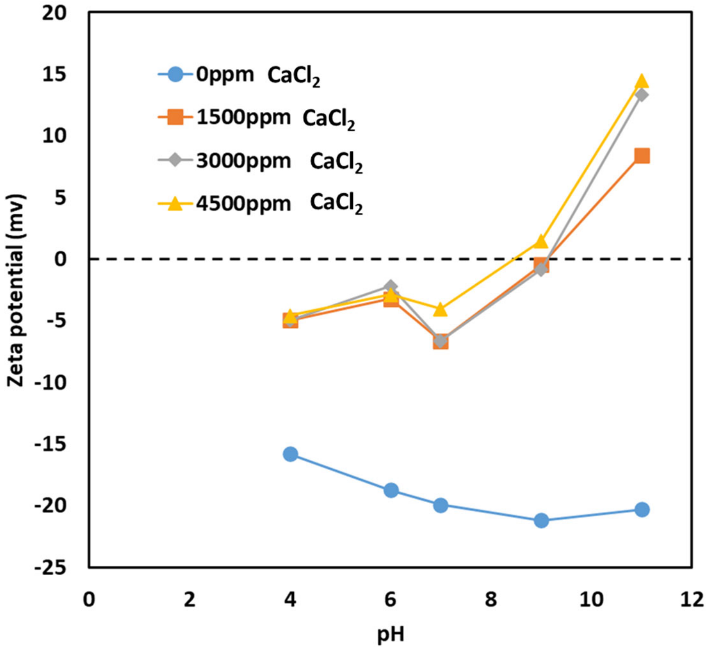


Figure 5S. Zeta potential measurements versus pH for solutions of kaolin at different $CaCl_2$ concentrations (Kashif et al., 2021).

2.5. Settling behaviour of kaolin containing ores

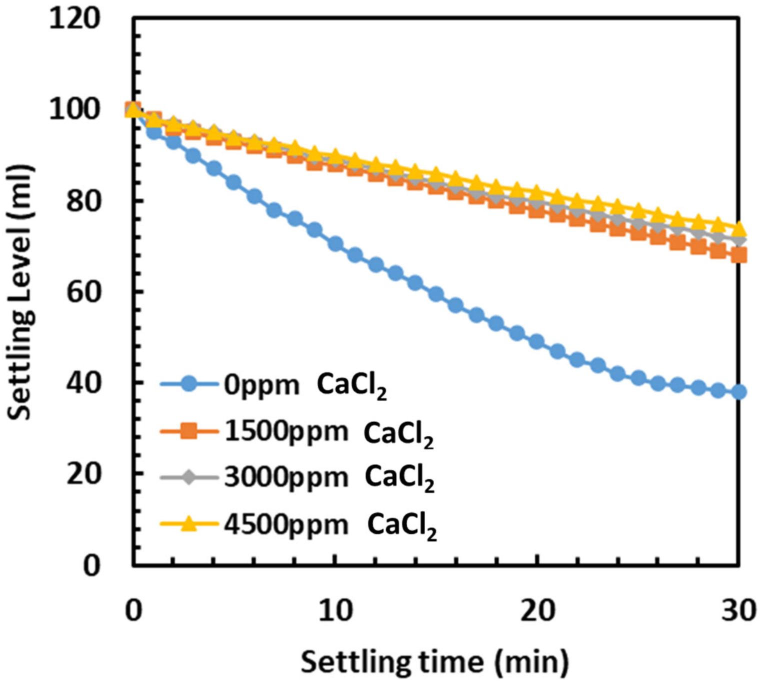


Figure. 6S. Settling behaviour after 30 min for 10% kaolin at different $CaCl_2$ concentrations.

References

Kashif, N., Albijanic, B., Xu, J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M.K., 2021. Detrimental effect of calcium on grinding performance of a kaolin-containing ore. Appl. Clay Sci. 215, 106307.

Kashif, N., Albijanic, B., Xu, J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M.K., 2023. Grinding of highly viscous bentonite containing slurries. Applied Clay Science 232, 106794.

Chapter VI

Influence of bentonite on flotation of minerals with different densities

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Abstract

While studies have investigated the influence of bentonite on flotation, the quantification of its impact on the flotation performance of minerals with different densities remains unexplored. The main objective of this study is to examine the influence of bentonite on the flotation performance of two minerals with significant differences in their densities (i.e., galena and sphalerite). The results showed that the presence of bentonite resulted in decreased flotation recoveries of both galena and sphalerite due to the increase in pulp viscosities. The detrimental impact of bentonite on the flotation of galena and sphalerite was reduced after the addition of Ca^{2+} ions, which resulted in a decrease in pulp viscosities. It was observed that the addition of Ca^{2+} ions had a more pronounced effect on the flotation performance of galena compared to sphalerite. These findings highlight the complex relationships among bentonite concentration, mineral densities, and the influence of Ca^{2+} ions in flotation processes.

Keywords: Flotation, bentonite, density of minerals, rheology

1. Introduction

Clay minerals, composed of fine-grained materials, are fundamental natural substances commonly encountered in mineralization as gangue minerals, presenting challenges across all stages of mineral processing (Taner and Onen, 2016). These minerals are widespread in the geological strata. The processing of low-grade ores, including those with a high clay content, has become more prevalent due to the depletion of high-grade ores (Yin et al., 2012; Chen and Peng, 2018; Xing et al., 2017; Yu et al., 2017). Processing high-clayey ores, however, presents new challenges, as these clay minerals have detrimental effects on the flotation of valuable minerals. It is well-documented that fine clay minerals adversely affect flotation, leading to a reduction in both mineral recovery and grade (Chen and Peng, 2018; Xing et al., 2017; Yu et al., 2017; Arnold, F.F. Aplan, 1986; Xu et al., 2003; Oats et al., 2010; Wang et al., 2014; Liu et al., 2014; Xing et al., 2019).

Challenges in processing of clay-containing slurries during flotation occurred due to the specific structures of clays (Wang et al., 2015; Taner and Onen, 2016). Clay minerals, characterized by arrangements of silica tetrahedral (T) and octahedral (O) sheets, form distinct 1:1 (T–O) and 2:1 (T–O–T) layer structures, resulting in three groups: kaolinite (T–O), montmorillonite (T–O–T), and mica (T–O–T) (Yin et al., 2012; Chen and Peng, 2018).

Bentonite contains mainly montmorillonite and is the most deleterious clay mineral where these layers are held together by the weak van der Waals forces allowing water molecules to enter into the interlayer spacing, leading to volumetric increase of bentonite (Luckham and Rossi, 1999; Xu et al., 2003; Zhang, 2016; Chen et al., 2020; Cruz et al., 2015). Therefore, challenges during flotation are particularly significant due to the presence of bentonite.

