Experimental Study of Morphology and Particle Size of Alumina Hydroxide Products

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Abstract

This project investigates the morphology and particle size of alumina hydroxide products, the objective being to replicate Wilhelmy's (1990) study by varying methanol and ethanol concentrations to produce different aluminium hydroxide crystal morphologies. Experiments focused on crystallising aluminium hydroxide from a synthetic potassium aluminate solution. Scanning electron microscopy (SEM) analysis provided insights into the crystals' shape under various conditions. Key findings include the successful production of nanoscale aluminium hydroxide crystals by adding an organic solvent under specific conditions, a novel achievement not previously documented in scientific literature from a potassium aluminate solution. These reproducible nanocrystals hold significant value in the adsorption and catalysis industry. A few drops of acid containing a significant impurity present in the ore were found to notably increase the solubility of aluminium hydroxide in potassium hydroxide. Therefore, it is recommended not to pre-treat the alunite ore as impurities in the ore enhance dissolution and improve leaching efficacy. This will minimise associated costs and conserve valuable resources for other critical aspects of the novel process.

1. Introduction

This project experimentally investigates the morphology and particle size of alumina hydroxide products for Impact Minerals. Impact Minerals is investigating a novel process using lacustrine clay aluminium salt feedstock, primarily composed of alunite ore ($KAl_3(SO_4)_2(OH)_6$), to produce high-purity alumina with 99.99% (4N) purity. Aluminium hydroxide is a precursor product to alumina, which is typically precipitated out of a sodium aluminate solution in the Bayer process under high temperatures and pressures. Potassium hydroxide was used in this research as it effectively leaches alunite ores and produces potassium sulphate as a valuable byproduct at relatively low temperatures and pressures.

The use of potassium hydroxide as the leachate to extract alumina currently has limited industrial application, and only within the last decade has received scholarly attention. The academic focus using potassium hydroxide has mainly been from China where alunite tailings from the copper industry have a great abundance of aluminium and potassium. There is limited understanding of the effects of reaction conditions on the morphology of aluminium hydroxide using potassium hydroxide as the leachate. Therefore, this research project explores this topic.

HPA requires specific physical properties including particle morphology. Morphology is the study of a crystal's shape and structure. The morphology of a crystal is usually shaped by the varying growth rates of its crystalline faces. The difference in growth rates is attributed to the variations in surface energy of different crystallographic planes. When a crystal forms, ions or molecules adhere to the surface of the crystal which contributes to its growth. These molecules or ions attach themselves more easily to faces with higher surface energy, which usually grow faster. The slower-growing faces have a lower surface energy, which attracts fewer molecules or ions. These faces maintain their relative size compared to the faster-growing faces which determines the overall shape (Perkins, n.d.).

Manipulating reaction conditions to produce desired crystal morphologies will allow Impact Minerals to target specific industries. HPA used in lithium-ion batteries requires a lamellar (plate-like) morphology (Altech, 2020). HPA used as a catalyst in the polymerisation industry and petrochemical industry in the cracking process needs to be porous with a high surface area, often in the form of nanospheres (Keijzer et al., 2023). Acicular (needle-like) aluminium hydroxide crystals are used as a nucleating agent for olefine resin, favouring its high specific surface area (Takemura & Nippa, 2004). The aluminium hydroxide in this case is employed as a filler in polyolefin to enhance its fire resistance and mechanical properties.

This research project was based on Wilhelmy's (1990) US Patent 4900537. The patent predicted the morphology of aluminium hydroxide crystals under various reaction conditions using sodium hydroxide. It was found that the concentration of methanol affected the morphology of aluminium hydroxide in a synthetic sodium aluminate solution. Methanol also enhances the precipitation rate by reducing the solubility of aluminium hydroxide in solution, thereby increasing the driving force for precipitation. Figure 1 illustrates that increasing methanol concentration results in a transition from acicular to lamellar crystals. For low diameter-to-length ratios, the crystals are characterised as acicular and for high diameter-to-length ratios the crystals are lamellar.

