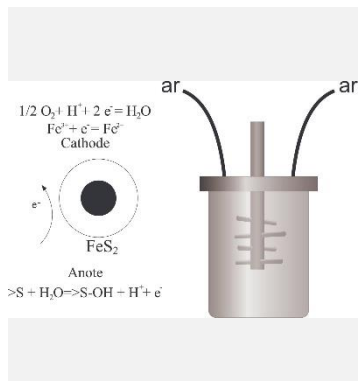


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Coal mining generates substantial waste materials, including the pyrite, leading to severe environmental issues, such as acid mine drainage. This study aimed to enhance the oxidation of pyrite in coal mining waste through mechanochemical activation, focusing on increasing the formation of heptahydrated ferrous sulfate. The oxidation process was conducted in a NETZSCH PE075 attritor mill, with periodic sampling. The characterization of the pyritic concentrate revealed the presence of key phases like pyrite, quartz, monohydrated ferrous sulfate (szomolnokite), and calcite. X-ray diffraction, X-ray fluorescence, and Mössbauer spectroscopy were employed for analysis, resulting in a pyrite content of 51%. The mechanochemical activation significantly reduced the particle size, enhancing the oxidation reactions. A notable 91% yield in sulfates was achieved, demonstrating the efficacy of this process conducted at room temperature. The results highlight the potential for valorizing pyritic coal mining waste, especially in terms of sulfates.

Introduction

Coal is the second most widely used source of energy worldwide, following oil, and plays a significant role in the economy of the southern region of Santa Catarina. However, coal extraction often results in the generation of waste materials, primarily composed of iron sulfides such as pyrite (FeS₂). Inadequate disposal of these waste materials leads to severe environmental problems, notably acid mine drainage (AMD). AMD is a consequence of pyrite oxidation, which, upon contact with air and water, produces sulfuric acid, thus acidifying both the soil and water resources, ultimately leading to the dissolution of heavy metals. The rate of pyrite oxidation is influenced by various factors, including surface area, pH, and the concentration of oxidizing agents [1,2]. The reactions involved in this process are intricate and multifaceted, and the underlying mechanisms remain not entirely comprehended. One of the fundamental reactions in this context is the conversion of pyrite to heptahydrated ferrous sulfate, as represented by Equation 1:



In addition to oxygen-driven oxidation, it is well-established that the ferric ion (Fe³⁺) also serves as a direct oxidizing agent in aerobic systems [3,4]. However, it is important to note that molecular oxygen also plays a significant role in these processes, as research indicates that the combination of Fe³⁺ and O₂ accelerates pyrite oxidation more effectively than when these components are added separately to the medium [5].

Based on these considerations, the present study aimed to investigate the acceleration of the pyrite oxidation process present in coal mining rejects by applying mechanochemical activation during comminution. This was done to enhance the formation of heptahydrated ferrous sulfate.

Material and Methods

The pyritic concentrate was supplied by a company specializing in coal ore beneficiation in the southern region of Santa Catarina. The samples underwent sieving, and the fraction that passed through a mesh with a 149 μm opening was characterized through X-ray diffraction (XRD) and fluorescence (XRF), Mössbauer spectroscopy, and laser diffraction particle size analysis. The monitoring of sulfate formation was conducted using the SMEWW 4500-SO₄ method.

The oxidation process of the pyritic concentrate was carried out in a NETZSCH PE075 attritor mill with a 500 cm³ working volume. Stainless steel balls with a diameter of 3 mm were used in a ball-to-powder ratio of 20:1, and the mill operated at a rotation speed of 700 rpm with continuous air supply during the shearing process. The mill feed consisted of pyritic concentrate and ferric sulfate, with pH controlled (maintained below 3.5) using 18 M sulfuric acid. Samples were collected at hourly intervals.