Several previous studies (Xu et al., 2003; Wang et al., 2015; Zhang and Peng, 2015; Basnayaka et al., 2017) have shown that the presence of bentonite significantly reduced the flotation recoveries of coal, copper sulfide and gold-bearing pyrite while kaolin showed no significant impact on flotation performance. The reason is because bentonite significantly reduced the pulp viscosities by increasing the shear stress and shear rate. Consequently, the bubble-particle collisions are reduced (Wang et al., 2015) attributed to the increased pulp viscosity and deteriorated froth stability (Yu et al., 2017).

Various techniques have been considered to mitigate the negative effects of bentonite on flotation. For example, the addition of calcium improved the flotation recovery of pyrite by 80% (i.e., the recovery increased from 43.44 to 78.28 %) in the case of the bentonite-containing ores (Basnayaka et al., 2017). Other approaches are to mechanically remove of bentonite prior flotation using hydro cyclones (Oats et al., 2010), reducing the pulp densities or using viscosity modifiers as a group of low molecular weight polymers (Taner and Onen, 2016).

Although the influence of bentonite on flotation have been studied, the influence of bentonite on flotation performance of galena and sphalerite have not yet been quantified. Comparison of flotation performance of these two minerals are also very important considering that these two minerals have a significant difference in density i.e., the density of galena is 1.9 times higher than the density of sphalerite. Therefore, the objective of this work is to study the flotation performance of galena and sphalerite in the presence of bentonite.

2. Materials and Methods

2.1. Materials

The synthetic ore samples for this study were created by mixing ground quartz (99.5% purity) with either 10% bentonite (Sibelco Group, Australia) or no bentonite and mixing with either 1% galena (Borieva Mine, Bulgaria) or 1% sphalerite (Krushev dol Mine, Bulgaria). Bentonite had 83% montmorillonite and 17.1% quartz as confirmed using XRD. The particle size of quartz, sphalerite, and galena were in the range between 38 μm and 106 μm.

2.2. Flotation

A 0.5 L mechanically agitated flotation cell (FLSmidth, USA) was used for all the experiments. The synthetic ore samples (30% solids) were transferred to the flotation cell and then the required amount of water was added. The impeller speed was kept constant as 400 rpm. The flotation pulps were conditioned using 30 g/ton of $CuSO_4$ activator (99% purity, Sigma Aldrich), 30 g/ton of PAX collector (90% purity, Orica, Australia Pty Ltd), and 10 g/ton of MIBC frother (Orica, USA). The flotation experiments were carried out at the pulp pH 6 and 9. NaOH (98% grade, Alpha Chemicals, Australia) and HCl (32% grade and distilled water, Alpha Chemicals, Australia) were used as a pH modifier. The flotation experiments were also performed in the absence and presence of Ca^{2+} using $CaCl_2$ (99% purity, Thermo Fisher Scientific, US). The air flowrate was 8 L/min. The flotation concentrates were collected after 4 mins. All the concentrates were filtered and dried. The repeated experiments showed that the experimental error was below 3%.

2.3. Rheological measurements

The rheological measurements of flotation tailings were performed in the laboratory using the available DV1 MLV viscometer (Brookfield, USA). The rheograms (shear stress vs shear rate) were obtained for all flotation tailings. These measurements were carried out at 20 ± 5°C.

The rheological properties of slurries can be described using the power-law model (King, 2002):

$$\tau = \mathrm{K}\gamma^{\mathrm{n}} \tag{1}$$

Where τ is the shear stress, γ represents the shear rate, K and n are the consistency index and the flow index, respectively.

2.4. Zeta potential

The zeta potential measurements were conducted using a Zetasizer Nano-ZS (Malvern, UK). These experiments were performed using both pure galena and pure sphalerite samples as a function of pH (5, 7, 8 and 10) in the absence and presence of Ca^{2+} ions. All experiments were performed using distilled water. All the samples were ground using the laboratory pulveriser (Rocklabs, New Zealand). Before the zeta potential experiments, the suspensions (0.05 % solid ratio) were kept for 3 min to allow the settling of the coarse particles. The supernatant solution containing fine particles was then used for the zeta potential measurements. The small amount of suspension was transferred to the measurement cell. Five measurements at each pH were performed, and the mean value of the measurements was used for further analysis. The experimental error did not exceed 7 %.

2.5. Settling experiments

The graduated cylinders of 100 ml were used to conduct the settling experiments. The slurries with 10% bentonite were prepared and transferred to the cylinders. All experiments were performed at 20 ± 5°C and a slurry pH was kept constant as 7.5. The experiments were conducted as a function of Ca^{2+}. The slurries were allowed to settle in the graduated cylinders after vigorous mixing. The changes in the solid-liquid interface were recorded for the 30 mins to study the settling behaviour of each slurry.

3. Results and Discussions

3.1. Effect of bentonite on galena performance

Table 1 shows the independent variables (Ca^{2+}, bentonite concentration, and pH), and the dependent variables the recoveries (R), the flow index (n), and the consistency index (K). ANOVA (analysis of variance) was employed to assess the significant impact of the independent variables on the dependent variables; the significance of each variable was assessed based on its p-value at a 95% confidence level. Additionally, the Tukey comparison pairwise method was utilized to illustrate the relationships between the independent variables and the dependent variables. Minitab statistical software was used to perform ANOVA and Tukey. Table 2 shows the ANOVA and the Turkey results.

Table 1. The experimental conditions and results for galena flotation and rheology.

Ca^{2+} (ppm)	**Bentonite (%)**	**pH**	**Recovery**	**Flow Index (n)**	**Consistency Index (K)**
3000	10	9	0.541	1.036	0.00132
3000	10	6	0.657	0.970	0.00144
3000	0	9	0.603	1.117	0.00072
3000	0	6	0.605	0.996	0.00195
0	10	9	0.216	0.678	0.02167
0	10	6	0.449	0.940	0.01534
0	0	9	0.564	1.016	0.00252
0	0	6	0.552	0.976	0.00054

3.1.1. Flotation results

Table 2 (a) presents the ANOVA results for the recovery. It is evident that Ca^{2+} concentration is the most significant variable, followed by bentonite concentration, with the pH of the slurry being the least significant variable. Tukey analysis (Table 2 (b)) revealed that increasing the concentration of bentonite and Ca^{2+} significantly impacted the recovery. Specifically, as the concentration of bentonite increased from 0% to 10%, the recovery decreased notably from 58% to 47%. This decline can be attributed to the increased viscosity of the pulp (see Figure 1 for rheology) resulting from the high-water absorption capacity and swelling properties of bentonite particles.

