Potassium release behavior from silicate rocks using sulfuric and citric acids media

Comportamento de liberação de potássio de rochas de silicato usando meio de ácidos sulfúrico e cítrico

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ABSTRACT
Potassium plays a pivotal role as a critical nutrient and essential for increasing crop productivity. Recent scientific studies have been directed toward investigating silicate minerals as a promising alternative source for this element. This study presents results derived from a preliminary exploration into the release of potassium behavior, alongside other present ions, extracted from silicate rocks originating from the region of Rio de Janeiro, Brazil. The efficacy of sulfuric and citric acids as potential agents for facilitating this release was examined. Employing an incomplete factorial design, the study systematically evaluated the influential variables temperature, time, and concentration, aiming to delineate their impact on potassium release across various sample-acid systems. The discussion delves into elucidating the hierarchical order of these variables concerning potassium liberation within each sample-acid configuration. The consequential insights derived from this meticulous analysis hold considerable significance,
contributing substantially to the prospective assessment of harnessing these rocks as a viable potassium resource for future agricultural applications.

**Keywords:** potassium, feldspar, fertilizer, silicate rocks, leaching.

**RESUMO**
O potássio desempenha um papel fundamental como nutriente crítico e essencial para aumentar a produtividade das culturas. Estudos científicos recentes têm sido direcionados para a investigação de minerais silicatos como uma fonte alternativa promissora para este elemento. Este estudo apresenta resultados de uma exploração preliminar na liberação de comportamento de potássio, ao lado de outros íons presentes, extraídos de rochas de silicato originárias da região do Rio de Janeiro, Brasil. Examinou-se a eficácia dos ácidos sulfúrico e cítrico como potenciais agentes para facilitar essa liberação. Empregando um desenho fatorial incompleto, o estudo avaliou sistematicamente as variáveis influentes temperatura, tempo e concentração, visando delinear seu impacto na liberação de potássio em vários sistemas de amostra-ácido. A discussão aprofunda-se em elucidar a ordem hierárquica dessas variáveis relativas à liberação de potássio dentro de cada configuração ácido-amostra. Os insights consequentes derivados dessa análise meticulosa têm significância considerável, contribuindo substancialmente para a avaliação prospectiva do aproveitamento dessas rochas como recurso viável de potássio para futuras aplicações agrícolas.

**Palavras-chave:** potássio, feldspato, fertilizante, rochas de silicato, lixiviação.

**1 INTRODUCTION**
Recent studies focusing on food supply forecasts have highlighted a prevailing global inclination toward heightened production across the world (D. Manning, 2017; D. A. C. Manning, 2010). Brazil stands prominently in this landscape as one of the largest agricultural producers worldwide. Consequently, a projected surge in fertilizer demand is anticipated not only in Brazil but also in other agricultural hubs in the years to come (OECD, 2018). Moreover, recent conflicts among producer nations have compounded concerns about future fertilizer supply (OECD, 2022), further intensifying the challenges ahead.

Of all agricultural fertilizers, potassium holds a pivotal role in bolstering plant immune systems and overall agricultural yield. Predominantly available in the market as soluble salts, potassium’s production is notably centralized in Canada, Russia, and China (Jasinski, 2023). The bulk of this production is originated from sedimentary deposits.

In the majority of soils worldwide, potassium primarily exists within silicate minerals like feldspars or feldspathoids, primarily formed through igneous or metamorphic processes. When compared to soluble compounds, potassium within these minerals exhibits an inherently slow-
release rate (D. A. C. Manning, 2010). This slow release is largely attributed to the stable silicate matrix, firmly encapsulating a significant portion of the potassium content within its rigid structure. However, the escalating demand for potassium has spurred extensive investigations into silicate minerals as an alternative source for this essential nutrient, captivating the attention of researchers globally.

Exploration of methods such as grinding these minerals for direct use in crops (remineralizers) has been a focal point of study (Gaian_Consulting, 2023). Other scholarly pursuits delve into the hydrothermal conditioning process of potassium within the silicate matrix, aiming for a higher release rate into the soil (Ciceri et al., 2017, 2019).

On a parallel track, various extractive metallurgy techniques have been under scrutiny for extracting potassium from these minerals (Jena, 2021; Jena et al., 2014; Ma et al., 2017; Nascimento & E Almendra, 2003; Samantray et al., 2020, 2022; Tanvar & Dhawan, 2020; Türk et al., 2021) to generate soluble compounds akin to the majority of currently marketed potassium products.