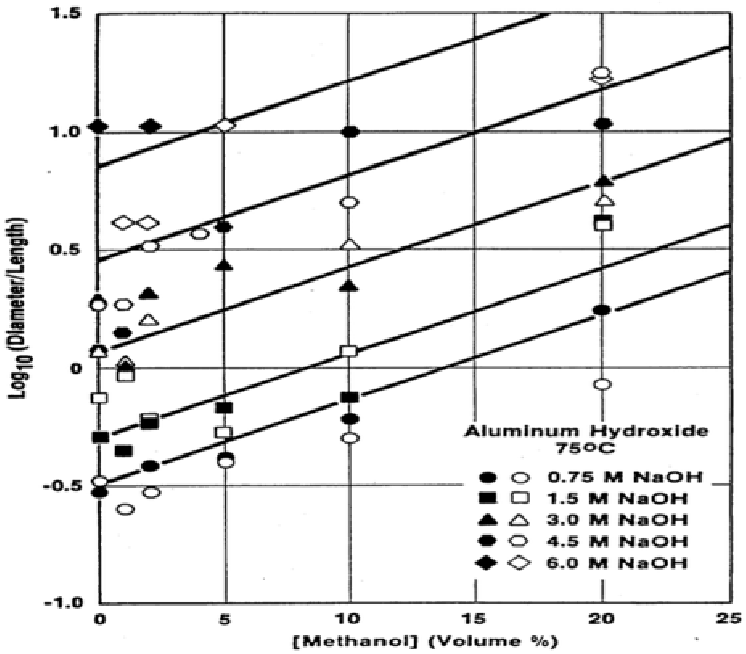

Figure 1 The effect of methanol concentration on the diameter-to-length ratio of aluminium hydroxide crystals (Wilhelmy, 1990).

1.2 Project Objectives

This project aims to establish the effect of reaction conditions on the particle size and morphology of aluminium hydroxide crystals precipitated from a synthetic potassium aluminate solution. The insights gained from these experiments will contribute to the current state-of-the-art knowledge in aluminium hydroxide crystallisation from a potassium aluminate solution. This knowledge will enable Impact Minerals to make informed decisions regarding process design, allowing them to strategically adjust reaction conditions to tailor the morphology of crystals, thereby optimising their suitability for specific industries.

2. Process

The overall methodology for this project began with an extensive literature review on the current understanding of aluminium hydroxide crystallisation from potassium aluminate solutions. This review informed the design of the experimental methodology, which involved varying amounts of organic solvents and specific temperature conditions to investigate their impact on crystal morphology.

The experiments began by producing a synthetic potassium aluminate solution through the combination of potassium hydroxide and aluminium hydroxide with heat and stirring on a magnetic stirrer hot plate. The solution was then filtered using a Buchner funnel to remove any undissolved aluminium hydroxide, as this research focused on non-seeded crystallisation. Specific amounts of organic solvents were then added to the filtered solution and stirred. The solution was aged for a period to facilitate crystal formation, after which it was filtered with a Buchner funnel to obtain the crystals. The morphology of the resulting crystals produced was then analysed using SEM.

Initial experiments were conducted by varying the amount of reagents added and the temperature of the solution. The insights gained were used to refine subsequent experiments. This included the amount of potassium hydroxide and methanol to add, the appropriate dissolution temperature for aluminium hydroxide, and the necessity of adding a specific acid to assist with aluminium hydroxide dissolution in potassium hydroxide. Once nanocrystals were successfully achieved, a reproducibility experiment was conducted to ensure the reliability and validity of producing nanocrystals under specific reaction conditions. Figure 2 provides a schematic diagram of the experiments conducted and the equipment used.