However, the addition of Ca^{2+} counteracted the adverse effects of bentonite on flotation performance, elevating the recovery from 45% to 60%. Prior research has indicated that the introduction of Ca^{2+} diminishes the swelling capacity of bentonite by replacing the interlayer Na+ ions, which have a larger ionic radius (116 pm), with smaller-radius Ca^{2+} ions (114 pm), thereby reducing the water absorption capacity of bentonite. Moreover, the penetration of water into the interlayers may have been restricted due to the potential formation of a stronger bond between bivalent Ca^{2+} ions and oxygen atoms in the bentonite crystal compared to monovalent Na+ ions (Kashif et al., 2023; Assemi et al., 2015; Cruz et al., 2015; Basnayaka et al., 2017 & 2018).

Table 2. Statistical analysis for flotation recovery of galena.

a) ANOVA

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Ca Conc./ Ca^{2+} (ppm)	1	0.0488	0.0488	22.63	0.132
Bentonite %	1	0.0265	0.0265	12.31	0.177
pH	1	0.0144	0.0144	6.68	0.235
Ca Conc./ Ca^{2+} (ppm)* Bentonite %	1	0.0243	0.0243	11.26	0.184
Ca Conc./ Ca^{2+} (ppm)* pH	1	0.0013	0.0013	0.62	0.576
Bentonite %*pH	1	0.0161	0.0161	7.49	0.223
Error	1	0.0022	0.0022		
Total	7	0.1336			

b) Tukey

Variables	Number of experiments	Mean Recovery
Ca^{2+}, 3000 ppm	4	0.60
Ca^{2+}, 0 ppm	4	0.45
Bentonite Conc., 0 %	4	0.58
Bentonite Conc., 10 %	4	0.47
pH, 6	4	0.56
pH, 9	4	0.50

3.1.2. Rheology results

Figure 1 shows the rheology results obtained for the flotation tailings. As seen in Figure 1, the increase in the bentonite concentration resulted in a higher viscosity attributed to the higher water swelling capacity of bentonite. A higher apparent viscosity resulted in reduced collisions between bubbles and particles due to reduced mobility of particles and air bubbles, leading to poor flotation performance. The addition of Ca^{2+} ions reduced the water swelling capacity of bentonite, leading to reduced viscosity. This is in agreement with the results of other studies (Basnayaka et al., 2017; Assemi et al., 2015; Cruz et al., 2015). The measurements of the rheological properties i.e., the consistency indexes and the flow indexes were used to better understand the relationship between the rheology and the flotation performance.

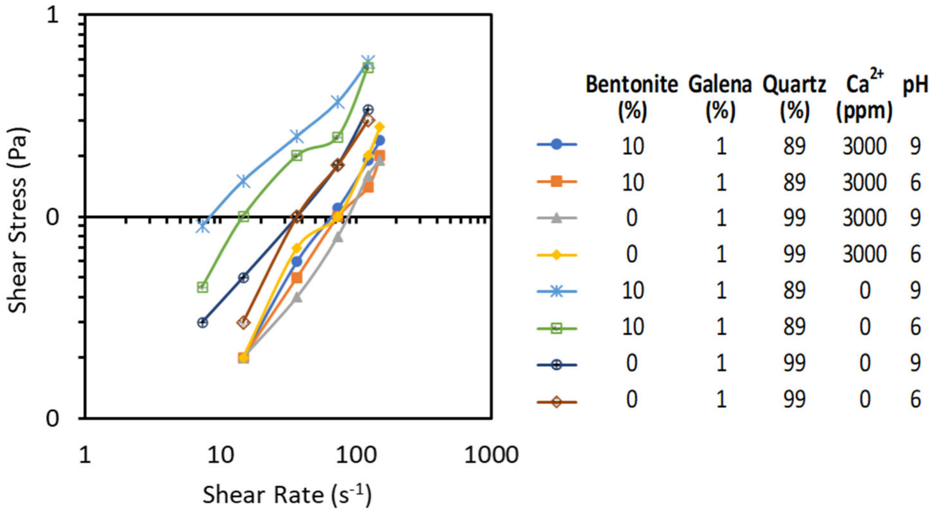


Figure 1. Galena flotation tailings rheograms.

Consistency index is a rheological property of the mineral suspensions that can be considered as a measure of yield stress. The ANOVA and Tukey results for consistency index are presented in Table 3 (a). The ANOVA results indicated that there is no statistically significant variable. The Tukey analysis showed that the consistency index decreased by increasing the concentration of Ca^{2+} from 0 to 3000 ppm considering that the presence of Ca^{2+} reduced the swelling of bentonite slurries. On the contrary, the consistency index increased with increasing in bentonite concentration given that the presence of bentonite made slurries more viscous. The flow index (n) indicates how the shear rate affects the shear stress. Both ANOVA and Tukey showed there are no significant variables (Table 3b).

Table 3. Statistical analysis for rheology of galena flotation tailings for a) consistency index and b) flow index.

a) Consistency index

ANOVA

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Ca Conc./ Ca^{2+} (ppm)	1	0.000147	0.000147	45.23	0.094
Bentonite %	1	0.000126	0.000126	38.63	0.102
pH	1	0.000003	0.000003	0.920	0.513
Ca Conc./ Ca^{2+} (ppm)* Bentonite %	1	0.000115	0.000115	35.30	0.106
Ca Conc./ Ca^{2+} (ppm)* pH	1	0.000003	0.000003	1.000	0.500
Bentonite %*pH	1	0.000003	0.000003	0.920	0.513
Error	1	0.000003	0.000003		
Total	7	0.000400			

Tukey

Variables	Number of experiments	Mean consistency index
Ca^{2+}, 3000 ppm	4	0.0012
Ca^{2+}, 0 ppm	4	0.0098
Bentonite Conc., 0 %	4	0.0015
Bentonite Conc., 10 %	4	0.0094
pH, 6	4	0.0050
pH, 9	4	0.0060

b) Flow index

ANOVA

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Ca Conc./ Ca^{2+} (ppm)	1	0.0329	0.0329	4.18	0.290
Bentonite %	1	0.0293	0.0293	3.72	0.304
pH	1	0.0002	0.0002	0.02	0.904
Ca Conc./ Ca^{2+} (ppm)* Bentonite %	1	0.0086	0.0086	1.10	0.485
Ca Conc./ Ca^{2+} (ppm)* pH	1	0.0205	0.0205	2.60	0.353
Bentonite %*pH	1	0.0155	0.0155	1.97	0.394
Error	1	0.0079	0.0079		
Total	7	0.1149			