Processes like leaching for potassium extraction from silicate minerals, as described in existing literature, are exhaustively deliberated, with extraction efficacy dependent of the silicate's nature, the reactive chemicals involved, and various other process parameters.

Inorganic acids, including sulfuric acid and hydrochloric acid, are commonly employed as lixiviant agents in hydrometallurgical processes. For instance, potassium feldspar samples underwent leaching with H$_2$SO$_4$-CaF$_2$ solution mixtures. Approximately 83% of the potassium was leached under specific conditions: 90°C, 40% H$_2$SO$_4$ concentration, a liquid/solid ratio of 4, and 2 g of CaF$_2$. The study reported that the presence of fluoride ions increases potassium release into the solution (Ma et al., 2017).

Leaching of silicates with organic acids has been a continually refined technique over the years, aiming to enhance the efficiency and feasibility of potassium extraction. Nonetheless, the extraction from silicate sources remains a persistent challenge. This method has emerged as an alternative route to acquiring potassium from unconventional mineral sources like agricultural residues and low-grade minerals (Basak et al., 2017).

Organic acids, such as acetic acid, citric acid (Lodi et al., 2022; Mcdonald et al., 2015; Ventura Machado et al., 2015), and oxalic acid (Duarte et al., 2022; Song & Huang, 1988), have been deployed for silicate leaching to releasing potassium. The efficiency of leaching is
contingent upon several factors, including the type of silicate, acid concentration, temperature, and reaction time.

Recent research indicates that silicate leaching with organic acids holds promise. Despite exhibiting relatively low recovery values, these studies exploring the role of organic acids in extracting potassium from silicate rocks are pivotal for initial assessments in shaping biohydrometallurgical pathways (Ashrafi Saeidloo & Rasouli Sadaghiani, 2017; Jena, 2021; Lian et al., 2008; Matias et al., 2019; Peng et al., 2017). Furthermore, leveraging organic acids in silicate leaching bears environmental benefits, given their reduced toxicity and corrosiveness compared to inorganic acids typically used in conventional processes.

Nonetheless, it's crucial to recognize that silicate leaching with organic acids remains an evolving field of study, with much yet to be explored. Challenges concerning purifying the liquid solution and eliminating impurities persist. Additionally, evaluating the economic feasibility of leaching techniques is imperative.

This research aimed to assess the release of potassium and other elements such as aluminum, silicon, and iron from various silicate rocks sourced from deposits in the state of Rio de Janeiro, Brazil. The findings are pivotal for appraising the future utilization of these rocks as potassium sources in agriculture and for furthering investigations into biohydrometallurgical processes aimed at soluble potassium production.

2 MATERIALS AND METHODS

The samples were identified as Tanguá, Itaguaí, and Magé according to their municipalities of origin in the state of Rio de Janeiro – RJ. Conducted X-ray diffraction tests identified the following main mineral phases (Bertolino & Licursi, 2023):

- Tanguá: Microcline, albite, biotite, hornblende, pyrite;
- Itaguaí: Quartz, biotite, orthoclase, albite, kaolinite, hornblende;
- Magé: Quartz, biotite, orthoclase, albite, kaolinite, hornblende.

Semi-quantitative analyses by X-Ray Fluorescence (XRF) were performed and Table 1 shows the contents of the main elements present. Granulometric classification results indicated that the samples had p80 between 0.49 and 0.56 mm (Figure 1).
Bench-scale chemical leaching (release) runs were conducted on silicate mineral samples containing potassium, using solutions of sulfuric acid and citric acid as lixiviant agents.

The effects of TIME (3 and 6 hours), TEMPERATURE (25 and 80°C), and CONCENTRATION (2 and 4 mol/L) of the lixiviant agent were evaluated. The variables of AGITATION and % SOLIDS were kept constant.

The experimental runs were performed using an incomplete factorial experimental design (23-1), resulting in 4 experiments and 4 replicates for each sample-lixiviant agent set, totaling 48 runs. Table 2 presents the experimental planning.

The runs were conducted in a reactor with a reaction vessel volume of up to 500 ml, fabricated with borosilicate glass. A glass condenser was attached to the reaction system to control lixiviant solution evaporation. The system was heated on a brand heating plate with temperature control. The reaction medium was stirred using a magnetic stirrer at a constant rate of 300 RPM.
Table 1. Results of XRF chemical analyses of the Magé, Itaguaí, and Tanguá samples (%/weight).

