Study of Red Mud Desulfurization and External Field Action

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Abstract

To further enhance red mud desulfurization, this paper analyzes red mud desulfurization under the action of ball mills and ultrasonic external fields and studies the red mud desulfurization mechanism. In this study, experiments were conducted using a bottom-blow stirred reactor device. The results show that the suitable red mud slurry concentration is 10 g/L. The raw red mud desulfurization can reach 100% absorption in the first 25 min, and the absorption capacity decreases gradually with the reaction time. The red mud desulfurization is mainly due to the dissolution of free alkali and metal oxides in the red mud. Under the action of the external field of the ball mill, the red mud particles can be refined to prolong the desulfurization time. Under the action of the external field of ultrasonic waves, the red mud slurry is dispersed more uniformly, which can accelerate the reaction rate. Under the effect of an ultrasonic external field, the red mud slurry is dispersed more uniformly, which can accelerate the reaction rate and dissolve more metal substances in the liquid phase.

1 Introduction

Red mud is an alkaline solid waste produced in the process of producing alumina from bauxite. The amount of red mud produced by alumina is determined by the taste of bauxite and the efficiency of alumina production (Xue et al. 2016). For every 1 ton of alumina produced, 1-2 tons of red mud is generated (Zhang et al. 2021; Pei et al. 2021). The production of red mud is growing at approximately 120 million tons per year (Power et al. 2011). Currently, most of the red mud is disposed of by stockpiling. Long-term storage of highly alkaline red mud will not only waste land resources but also cause environmental pollution (Zhu et al. 2015; Xue et al. 2019).

According to the characteristics of red mud, it is of great significance to reasonably treat and reuse red mud resources. Red mud has high surface reactivity, a large specific surface area, and a porous structure, which can adsorb or acidify red mud to adsorb harmful metals, phosphates, and other inorganic salts and organic matter in aqueous solutions (Guo et al. 2018; Nadaroglu et al. 2010; Smičiklas et al. 2014). Red mud contains a large amount of Al, Fe, Ti, Na, and other metal elements, and valuable metal elements in red mud can be recovered (Liu et al. 2012; Maria et al. 2002). The residual iron oxide, quartz, and sodium silica-aluminate in red mud can be used as additives to condition and improve the soil. It fixes metals and reduces soil pH through adsorption physical and chemical mechanisms (Lockwood et al. 2014; Hua et al. 2016; Feigl et al. 2012; Gray et al. 2006). Red mud is used to construct ceramics (Sglayo et al. 2000), ceramic glazes (Yalcin et al. 2000), bricks, roof tiles (Akinci et al. 2008; Piskin et al. 2013), cement (Tsakiridis et al. 2004), geopolymers (Li et al. 2019), and other building materials. The characteristics of red mud, such as strong alkalinity, fine particles, and large specific surface area, allow for mineralized sequestration of CO₂ (Yadav et al. 2010). It can also be used to absorb and treat acidic waste gases such as nitrides (Xiao et al. 2019; Apeksha et al. 2018), H₂S (Ramesh et al. 2011), SO₂, fluoride, etc. (Nath et al. 2018).

SO₂, as an irritant gas, is harmful to the human body and the environment. Flue gas desulfurization technologies are dry desulfurization, semidry desulfurization, and wet desulfurization (Li 2022). Red mud desulfurization technology can be used for dry adsorption desulfurization by using the characteristics of red mud, such as a large specific surface area and porous structure. At present, research on the dry desulfurization of red mud is shown as follows. Jin Yan (2021) used red mud instead of CaO for desulfurization in a circulating fluidized bed with the highest desulfurization rate of more than 94%. Hongtao Liu (2011) used red mud-modified limestone for desulfurization by adsorption in a tube furnace. Jian Niu (2021) used red mud as an additive to activated carbon to improve the desulfurization capacity of activated carbon, and the maximum sulfur capacity was increased by 17.9% compared with activated carbon alone. Red mud is highly alkaline, and the slurry made from red mud for desulfurization is a wet desulfurization process. In red mud slurry desulfurization, Xinke Wang (2014) studied the effect of red mud slurry desulfurization and decarbonization on red mud dealkalization. The main components of red mud residue after desulfurization and decarbonization are SiO₂, Fe₂O₃, and AlOOH. Wei Peng (2012) obtained the optimal operating conditions for desulfurization of an absorption tower with red mud slurry in an absorption tower. The desulfurization rate was above 95%, and the red mud slurry lost its desulfurization capacity after 10 h. Jinji Yang (2012) performed red mud slurry desulfurization in a desulfurization absorption tower and obtained the optimum operating conditions with a maximum desulfurization rate of 98.8%. Bin Li (2020) used ozone preoxidation of red mud slurry desulfurization and denitrification in a spray absorption tower, and the desulfurization rate was stabilized at 98% within 1 h. The reaction mechanism of desulfurization and denitrification was investigated. Lei Tao (2019) used red mud slurry desulfurization in a bubbling reactor and found that the liquid/solid ratio had the most significant effect on the desulfurization process. Yu Liu (2022) used a yellow phosphorus emulsion coupled with red mud for desulfurization and denitrification to optimize the reaction conditions. Under the optimized conditions, the optimal desulfurization and denitrification rates were as high as 97.9% and 100%, respectively. Yuwei Zhang (2021) established an industrial demonstration of red mud limestone with a desulfurization rate of 98.9%, which can meet ultralow emissions requirements.