Tukey

Variables	Number of experiments	Mean flow index
Ca^{2+}, 0 ppm	4	0.903
Ca^{2+}, 3000 ppm	4	1.031
Bentonite Conc., 0 %	4	1.027
Bentonite Conc., 10 %	4	0.906
pH, 6	4	0.972
pH, 9	4	0.962

3.1.3. Zeta potential results

Figure 2 shows the zeta potentials for galena and bentonite with and without of Ca^{2+}. As seen in Figure 2, with pure bentonite and galena, pH increases lowered zeta potential, likely due to OH- ion adsorption. The presence of Ca^{2+} ions led to a less negative zeta potential of both galena and bentonite due to the adsorption of different calcium ions on galena and bentonite. Ca^{2+} ions did not change zeta potential up to pH 8, potentially because Ca^{2+} replaced Na^{+} in bentonite interlayers, limiting available Ca^{2+} for adsorption. Ca^{2+} and $Ca(OH)^{+}$ ions are prevalent species when the pH is below 12.6, whereas $Ca(OH)_2$ become predominant when the pH exceeds 12.6 (Zhang et. al., 2019). It means that the addition of Ca^{2+} significantly reduced the repulsive forces between particles due to the less negative zeta potential of bentonite and galena, leading to a higher settling rate (see Figure 3).

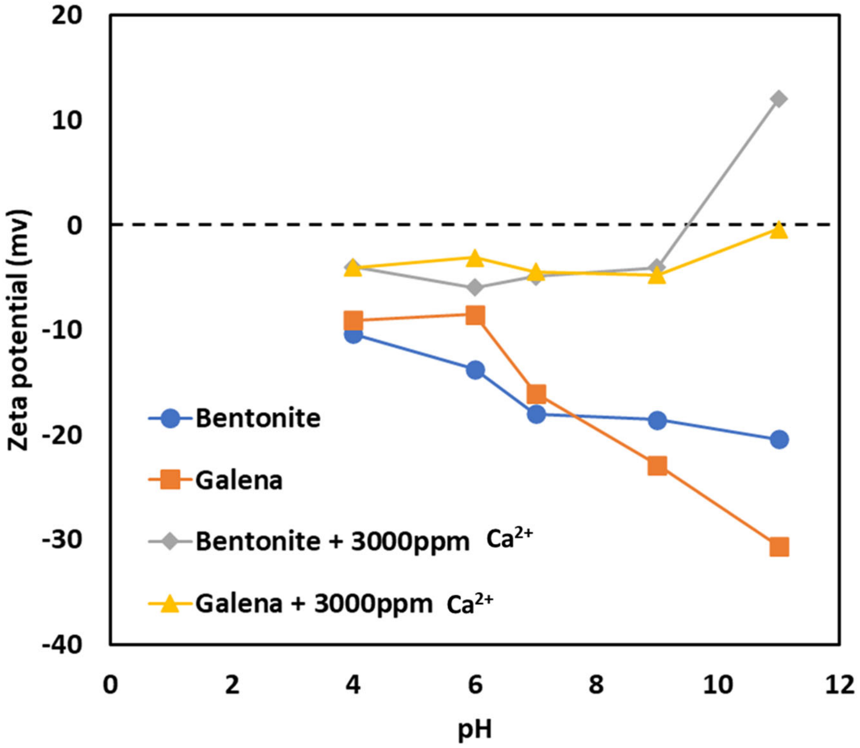
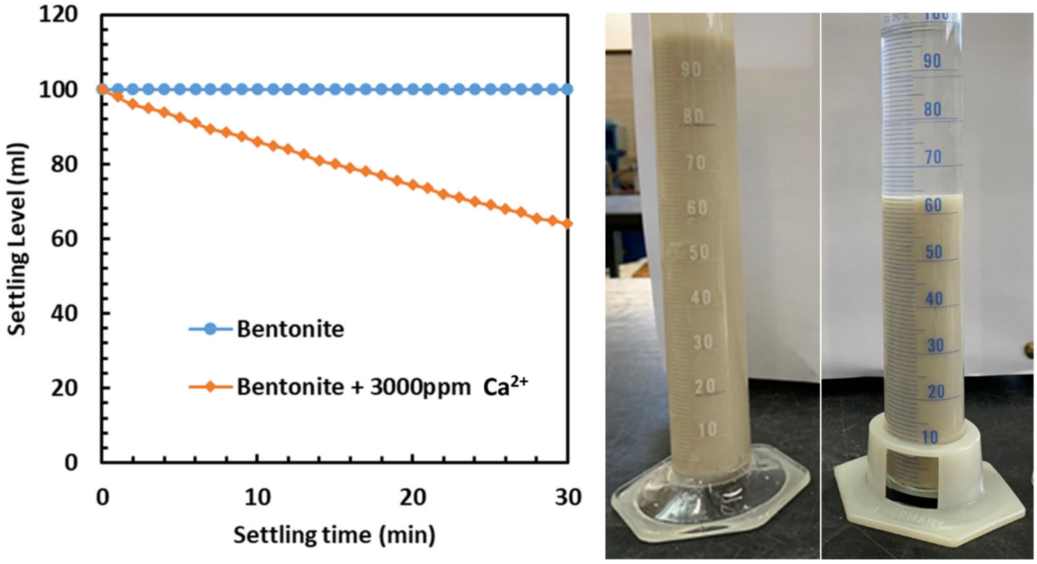


Figure 2. Zeta-potential of galena and bentonite in the presence and absence of Ca^{2+}

3.1.4. Settling tests results

Figure 3 shows that the presence of Ca^{2+} significantly increased the settling rate. The reason is that the presence of Ca^{2+} reduced the swelling properties of bentonite (Kashif et al., 2023; (Assemi et al., 2015; Cruz et al., 2015). Moreover, the repulsive forces between bentonite particles reduced significantly at pH 8 (see Figure 3), leading to the faster settling rate.



(a) **(b)**

Figure 3. Settling tests after 30 min for 10% bentonite at Ca^{2+} concentration at pH=7.5±0.5 (a) 0 ppm (b) 3000 ppm.

3.2. Effect of bentonite on sphalerite performance

Table 4 displays the independent variables, including Ca^{2+} concentration, bentonite concentration, and pH, alongside the dependent variables, i.e. recoveries (R), flow index (n), and consistency index (K). ANOVA (analysis of variance) was utilized to evaluate the significant influence of these independent variables on the dependent variables. Table 5 presents the results of ANOVA and Tukey analysis.