<table>
<thead>
<tr>
<th>Element (oxide base)</th>
<th>Magé</th>
<th>Santa Luzia</th>
<th>Tanguá</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>3.3</td>
<td>3.8</td>
<td>4.0</td>
</tr>
<tr>
<td>MgO</td>
<td>3.8</td>
<td>1.4</td>
<td>0.69</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.3</td>
<td>14.6</td>
<td>18.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>56.1</td>
<td>67.6</td>
<td>58.7</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.1</td>
<td>0.25</td>
<td>0.16</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.17</td>
<td>0.13</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.7</td>
<td>3.4</td>
<td>8.1</td>
</tr>
<tr>
<td>CaO</td>
<td>6.1</td>
<td>3.1</td>
<td>2.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.7</td>
<td>0.69</td>
<td>1.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.4</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td>MnO</td>
<td>0.13</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>SrO</td>
<td>0.18</td>
<td>&lt;0.1</td>
<td>0.18</td>
</tr>
<tr>
<td>BaO</td>
<td>0.18</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>PPC</td>
<td>0.79</td>
<td>0.39</td>
<td>1.2</td>
</tr>
<tr>
<td>Total</td>
<td>100.05</td>
<td>100.07</td>
<td>99.95</td>
</tr>
</tbody>
</table>

Source: Bertolino & Licursi (2023)

In each run, 30 g of each mineral sample and volumes of 150 ml of reagent solution were used. The mineral sample, water volume, and leaching reagent for each test were placed in the reactor under agitation and heated until reaching the reaction temperature. The reaction time was then initiated. Upon completion, the mixture was cooled to 50°C (in cases of assays at 80°C) and filtered through a Büchner funnel with quantitative filter paper. The mixture was then washed with 150 ml of distilled water, and the wash water was collected along with the leaching solution. The final solutions were stored in plastic bottles for subsequent chemical analysis. Quantitative chemical analyses were conducted for the elements K, Fe, Al, and Si, using the Atomic Absorption Spectrometry technique – AAS (Analytik Jena). The filter paper containing the final reaction residue was dried in an oven for 24 hours at a temperature of 80°C. After this period, it was cooled and weighed to measure the mass of the final residue.

Table 2. Experimental planning of experiments.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Concentration (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Source: original material from authors.
3 RESULTS

The averages of the release percentages were represented in bar charts in Figures 2 to 5. If all the release percentages are taken into account, the sulfuric leaching tests show a preference mainly for the release of iron and potassium in the samples. In these samples, potassium occurs in the form of biotite, orthoclase, and hornblende, while particularly in the Tanguá sample, the element occurs in the phases of biotite, microcline, and hornblende. For aluminum, the observed release order was Magé > Tanguá > Itaguaí. And for silicon, Tanguá > Itaguaí > Magé. Previous work results report that the biotite phase shows greater propensity for the release of potassium through acid leaching than mineral phases such as microcline or orthoclase (Snäll & Liljefors, 2000). These phases are present in the tested samples.

Statistical analysis was conducted for the potassium release results. These outcomes were presented through Pareto diagrams, illustrating the order of influence on potassium release (estimated effects) from the group of tested process variables.

Figure 2. Percentages of K release (% Extr.) for the experimental runs carried out (Legend: Sulf – sulfuric acid; Cit – citric acid).
Figures 6 and 7 display Pareto diagrams illustrating the effects of variables on potassium release from the Tanguá sample, respectively from sulfuric leaching and citric leaching. In terms of potassium release results, few differences were observed for the Tanguá sample. These values, in percentage terms, varied between 1.42% and 10.19% for sulfuric leaching runs and 1.10% and 1.68% for citric leaching runs. Always within the levels of studied variables and regarding the investigation of influential variables, the Pareto diagrams show differences. In sulfuric leaching (Figure 6), temperature is the most influential variable, with an effect almost twice as significant as the second variable in order of importance, which was the time. Its effect is positive, which could suggest that potassium release by sulfuric acid could be favored by an increase in
temperature; however, none of the presented effects were significant at a confidence level of 90%.

