ELECTROCHEMICAL SEPARATION OF SULFURIC ACID FROM MAGNESIUM SULFATE SOLUTIONS: APPLICATION FOR NICKEL LATERITE PROCESSING

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ABSTRACT

Nickel is used in various applications, especially in energy storage. To extract nickel from certain ores, a lot of sulfuric acid is needed, mainly because of minerals like magnesium silicates which consume the acid during extraction. This process creates waste solutions containing magnesium sulfate, which is harmful to the environment. However, electrochemical separation can help. It converts these waste solutions into sulfuric acid, which can be reused for nickel extraction, and magnesium hydroxide, which can be used for carbon capture or in the nickel extraction process.

In our recent study, we used a single membrane electrolyser to carry out this conversion. We evaluated its performance by looking at factors like efficiency, energy intensity, current density, and sulfate recovery. We found that starting with low concentrations of magnesium sulfate and applying a specific voltage maintained high efficiency. However, using higher voltages or concentrations had drawbacks like water splitting and excessive precipitation of magnesium hydroxide, which can cause operational issues.

After testing, we found that sulfate recovery ranged from 43-49% after 4 hours, depending on the initial concentration of magnesium sulfate in the solution. The energy required for producing sulfuric acid ranged from 2.94 to 4.44 kWh per kilogram of sulfuric acid produced.

INTRODUCTION

As the demand for nickel rises, particularly for its use in lithium-ion batteries powering electric vehicles and renewable energy systems, there's a pressing need to optimize nickel production and recycling processes. Nickel extraction from ores, especially from laterites, involves the use of sulfuric acid. However, laterite ores, rich in magnesium, present significant challenges during extraction and generate considerable waste. Traditionally, nickel production heavily relied on sulfide ores due to their easier processing compared to laterites. But as sulfide ore reserves dwindle, attention has shifted to laterites, which accounted for half of global nickel production by 2009. Yet, extracting nickel from laterites poses challenges, primarily due to their magnesium-rich composition.

During the extraction process, sulfuric acid leaching is used, resulting in the formation of magnesium sulfate waste streams. These waste streams not only impact the economic feasibility of processing such ores but also pose environmental concerns when disposed of, often into the ocean or stored in evaporation ponds. One promising solution to address the acid consumption in laterite ores, especially due to their high magnesium content, is electrochemical separation. This process involves converting the waste magnesium sulfate into sulfuric acid (H₂SO₄) and magnesium hydroxide (Mg(OH)₂) through electrochemical reactions. By doing so, it reduces the need for fresh acid in the leaching process, thus improving efficiency and reducing costs. Moreover, electrochemical separation enables the utilization of the generated magnesium hydroxide for various purposes. For instance, it can be used to precipitate nickel from the solution or in carbon capture processes to produce magnesium carbonates. Additionally, this approach eliminates the need for tailing neutralization, offering both environmental and economic benefits. Hence, electrochemical separation holds immense potential in enhancing the sustainability and efficiency of nickel production. By mitigating acid consumption, reducing waste, and enabling the reuse of by-products, it represents a promising pathway towards a more environmentally friendly and economically viable nickel industry.

The process of separating magnesium sulfate involves splitting sulfate from a neutral solution to create magnesium hydroxide and sulfuric acid. This is typically done in a two-chamber system, where the magnesium sulfate is introduced into the cathodic compartment. This setup helps prevent magnesium scaling on a membrane and reduces internal resistance. During the process, water electrolysis occurs, leading to hydrogen evolution at the cathode and oxygen evolution at the anode. Protons are consumed at the cathode, and hydroxide ions are consumed at the anode, causing ion migration. Sulfate transport from the catholyte to the anolyte is facilitated by an anion exchange membrane (AEM), which prevents magnesium diffusion to the anolyte. As the pH increases in the catholyte and decreases in the anolyte, and sulfate depletes in the catholyte, the faradaic efficiency (FE) decreases due to water splitting (H+/OH- migration). However, there's an initial period where high FE (>80%) is achieved before water splitting becomes dominant. This period is crucial for steady-state operation as it maximizes process efficiency and economic viability. Maintaining high FE is important as it ensures that the current passing through the electrolyzer is primarily utilized for sulfate transport. The type of AEM used, along with operational parameters like cell potential and influent concentrations, significantly influences sulfate transport efficiency. While our study focuses on operational parameters to determine sulfate transport efficiency and energy requirements, the choice of membrane properties, particularly a sulfate-specific AEM, plays a crucial role in the process.