Table 4. The experimental conditions and results for sphalerite flotation and rheology.

Ca^{2+} (ppm)	Bentonite (%)	pH	Recovery	Flow Index (n)	Consistency Index (K)
3000	10	9	0.57	1.167	0.00099
3000	10	6	0.66	1.033	0.00159
3000	0	9	0.63	0.997	0.00174
3000	0	6	0.62	1.049	0.00132
0	10	9	0.51	0.630	0.03570
0	10	6	0.54	0.750	0.02200
0	0	9	0.65	0.946	0.00325
0	0	6	0.63	0.999	0.00273

3.2.1. Flotation results

In Table 5(a), the ANOVA results for the recovery are presented. It is discernible that the concentration of bentonite appears as the most significant variable, followed by Ca^{2+} concentration, whereas the pH of the slurry exhibits the least significance. Subsequent Tukey analysis (Table 5(b)) showed that the recovery was significantly affected by increasing the concentrations of bentonite and Ca^{2+}. More precisely, increasing the concentration of bentonite from 0% to 10%, resulted in a substantial decline in recovery from 63% to 56%. This decrease can be attributed to the pronounced high water absorption capacity and swelling properties of bentonite particles that led to a significant rise in pulp viscosity (refer to Figure 4 for rheology). However, the presence of Ca^{2+} reduced the adverse effects of bentonite on flotation efficiency, resulting in an elevation of recovery from 58% to 62%.

Table 5. Statistical analysis for flotation recovery of sphalerite.

a) ANOVA

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Ca Conc./ Ca^{2+} (ppm)	1	0.00302	0.00302	7.60	0.222
Bentonite %	1	0.00772	0.00772	19.41	0.142
pH	1	0.00096	0.00096	2.41	0.365
Ca Conc./ Ca^{2+} (ppm)* Bentonite %	1	0.00634	0.00634	15.93	0.156
Ca Conc./ Ca^{2+} (ppm)* pH	1	0.00033	0.00033	0.82	0.531
Bentonite %*pH	1	0.00240	0.00240	6.02	0.246
Error	1	0.00040	0.00040		
Total	7	0.02116			

b) Tukey

Variables	Number of experiments	Mean Recovery
Ca^{2+}, 3000 ppm	4	0.62
Ca^{2+}, 0 ppm	4	0.58
Bentonite Conc., 0 %	4	0.63
Bentonite Conc., 10 %	4	0.56
pH, 6	4	0.61
pH, 9	4	0.59

3.2.2. Rheology results

Figure 4 presents the rheological analysis conducted on sphalerite flotation tailings. It is evident from Figure 4 that the increase in bentonite concentration corresponds to a rise in pulp viscosity, attributed to the increased water swelling capacity of bentonite. The increased pulp viscosity resulted in decreased mobility of both bubbles and particles within the flotation cell, thereby reducing the frequency of bubble-particle collisions and negatively impacting flotation performance. The introduction of Ca^{2+} ions mitigated the water swelling capacity of bentonite, and thus reduced the pulp viscosity. These observations align with prior research findings (Basnayaka et al., 2017; Assemi et al., 2015; Cruz et al., 2015).

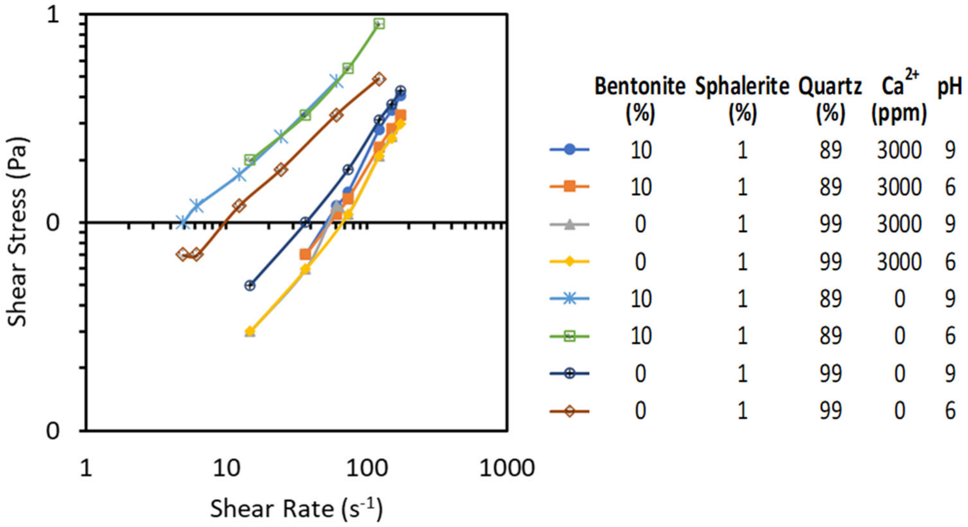


Figure 4. Sphalerite flotation tailings rheograms.

Table 6a presents the ANOVA and Tukey results for the consistency index. The ANOVA results revealed no statistically significant variables. However, the Tukey analysis revealed a decrease in the consistency index with increasing Ca^{2+} concentration from 0 to 3000 ppm, attributed to the mitigated swelling of bentonite slurries in the presence of Ca^{2+}. Conversely, the consistency index exhibited an increase with increasing bentonite concentration, as the presence of bentonite rendered the slurries more viscous. Regarding the flow index (n), both ANOVA and Tukey analyses demonstrated no significant variables (Table 6b).

Table 6. Statistical analysis for rheology of sphalerite flotation tailings for a) consistency index and b) flow index

a) Consistency index

ANOVA

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Ca Conc./ Ca^{2+} (ppm)	1	0.000346	0.000346	36.05	0.105
Bentonite %	1	0.000256	0.000256	26.70	0.122
pH	1	0.000008	0.000008	0.85	0.526
Ca Conc./ Ca^{2+} (ppm)* Bentonite %	1	0.000267	0.000267	27.84	0.119
Ca Conc./ Ca^{2+} (ppm)* pH	1	0.000009	0.000009	0.93	0.512
Bentonite %*pH	1	0.000006	0.000006	0.59	0.583
Error	1	0.000010	0.000010		
Total	7	0.000902			