Results and Discussion

XRD analysis enabled the qualitative identification of four primary phases in the pyritic concentrate sample, namely pyrite (FeS₂), quartz (SiO₂), monohydrated ferrous sulfate - szomolnokite (FeSO₄·H₂O), and calcite (CaCO₃). These findings were corroborated by XRF analysis, which confirmed the predominant presence of sulfur and iron while also identifying the occurrence of silicon and calcium. Additionally, this information was combined with Mössbauer spectroscopy, showed in Figure 1, for quantifying the pyrite content in the sample, revealing a mass percentage of 51%. Table 1 presents the hyperfine parameters from the Mössbauer spectrum, which identified the FeS₂ and FeSO₄·nH₂O phases with hydration degrees ranging from 0 to 7.

The average particle size of the pyritic concentrate sample before the milling process was 24.38 μm. Figure 2 illustrates the reduction in particle size over an 8-hour processing period. It was observed that a rapid decrease in

particle size occurred during the initial stages of milling and the average diameter reached equilibrium at 0.84 μm .

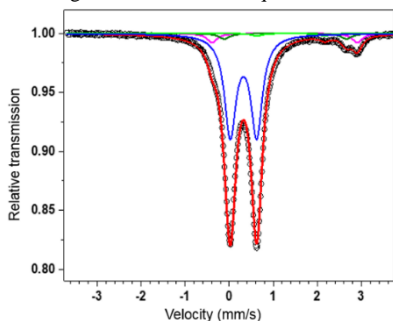
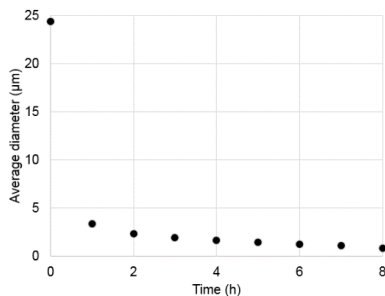


Figure 1. Mössbauer spectrum of the pyritic concentrate (27 °C)

Table 1. Hyperfine parameters from the Mössbauer analysis.

Subspectrum	Γ^*	δ^*	QS *	Area (%)	Phase
Doublet 1 (blue)	0,32	0,32	0,60	88,0	FeS_2
Doublet 2 (pink)	0,27	1,26	3,29	6,0	$\text{FeSO}_{4,n}\text{H}_2\text{O}$ (n=4 or 7)
Doublet 3 (green)	0,30	1,27	2,77	4,0	$\text{FeSO}_{4,n}\text{H}_2\text{O}$ (n=0 or 1)
Doublet 4 (pale green)	0,27	1,40	1,54	2,0	Fe^{2+}



Conclusions

Mechanochemical activation appears to favor weakening the bonds in pyrite and increasing the contact surface, as it also removes the product formed, which is adsorbed on the surface, through shear forces. A high yield in terms of sulfates in a process conducted at room temperature demonstrates that this is a promising alternative for the valorization of pyritic coal mining reject.

References

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Figure 2: Average particle diameter as a function of time.

Figure 3 illustrates the increase in sulfate concentration, which aligns with the reduction in particle size over 8 hours. A plausible explanation is that mechanochemical activation enhances the degree of amorphization and weakens the bonds on the surface of pyrite, facilitating oxidation reactions and increasing the surface area through particle size reduction.

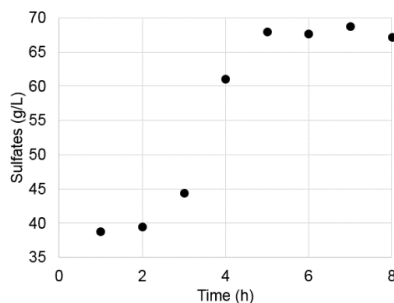


Figure 3. Sulfate concentration over time.

The reaction yield in terms of heptahydrated ferrous sulfate was 91%. This parameter was determined through the mass balance, considering the mass of pyritic concentrate added and the concentrations of iron (XRF) and sulfates (Mössbauer spectroscopy). This estimation accounted for the mono- and heptahydrated sulfates already present in the initial sample and the amount of sulfate generated from the addition of ferric sulfate. This high yield is noteworthy, as there are multiple possible reactions of iron sources not fully identified in the characterization analyses. But the mechanochemical activation appears to favor the formation of ferrous sulfate, which is the desired product.