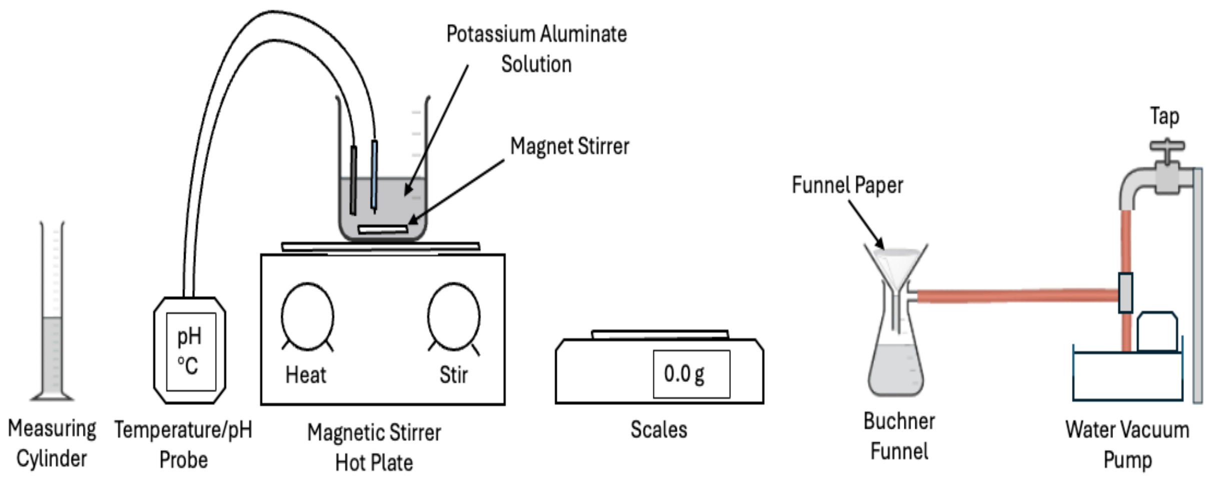

Figure 2 Experiment schematic diagram.

3. Results and Discussion

None of the cases from the first experiment resulted in the precipitation of any crystals. This outcome was attributed to the limited solubility of aluminium hydroxide in potassium hydroxide. Consequently, a significant portion of the added aluminium hydroxide powder remained undissolved and was subsequently filtered out. The insufficient dissolution of aluminium hydroxide in the potassium hydroxide solution hindered the formation of aluminium hydroxide crystals. While aluminium hydroxide is insoluble in water, limited literature exists regarding the solubility of aluminium hydroxide in potassium hydroxide, resulting in a lack of prior expectations regarding its dissolution behaviour.

Interestingly, the raw feedstock demonstrated notable solubility in potassium hydroxide solution observed by Impact Minerals under comparable temperatures and concentrations. It was hypothesised that impurities within the ore facilitate this dissolution process. Subsequently, an experiment was conducted to determine if introducing a significant impurity in the ore in the form of an acid would enhance the dissolution of aluminium hydroxide in solution. The results showed that adding this acid increased the amount of dissolved aluminium hydroxide by three times the amount compared to without acid.

A significant finding emerging from this experiment, despite no crystals forming, underscores the unnecessary nature and potential detriment of ore processing steps aimed at removing impurities. Such processes have the potential to diminish the solubility of aluminium hydroxides in the ore from potassium hydroxide solution, thereby compromising the efficacy of the leaching step.

This finding informed the methodology for subsequent experiments, where aluminium hydroxide was successfully dissolved and crystalised from solution. These experiments varied the amount of organic solvent added and dissolution temperature, leading to the production of aluminium hydroxide nanocrystals under specific conditions. Figures 3 and 4 depict the morphology of the aluminium hydroxide reagent used to produce the potassium aluminate solution, while Figures 5 and 6 show the resulting nanocrystals produced. These nanocrystals possess exceptionally high surface area, making them valuable in catalysis and adsorption applications. The value of these nanocrystals requires negotiation with potential clients.