Tukey

Variables	Number of experiments	Mean consistency index
Ca^{2+}, 3000 ppm	4	0.00141
Ca^{2+}, 0 ppm	4	0.01456
Bentonite Conc., 0 %	4	0.00233
Bentonite Conc., 10 %	4	0.01365
pH, 6	4	0.00900
pH, 9	4	0.00698

a) Flow index

ANOVA

Variables and the interactions between them	DF	Adj SS	Adj MS	F-value	p-value
Ca Conc./ Ca^{2+} (ppm)	1	0.1060	0.1060	13.28	0.170
Bentonite %	1	0.0212	0.0212	2.65	0.351
pH	1	0.0010	0.0010	0.13	0.779
Ca Conc./ Ca^{2+} (ppm)* Bentonite %	1	0.0647	0.0647	8.11	0.215
Ca Conc./ Ca^{2+} (ppm)* pH	1	0.0082	0.0082	1.02	0.496
Bentonite %*pH	1	0.0018	0.0018	0.22	0.719
Error	1	0.0080	0.0080		
Total	7	0.2107			

Tukey

Variables	Number of experiments	Mean flow index
Ca^{2+}, 0 ppm	4	0.831
Ca^{2+}, 3000 ppm	4	1.062
Bentonite Conc., 0 %	4	0.998
Bentonite Conc., 10 %	4	0.895
pH, 6	4	0.958
pH, 9	4	0.935

3.2.3. Zeta potential

Figure 5 illustrates the zeta potentials observed for sphalerite and bentonite in the presence and absence of Ca^{2+}. As depicted in Figure 5, when pure bentonite and sphalerite are considered, increasing pH levels resulted in lower zeta potential values, likely attributed to the adsorption of OH^- ions. The addition of Ca^{2+} ions induced a less negative zeta potential for both sphalerite and bentonite, owing to the adsorption of different calcium ions on sphalerite and bentonite particles. However, up to a pH of 8, Ca^{2+} ions did not lead to any notable changes in zeta potential, possibly due to the replacement of Na^+ ions in bentonite interlayers by Ca^{2+}, thus limiting the availability of Ca^{2+} ions for adsorption. At pH below 12.6, Ca^{2+} and $Ca(OH)^+$ ions prevail, whereas $Ca(OH)^{-2}$ becomes predominant beyond this pH threshold (Zhang et al., 2019).

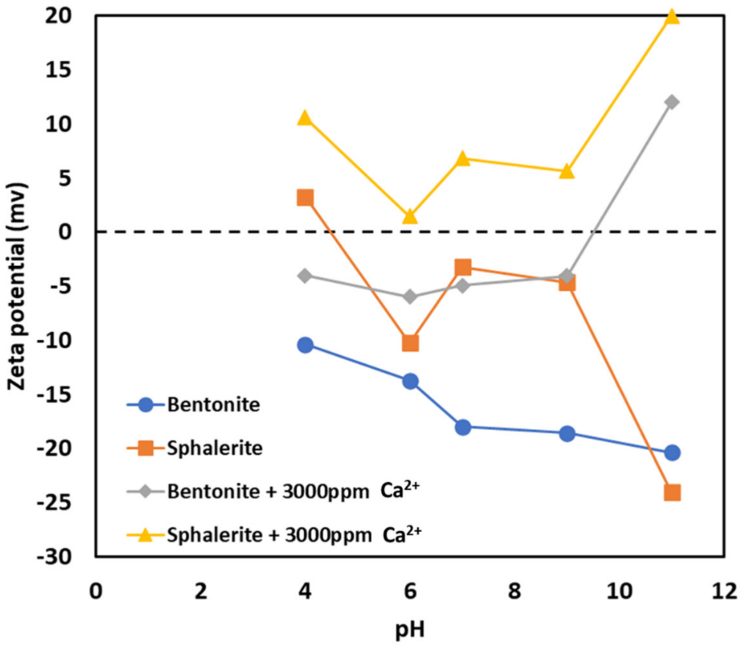
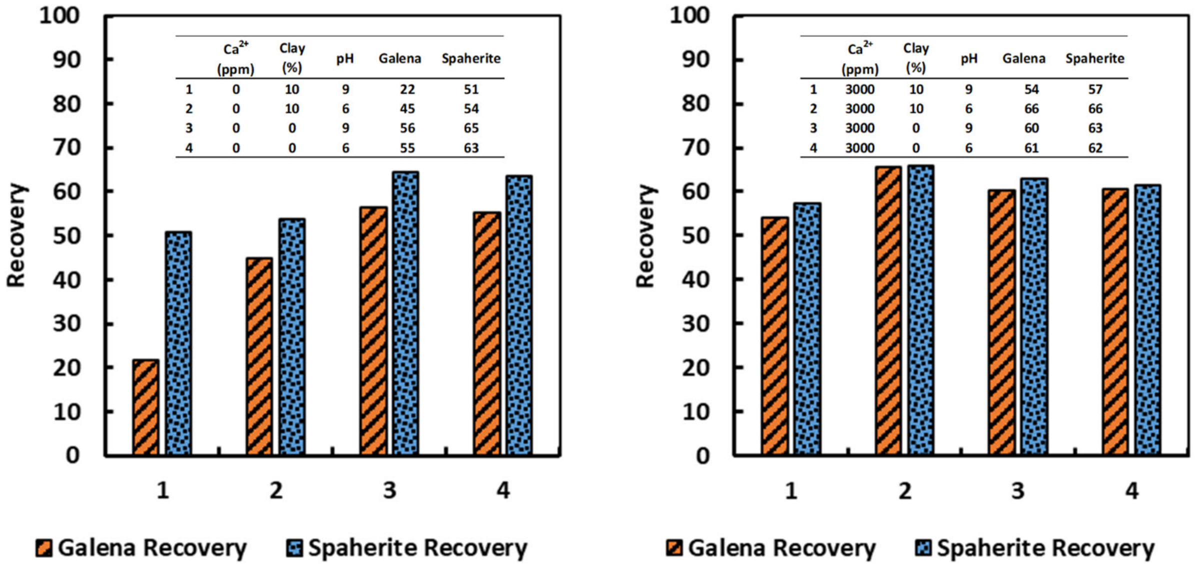


Figure 5. Zeta-potential of sphalerite and bentonite in the presence and absence of Ca^{2+}

3.3. Comparison of galena and sphalerite performance in the presence of bentonite

Figures 6 and 7 compares the flotation performances of galena with those of sphalerite in the presence of bentonite. As seen in Figures 6 and 7, in the absence of Ca^{2+}, the flotation recoveries of galena were lower than those of sphalerite. In the absence of Ca^{2+}, the flotation recovery of galena decreased significantly more than the flotation recovery of sphalerite with increasing the consistency index (see Figure 7a). The high consistency index coupled with the high galena density (i.e., galena has 1.876 times greater density than sphalerite), suggests that galena is more likely to detach from bubbles compared to sphalerite, reducing the recovery of galena. However, in the presence of Ca^{2+}, there is no significant difference in the flotation recoveries of galena and sphalerite (see Figures 6b and 7b). This is likely attributed to the reduced consistency index, which enhances the mobility of bubbles and particles during flotation, consequently resulting in higher flotation recoveries.