RESULTS & DISCUSSION

Effect of electrolyser potential

The study delved into exploring how the voltage applied to an electrolyser affects the transportation of sulfate ions. We conducted experiments using specific concentrations of electrolytes to understand how different voltages impact this process. Sulfate ion transport is influenced by several factors, including the potential gradient (migration), concentration gradient (diffusion), and pressure gradient (convection). Essentially, higher voltage leads to a greater rate of sulfate ion migration. However, there are drawbacks to consider. Higher voltages can reduce the efficiency of the process due to increased transport of non-target ions and greater internal resistance caused by conductivity limitations.

To understand these effects, we examined a range of voltages, from 3V to 5V. We observed that as the voltage increased, sulfate recovery and current density also increased. This suggests that higher voltage promotes more efficient sulfate transportation. However, we also found that FE, which measures how effectively the current is utilized for sulfate transport, decreased over time. This decrease in FE was attributed to membrane leakage, where non-target ions such as hydroxides from the catholyte and protons from the anolyte crossed the membrane. Interestingly, we noted that FE was highest at the beginning of the experiment but declined as the experiment progressed. This decline was more significant at higher voltages, especially beyond 40 minutes of operation. This is because at higher voltages, more water splitting occurs, contributing to the decline in FE.

The study also highlighted the importance of maintaining a low concentration of sulfuric acid in the anolyte to achieve high FE. We found that by keeping the anolyte concentration around 0.16M H2SO4, FE could exceed 80%. However, we noted that differences in temperature and pH between compartments could affect FE. Additionally, we found that energy intensity increased with higher voltage. This means that while higher voltages led to greater sulfate recovery, we also consumed more energy. For example, recovering 24% of sulfate over 1 hour at 5V consumed more energy compared to recovering only 5% at 3V. Finally, while higher voltage can enhance sulfate recovery, it also comes with increased energy consumption. Therefore, it's essential to strike a balance between efficiency and energy cost when optimizing sulfate transport processes.

Effect of initial catholyte concentration

The concentration of the catholyte, or the solution in the cathode compartment, significantly impacts the overall performance of the electrolyser. This concentration affects various aspects of the electrolysis process, including the concentration gradient, conductivity, ion pairing, solubility of reaction products, membrane fouling, and electrode scaling. To comprehensively understand these effects, the

researchers tested three different concentrations of magnesium sulfate (0.5M, 1M, and 1.5M) at two different potentials (4V and 5V).

One crucial finding was that increasing the concentration of the catholyte led to a greater flux of sulfate ions to the anolyte (the solution in the anode compartment). This was primarily due to the larger concentration gradient created by higher catholyte concentrations. Additionally, higher concentrations resulted in greater conductivity, leading to enhanced ion transport. This increase in conductivity was attributed to the availability of more charge carriers (sulfate ions), which reduced the solution's ohmic resistance. However, it was noted that increasing the concentration gradient does not always directly correlate with higher flux. For instance, while a concentration of 1M exhibited approximately 1.7 times higher flux than a concentration of 0.5M at a potential of 5V, the flux was lower for a concentration of 1.5M compared to 1M at all tested potentials. This suggests that there's an optimal concentration range for maximizing sulfate flux. Moreover, it was observed that electrode blockage, or scaling, occurred when the catholyte concentration exceeded 1M. This led to decreased current density, indicating less effective ion movement towards the anode. Significant deposition of magnesium hydroxide on the cathode was also observed at higher concentrations, particularly at 5V and 1.5M concentration. This deposition was attributed to the elevated concentration of magnesium ions (Mg2+) and the high pH of the cathodic compartment. Regarding faradaic efficiency, it was noted that increasing the catholyte concentration resulted in a higher rate of H+/OH- migration, which can decrease FE. This decrease in FE was observed across all tested concentrations when the voltage was increased to 5V. Conversely, energy intensity, which measures energy consumption, followed an opposite trend to FE. Higher FE resulted in lower energy consumption. For example, at 4V, the energy intensity was lower (2.3 kWh/kg) compared to 5V (3.4 kWh/kg). In short, while higher catholyte concentrations can enhance sulfate transport efficiency, they must be carefully controlled to avoid electrode scaling and maintain high FE and low energy consumption. These findings highlight the importance of optimizing catholyte concentration for efficient electrolyzer performance.