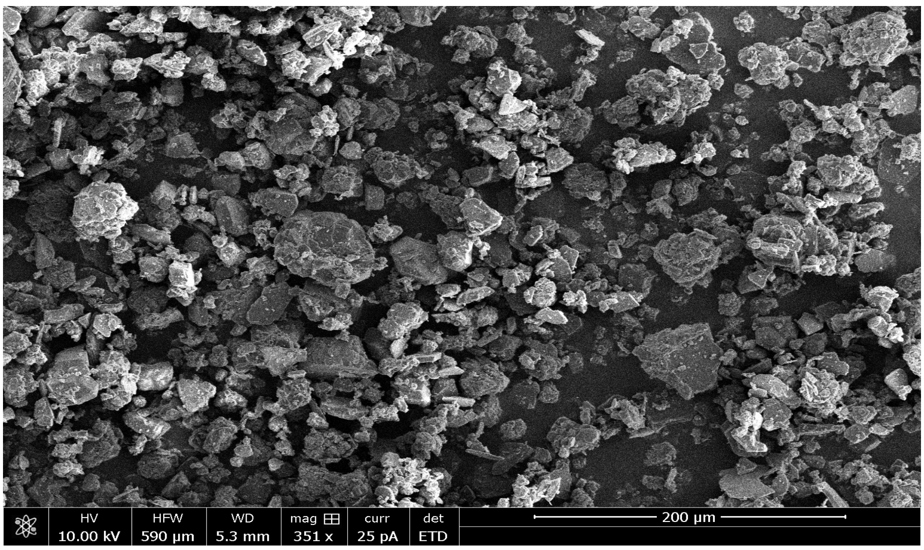

Figure 3 Overview of aluminium hydroxide reagent morphology.

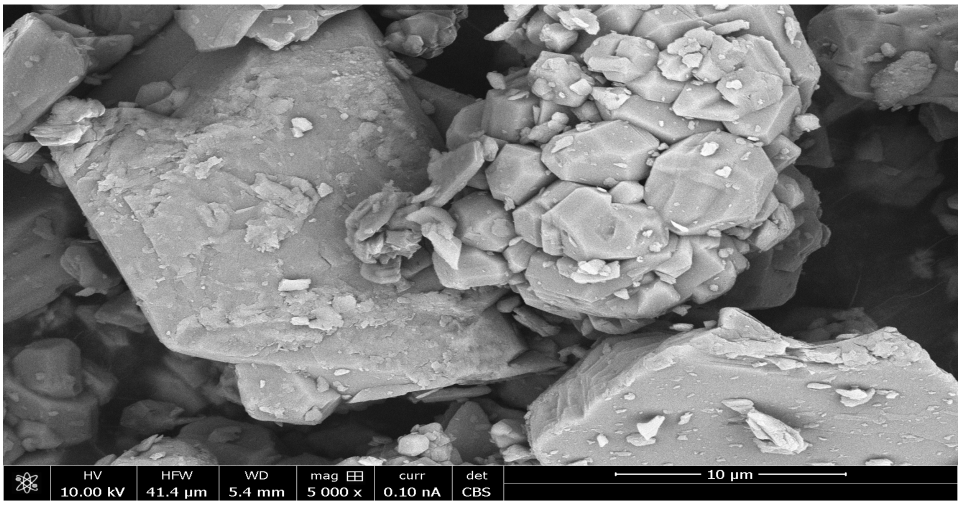

Figure 4 Close-up of aluminium hydroxide reagent morphology.