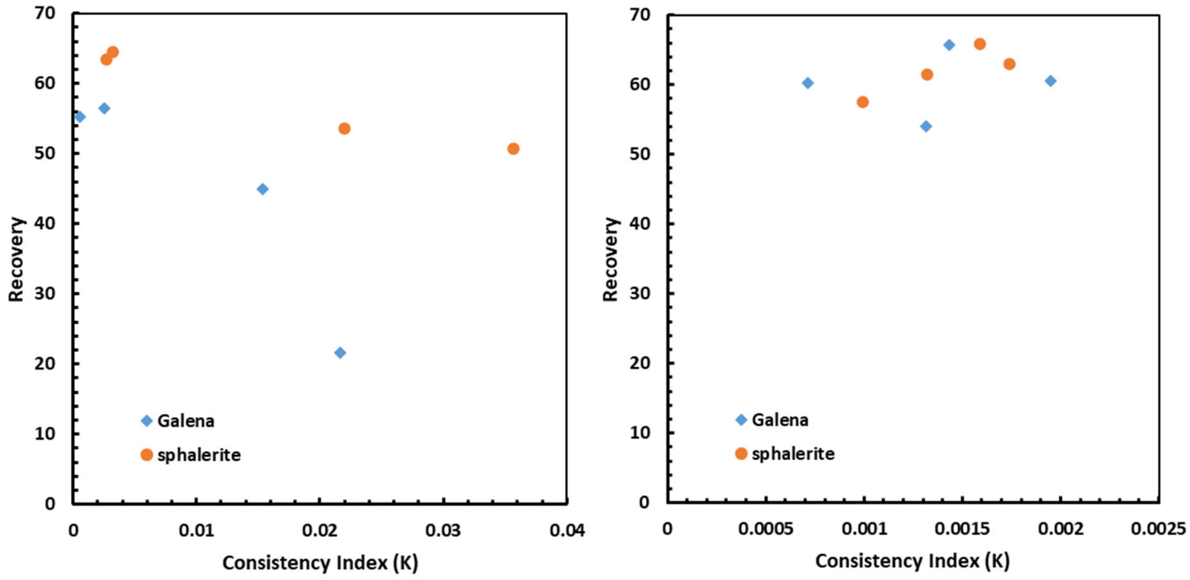
	Ca^{2+} (ppm)	Clay (%)	pH	Galena	Spaherite
1	0	10	9	22	51
2	0	10	6	45	54
3	0	0	9	56	65
4	0	0	6	55	63

	Ca^{2+} (ppm)	Clay (%)	pH	Galena	Spaherite
1	3000	10	9	54	57
2	3000	10	6	66	66
3	3000	0	9	60	63
4	3000	0	6	61	62

(a)

(b)

Figure 6. Comparison of the flotation recoveries of galena and sphalerite a) in the absence of Ca^{2+} and b) in the presence Ca^{2+}.



(a)

(b)

Figure 7. The relationship between the flotation recovery and the consistency index a) in the absence of Ca^{2+} and b) in the presence Ca^{2+}.

4. Conclusions

This paper investigated the flotation performance of galena and sphalerite in the presence bentonite, while also examining the influence of their different densities on their respective flotation behaviours. The presence of bentonite led to decreased flotation recoveries of both galena and sphalerite, attributed to an increase in pulp viscosities. After the addition of Ca^{2+} ions, which caused a decrease in pulp viscosities, the adverse effect of bentonite on the flotation of galena and sphalerite was mitigated. The zeta potentials of galena, sphalerite, and bentonite were notably reduced after the addition of Ca^{2+} ions, resulting in decreased repulsive forces between the particles and subsequently reducing the pulp viscosities. The positive impact of Ca^{2+} ions was confirmed through settling tests, where it was observed that the settling rate significantly increased after adding Ca^{2+} ions. In the absence of Ca^{2+}, the flotation recoveries of galena decreased more significantly than that of sphalerite attributed to the increase in the consistency index. The increased consistency index together with the high galena density, may have caused galena particles to detach from bubbles, reducing the recovery of galena. In the presence of Ca^{2+}, there is no notable difference in the flotation recoveries of galena and sphalerite. A considerable amount of additional work is necessary to explore the impact of bentonite on the recovery of minerals with different densities, using not only flotation but also other separation techniques like hydrocyclone.

References

Arnold, B.J., Aplan, F.F., 1986. The effect of clay slimes on coal flotation, part I: The nature of the clay. Int. J. Miner. Process., 17: 225-242.

Assemi, S., Sharma, S., Tadjiki, S., Prisbrey, K., Ranville, J., Miller, J.D., 2015. Effect of surface charge and elemental composition on the swelling and delamination of montmorillonite nanoclays using sedimentation field-flow fractionation and mass spectroscopy. Clay Clay Miner. 63 (6), 457–468.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2017. Influence of clays on the slurry rheology and flotation of a pyritic gold ore. Appl. Clay Sci. 136, 230–238.

Basnayaka, L., Subasinghe, N., Albijanic, B., 2018. Influence of clays on fine particle filtration. Appl. Clay Sci. 156, 45–52.

Chen, L., Zhao, Y., Bai, H., Ai, Z., Chen, P., Hu, Y., Song, S., Komarneni, S., 2020. Role of Montmorillonite, Kaolinite, or Illite in Pyrite Flotation: Differences in Clay Behavior Based on Their Structures. Langmuir. 36 (36), 10860-10867 DOI: 10.1021/acs.langmuir.0c02073

Chen, X., Peng, Y., 2018. Managing clay minerals in froth flotation-a critical review, Miner. Process. Extr. Metall. Rev. 2. 1–19.

Cruz, N., Yongjun, P., Wightman, E., Xu, N., 2015. The interaction of clay minerals with gypsum and its effects on copper–gold flotation. Min. Eng. 77, 121–130.

Kashif, N., Albijanic, B., Xu, J., Syahida, S., McGrath, T., Tadesse, B., Nazir, M.K., 2023. Grinding of highly viscous bentonite containing slurries. Applied Clay Science 232, 106794.

King, R.P., 2002. Introduction to Practical Fluid Flow. first ed. Butterworth-Heinemann, Oxford.

Liu, D., Peng, Y., 2014. Reducing the entrainment of clay minerals in flotation using tap and saline water, Powder Technol. 253, 216–222.

Luckham, P.F., Rossi, S., 1999. The colloidal and rheological properties of bentonite suspensions. Adv. Colloid Interf. Sci. 82 (1–3), 43–92.