Figure 5. Percentages of Fe release (% Extr.) for the experimental runs carried out (Legend: Sulf – sulfuric acid; Cit – citric acid).

Source: original material from authors.

Analyzing the results obtained from the application of citric acid solution as a lixiviant agent, which, in terms of dissociation, is considered a weaker acid than sulfuric acid, temperature was identified as the most influential variable (Figure 7). Furthermore, it was the variable that fell within the 90% significance interval. Its influence is positive, indicating that a potential increase in temperature would favor the release of potassium from the Tanguá sample.
The potassium extraction results in the Itaguaí sample varied between 8.32% and 28.01% for runs conducted with sulfuric acid and between 0.89% and 9.52% for runs with citric acid. Figures 8 and 9 show Pareto diagrams illustrating the effects of variables on potassium release from the Itaguaí sample, respectively from sulfuric leaching and citric leaching.

For sulfuric leaching in the Itaguaí sample (Figure 8), the increase in potassium release to the solution was more favored by raising the reaction temperature. The other effects of the analyzed variables were positioned outside the 90% significance interval.

Observing Figure 9, which depicts the Pareto diagram outlining the variable effects in the leaching trials of the Itaguaí sample with citric acid, it's notable that each variable exhibited considerable significance, showcasing their effects distinctly surpassing the 90% significance level. Particularly striking is the pronounced impact of temperature, markedly outweighing the effects of other variables under analysis. Additionally, all variables demonstrated a positive effect, signaling that any elevation in the tested variables values would likely yield a more pronounced release of potassium into the solution, accentuating the potential for enhanced leaching efficacy and potassium yield.
Figures 8 and 9, represented as Pareto diagrams, provide a comprehensive analysis of the variables effects in both sulfuric and citric leaching procedures conducted on the Magé sample. In the domain of sulfuric leaching, the potassium release spectrum for this specific sample exhibited a range from 8.09% to 32.5%, whereas in the citric leaching realm, this range appeared narrower, oscillating between 0.97% and 10.26%. Figure 10 elucidates that within the purview of sulfuric leaching, temperature emerges as the foremost influential factor,
unequivocally displaying a positive impact on the outcomes. This substantiates the direct correlation between increased reaction temperature and heightened potassium liberation into the leachate. Moreover, the concentration parameter exhibited a similarly pronounced positive influence on the process. Notably, the substantial effects of these two variables retained their significance, maintaining a commendable confidence level of 90%.

![Figure 10. Estimated effects of K releasing by sulfuric acid: Magé sample.](image)

Source: original material from authors.

Delving into the dynamics of citric leaching, particularly for the Magé sample (Figure 11), it becomes evident that the effects of each variable were statistically significant, underlining their substantial roles at a 90% confidence threshold. The escalation in temperature remained the primary driving force behind the amplified potassium release, asserting its pivotal influence. Subsequently, the temporal factor emerged as the second most influential variable, demonstrating a discernible impact on the leaching process, closely trailed by the concentration factor. Remarkably, all variables displayed a positive effect, collectively contributing to the intricate mechanisms governing the leaching process.
4 CONCLUSIONS

Sulfuric and citric acids were used as leaching agents to evaluate the release of potassium from silicate rocks originating from the municipalities of Tanguá, Itaguaí, and Magé in the state of Rio de Janeiro. Technological characterization analyses revealed that potassium contents in the samples primarily occurred in mineral phases such as biotite, microcline, orthoclase, and hornblende.

Leaching tests were conducted to assess potassium release through an incomplete factorial experiment design, investigating reaction temperature, time, and concentration of leaching acids. It was observed that for the tested samples, sulfuric acid was the most effective leaching agent for potassium release. The preference order for potassium release was Magé > Tanguá > Itaguaí with sulfuric acid solutions, while with citric acid solutions, the potassium release order was Magé > Itaguaí > Tanguá.

Statistical analysis of the variables revealed an order of influence on each sample-leaching agent system. This order is summarized as follows:

- Tanguá – sulfuric acid: Temperature > Time > Concentration;
- Tanguá – citric acid: Temperature > Concentration > Time;
- Itaguaí – sulfuric acid: Temperature > Concentration > Time;
- Itaguaí – citric acid: Temperature > Concentration > Time;
- Magé – Sulfuric acid: Temperature > Concentration > Time;

Source: original material from authors.
Magé – Citric acid: Temperature > Time > Concentration.

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REFERENCES