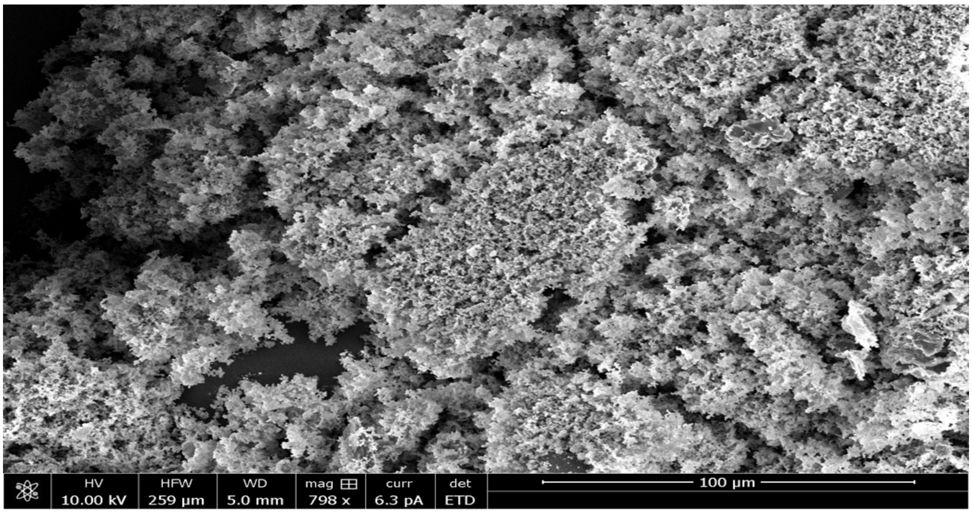

Figure 5 Overview of aluminium hydroxide nanocrystals.

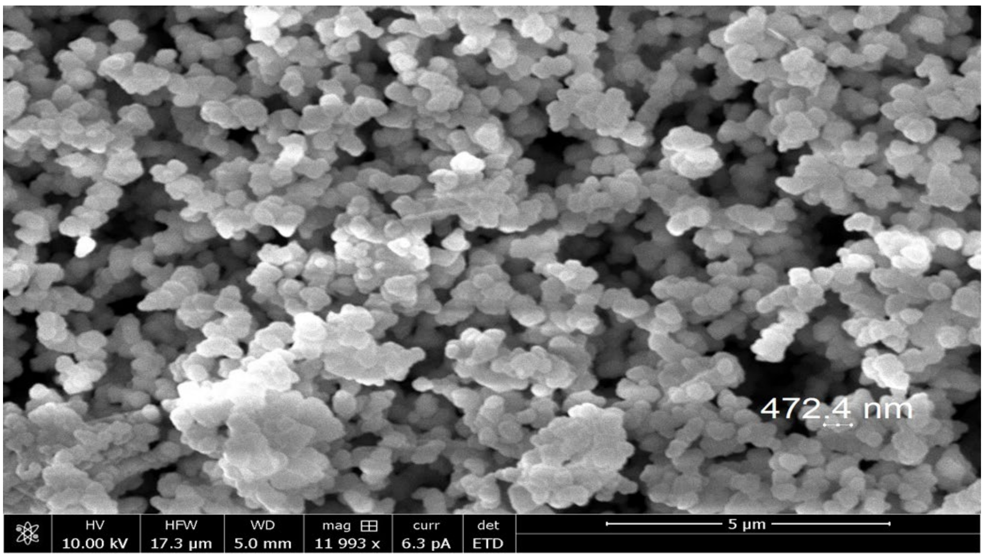

Figure 6 Close-up of aluminium hydroxide nanocrystals.

4. Conclusions and Future Work

This project found specific reaction conditions to precipitate aluminium hydroxide nanocrystals from a synthetic potassium aluminate solution. A reproducibility experiment conducted under identical conditions yielded consistent nanocrystal formation. This is the first time nano aluminium hydroxide crystals have been precipitated from a potassium aluminate solution based on the reviewed literature. Nanocrystals hold significant value in the adsorption and catalysis industry due to their high surface area.

Initial experiments found aluminium hydroxide exhibits low solubility in potassium hydroxide, where the addition of a significant impurity in the ore in the form of an acid improved dissolution by three times the amount. Pre-treating the alunite ore to remove impurities before leaching with potassium hydroxide could decrease the solubility of aluminium hydroxide in the ore, thereby compromising leaching efficacy. It is recommended to avoid pre-treatment of the ore before leaching. This will minimise associated costs and conserve valuable resources for other critical aspects of the novel process.

Future work may involve optimising the process for producing nanocrystals by exploring the limits of nanocrystal production from reagent addition. This should be done using a single large batch of potassium aluminate to enhance experimental accuracy. Also, examine the impact of acid addition on crystal morphology using SEM energy dispersive x-ray spectroscopy (EDS) or transmission electron microscopy (TEM) EDS analysis. This investigation will aim to determine the presence, if any, of the acid's primary element within the nanocrystals.

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