Oats, W. J., Ozdemir, O., Nguyen, V. A., 2010. Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation, Minerals Engineering, Volume 23, Issue 5, Pages 413-419, ISSN 0892-6875, https://doi.org/10.1016/j.mineng.2009.12.002

Taner, H., Önen, V., 2016. Control of clay minerals effect in flotation. A review. E3S Web of Conferences. 8. 01062. 10.1051/e3sconf/20160801062.

Wang, B., Y. Peng, Y., 2014. The effect of saline water on mineral flotation – a critical review, Miner. Eng. 66–68, 13–24.

Wang, Y., Peng, Y., Nicholson, T., Lauten, R. A., 2015. The different effects of bentonite and kaolin on copper flotation, Applied Clay Science 114, 48–52.

Xing, Y., Gui, X., Pan, L., Pinchasik, B., Cao, Y., Liu, J., Kappl, M., Butt, H. J., 2017. Recent experimental advances for understanding bubble-particle attachment in flotation, Adv. Colloid Interf. Sci. 246, 105–132.

Xing, Y., Xu, X., Gui, X., Cao, Y., Xu, M., 2017. Effect of kaolinite and montmorillonite on fine coal flotation, Fuel 195, 284–289.

Xing, Y., Xua, M., Guoa, F., Luo, J., Zhang, Y., Cao, Y., Gui, X., 2019. Role of different types of clay in the floatability of coal: Induction time and bubble-particle attachment kinetics analysis. Powder Technology 344, 814–818.

Xu, Z., Liu, J., Choung, J., Zhou, Z., 2003. Electrokinetic study of clay interactions with coal in flotation, Int. J. Miner. Process. 68, 183–196.

Yin, X., Gupta, V., Du, H., Wang, X., Miller, J., 2012. Surface charge and wetting characteristics of layered silicate minerals, Adv. Colloid Interf. Sci. 179–182, 43–50.

Yu, Y., Ma, L., Cao, M., Liu, Q., 2017. Slime coatings in froth flotation: a review, Miner. Eng. 114, 26–36.

Zhang, C., Xu, Z., Hu, Y., He, J., Tian, M., Zhou, J., Zhou, Q., Chen, S., Chen, D., Chen, P., Sun, W., 2019. Novel Insights into the Hydroxylation Behaviors of α-Quartz (101) Surface and its Effects on the Adsorption of Sodium Oleate. Minerals, 9, 450. https://doi.org/10.3390/min9070450

Zhang, M., 2016. The Effect of Clay Minerals on Copper and Gold Flotation. PhD Thesis. The University of Queensland.

Zhang, M., Peng, Y., 2015. Effect of clay minerals on pulp rheology and the flotation of copper and gold minerals. Miner. Eng. 70, 8–13.

Chapter VII

Conclusions and recommendations for future work

1. Conclusions

The influence of Ca^{2+} ions was studied on the grinding performance of kaolin-containing ores by analyzing grinding efficiency, particle size distributions, rheology, zeta potentials, and settling behavior. The findings indicate that Ca^{2+} ions negatively affect grinding performance when kaolin content is high (40%) and solid percentage is elevated (70%). Ca^{2+} ions reduced zeta potentials, decreasing repulsion forces between kaolin particles, and negatively impacting settling rates due to particle agglomeration. Rheological studies show increased shear stress in the presence of Ca^{2+} ions at high clay percentages. The study highlights the need to optimize Ca^{2+} concentrations in plant water for kaolin ores.

This thesis also demonstrated that bentonite negatively influenced grinding performance due to its high swelling capacity. Grinding efficiency decreased significantly when the solid percentage of bentonite-containing slurries exceeded 62%. However, adding Ca^{2+} ions improved performance by reducing bentonite swelling, as confirmed by rheological measurements. Higher solid percentages consistently resulted in lower grinding performance, with Ca^{2+} dosage being the most influential factor. The research suggests that optimizing solid percentage or Ca^{2+} dosage can enhance grinding performance for bentonite-containing ores, providing valuable insights for developing methods to mitigate bentonite adverse effects in industrial grinding processes.

The drying performance of kaolin and bentonite-containing slurries were investigated through various analytical techniques, revealing that adding Ca^{2+} ions improved the drying performance of bentonite slurries by lowering viscosity and improving stability and dispersion, as confirmed by rheology, zeta potential, FTIR, DTA-TGA, and SEM analyses. The Ca^{2+} ions reduce the swelling capacity of bentonite, resulting in faster drying rates. In contrast, Ca^{2+} ions have minimal impact on kaolin slurries, causing slight agglomeration without significantly improving drying rates. Three drying regions were identified for both kaolin and bentonite-containing slurries, with temperature being the predominant factor influencing drying kinetics. These findings are valuable for improving industrial drying processes of bentonite and kaolin slurries, potentially reducing product handling costs.

The flotation performance of galena and sphalerite was investigated to study the influence of bentonite and the influence of different densities of two minerals. Bentonite reduced the flotation recoveries of both minerals by increasing pulp viscosities. Adding Ca^{2+} ions mitigated this adverse effect by lowering zeta potentials, thus reducing repulsive forces between particles and hence reduced pulp viscosities. The improved flotation performance with Ca^{2+} was confirmed by increased settling rates. In the absence of Ca^{2+}, galena recoveries decreased more than sphalerite due to higher consistency index and density, causing particle detachment from bubbles. With addition of Ca^{2+}, no significant difference in recoveries of two minerals (i.e. galena and sphalerite) was observed.

This thesis confirmed that understanding of behaviour of clay-containing slurries using grinding, flotation and drying is very important for improving mineral processing performance of clay-containing ores.

2. Future research opportunities/ recommendations

- This thesis examined the individual effects of kaolin and bentonite clays on different mineral processes (i.e. grinding, drying and flotation). It is suggested to investigate the combined influence of these two clay types in different proportions by preparing synthetic ores.
- The influence of Ca^{2+} ions was investigated on selected mineral processes. More research is recommended to examine the interactions between clay particles and other bivalent cations (Mg^{2+}) and trivalent cations (Al^{3+}).
- This thesis underscores the need for optimizing Ca^{2+} levels in grinding operations of kaolin-containing ores and further investigation is required to study the impact of different ions (i.e. sulphate ions) to mitigate the negative effect of Ca^{2+} ions on grinding performance of kaolin-containing ores.
- The study examined the flotation performance of galena and sphalerite to understand the effects of bentonite and varying mineral densities, however further research is required to investigate the effect of bentonite on mineral recovery using methods other than flotation such as hydrocyclones.