Effect of initial anolyte concentration

The concentration of sulfate ions in the anolyte, or the solution in the anode compartment, has both positive and negative effects on the electrolyzer system. This was tested by comparing anolyte solutions with different concentrations of sulfuric acid (H2SO4) - 0M, 0.1M, and 0.2M - at a voltage of 4V.

We found that a 0.1M concentration resulted in more sulfate recovery compared to 0.2M due to a higher concentration gradient. Although the 0.2M solution had slightly higher current density due to increased conductivity, most of this current was used for water splitting rather than transporting sulfate, resulting in lower faradaic efficiency (FE). Consequently, the 0.2M solution required about 45% more energy to transfer sulfate within the same time frame. To determine the minimum anolyte concentration and conductivity needed to maximize sulfate transport, we conducted experiments using 1M MgSO4 catholyte and ultra-pure water anolyte (0M) at 4V. We found that having high initial solution resistance in the anolyte led to lower initial FE. However, over time, conductivity in the anolyte increased, eventually decreasing internal resistance and maximizing sulfate transport.

The experiments showed that a minimum sulfate concentration of 0.05M and a corresponding conductivity of 30 mS/cm were needed to achieve maximum FE. Above 0.15M, FE declined due to sulfate accumulation in the anolyte. Both anolyte concentrations eventually achieved the same current density of approximately 25mA/cm2. After 4 hours, 49% sulfate recovery was achieved at 0M compared to 43% at 0.1M, with the difference primarily due to a larger concentration gradient. The average energy intensity for the 0.1M experiment was 2.94 kWh/kg, while it was 4.44 kWh/kg for the 0M experiment. In essence, maintaining an optimal sulfate concentration and conductivity in the anolyte is crucial for maximizing sulfate transport efficiency and minimizing energy consumption in the electrolyzer system.

Energy intensity analysis

Sulfuric acid holds a pivotal role across various industries worldwide, earning it the status of one of the most indispensable chemicals in industrial processes. However, its conventional production method involves energy-intensive procedures like the oxidation of elemental sulfur, typically sourced as a byproduct of oil and gas extraction. This method is associated with high temperatures, pressure, and sulfur emissions, contributing to its high energy intensity, which is approximately 1.67 kWh/kg H2SO4.

In recent times, there has been growing interest in exploring electrochemical alternatives for sulfuric acid production. These alternatives aim to produce diluted sulfuric acid with lower energy intensity. providing potential downstream benefits such as easier concentration. The thermodynamic limit for energy intensity in such electrochemical processes is around 0.82 kWh/kg H2SO4, significantly lower than conventional methods. However, current electrochemical methods have not yet matched the capacity and purity levels achieved by conventional technologies. The chlor-alkali process serves as a benchmark in the industry, setting standards for current density (often exceeding 100 mA/cm2) and energy intensity (ranging from 2 to 4.5 kWh/kg H2SO4 equivalent). In a comparative analysis, energy intensity associated with electrochemical sulfuric acid production was found to be within the bounds of the chlor-alkali process. Interestingly, higher current densities were linked with lower energy intensity, suggesting potential efficiency gains with improvements in electrochemical processes. To enhance current densities in electrochemical sulfuric acid production, several strategies are being explored. These include modifications to electrode designs, such as increasing surface area and implementing anti-fouling surface treatments. Adjusting the local reaction environment and reducing the gap between electrodes are also promising avenues for improving performance. Additionally, optimizing operating conditions, such as controlling catholyte temperature, can help mitigate issues like magnesium fouling on cathodes by enhancing the solubility of magnesium compounds. Maintaining high faradaic efficiency (FE) is crucial for efficient sulfuric acid production. FE can be optimized by carefully controlling the sulfuric acid concentration in the anolyte, ensuring that electrochemical processes remain efficient and cost-effective. These ongoing advancements in electrochemical sulfuric acid production hold promise for reducing energy consumption and environmental impact in the industrial production of this vital chemical.

Economic analysis

Electrolysis represents a promising avenue for industrial processes, offering energy-efficient operations with significantly lower carbon emissions compared to conventional methods. This advantage becomes even more pronounced when renewable energy sources like solar and wind are employed, which are becoming increasingly affordable, particularly in regions like Australia. As the costs of electricity generation from renewables continue to decline due to advancements in technology and increased market penetration, the overall economics of electrochemical processes, including acid recycling, are expected to improve. The key economic factors influencing electrochemical acid recycling are the capital cost of electrolyzers and electricity expenses. By comparing two electricity scenarios - one based on fossil fuels and the other on renewable sources - it becomes evident that utilizing renewable energy can significantly reduce the cost of acid production. For example, the average cost of generating acid using renewable energy was found to be A\$143 per tonne, while the cost using fossil fuels was substantially higher at A\$477 per tonne. Even when considering an average acid purchase cost of A\$200 per tonne, electrochemical acid generation proves to be a more economically attractive option. Batch experiments were conducted to determine critical operational parameters for industrial applications, such as sulfate flux, faradaic efficiency (FE), power consumption, and the onset of side effects like magnesium hydroxide precipitation. These experiments not only provided insights into the initial costs of acid production but also revealed that the cost decreases over time as the concentration of acid in the anolyte increases. Based on these findings, a basic economic assessment was conducted to evaluate the cost savings associated with producing nickel using sulfuric acid generated through electrolysis with renewable energy. The analysis showed a potential cost reduction of 22% compared to purchasing acid. Furthermore, utilizing magnesium hydroxide generated by the electrolyzer could further decrease costs associated with nickel precipitation. Additionally, carbon capture presents another avenue for cost minimization through potential reductions in carbon taxes.





Figure 2. a) sulfuric acid energy intensity as a function of time-average current density at 0.5, 1 and 1.5M MgSO4 and 0.1M H2SO4 compared to data obtained from Lammers et al.[19] using 1M MgSO4 b) sulfuric acid cost using different electricity prices (utilizing the energy intensity data from the first 20 minutes of batch experiments at 4V and 0.1M H2SO4) across a MgSO4 feed range of 0.5 to 1.5M and 0.1M H2SO4 initial anolyte concentration c) sulfuric acid cost using different electricity prices as a function of the recovered acid concentration in the anolyte at 0.5, 1 and 1.5M MgSO4 catholyte concentration and 0.1M H2SO4 initial anolyte concentration d) acid production cost (calculated using average renewable energy price in Australia, A\$0.06/kWh) and anolyte concentration as a function of time

CONCLUSIONS

Our study found a strong relationship between faradaic efficiency (FE) and the concentrations of sulfuric acid (H2SO4) in the anolyte and magnesium sulfate (MgSO4) in the catholyte. Lower anolyte concentrations tended to result in higher FE, especially at specific catholyte concentrations and potentials. For example, with a 1M catholyte and 4V potential, FE could exceed 90% until the anolyte concentration reached 0.16M, indicating a good starting point for continuous operation. Increasing the potential difference between the electrodes improved sulfate mass flux per membrane area within a limited range of feed concentrations. However, feed concentrations beyond 1M led to magnesium hydroxide deposition on the electrode, reducing its surface area.

We found that the minimum anolyte concentration required to achieve the highest sulfate FE was 0.05M at a 1M catholyte concentration. In our experiments, operating for 4 hours at 4V with an initial catholyte concentration of 1M resulted in recovering 49% and 43% of sulfate at starting anolyte concentrations of 0M and 0.1M, respectively. The corresponding energy consumption values were 4.44 kWh/kg H2SO4 for 0M and 2.94 kWh/kg H2SO4 for 0.1M. Our study highlights the importance of using renewable energies for the economic viability of acid recycling. However, we also identified that the current density obtained may not be sufficient for seamless integration with renewables, indicating the need for attention to electrolyzer design. Additionally, addressing electrode scaling is crucial to unlocking the full potential of the electrolyzer.

REFERENCES

The information reported in this paper is taken from the following manuscript:

M. H. Ibrahim, D. Batstone, J. Vaughan, and K. Steel, "Electrochemical separation of sulfuric acid from magnesium sulfate solutions: Application for nickel laterite processing," Sep. Purif. Technol., vol. 336, p. 126291, 2024, doi: https://doi.org/10.1016/j.seppur.2024.126291.