In this paper, red mud slurry wet desulfurization is used to study the desulfurization mechanism in a bottom-blow stirred reactor. The existing studies on red mud desulfurization are all about the process of desulfurization, and there is no research on red mud desulfurization under the action of external field intensification. Therefore, to better enhance the promotion of red mud slurry desulfurization, the external field of mechanical energy of the ball mill and the external field of the ultrasonic mechanical wave were used in this paper. The effect of the external field on the desulfurization of red mud slurry was studied.

2 Experimental Section

2.1 Experimental procedures

In this study, the red mud slurry desulfurization reaction was carried out in a bottom-blow stirred reactor. The experimental setup is shown in Fig. 1. It mainly includes a gas supply device, absorption device, and

analysis device. The specific experimental process is as follows: SO₂ gas is supplied by a compressed stainless steel bottle, controlled by a gas flow meter, and the SO₂ inlet flow rate is 400 ml/min. SO₂ is refined by aeration stones, and bubbles escape at the bottom of the reactor to react with the red mud slurry. The stirring paddle in the reactor continuously disperses the red mud and renews the absorption reaction interface. The speed of the stirring paddle was controlled at 350 r/min. The pH change of the slurry was measured by a Thunder Magnetic pH Meter (PHSJ-3F, Shanghai Jingke Company) during the absorption reaction. The SO₂ gas after the reaction was measured by a SO₂ detector (Leibo 3040, Jiangsu Leibo Scientific Instruments Co., Ltd.) for concentration. The unreacted SO₂ tail gas is passed into the NaOH solution. The desulfurized red mud residue was filtered and dried for characterization and determination.

The absorption reactor was a 1 L four-neck flask with a red mud slurry volume of 700 mL. The red mud is mechanically refined by a planetary high-energy ball mill (Fritz Instrument Equipment Co., Ltd., Germany) to refine the particles. The ball milling speed was 300 r/min, and the ball milling time was 1 h. The ultrasonic mechanical wave for the reaction process was provided by a 40 kHz ultrasonic cleaner (CJ-060B, Shenzhen Super Clean Technology Industrial Co., Ltd.).

There are also some testing devices as follows: X-ray fluorescence spectrometer (XRF, ZSXPrimus, Rigaku Corporation, Japan), Specific surface area physical adsorption instrument (ASAP2020, Micromeritics Instrument Company, America), X-ray diffractometer (XRD, Bruker, Germany), Field emission scanning electron microscope (SEM, ZEISS Sigma 300, UK), Fourier transform infrared spectrometer (Nicolet IS 50, Thermo Fisher, America).

2.2 Experimental materials

The concentration of SO₂ gas used in the experiment was 5%, balanced with N₂ (Shenyang Shuntai Special Gas Co., Ltd.). The red mud used in the experiment came from an aluminum factory in Shanxi. The ingredients of the raw materials are listed in Table 1, and the main components are shown in Fig. 7. To better promote the absorption of SO₂ in red mud, the red mud particles were broken by mechanical ball milling. The absorption reaction rate can be improved by refining the particles and increasing the specific surface area of the particles from a macroscopic point of view. The adsorption-desorption isotherms before and after ball milling are shown in Fig. 2. The curves of the red mud samples before and after ball milling showed a typical type IV adsorption-desorption isothermal curve. According to the adsorption-desorption isotherm, the specific surface area of the raw red mud is 98.3489 m²/g, and the specific surface area after ball milling is 32.4629 m²/g by the Brunauer–Emmett–Teller (BET) gas adsorption method (1990).

Table 1
Compositions of raw red mud

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Na_2O	CaO	SO_3
Raw red mud	17.78	11.88	39.82	6.93	5.94	2.38	0.48

From Fig. 3, it can be seen that the original red mud is formed by cohesions, agglomerates, and agglomerates to form a loose structure. There are spherical particles of Na_2O and other substances attached to the surface. In addition, some particles have agglomeration behavior. After ball milling, the red mud agglomerates with sphere-like particles. After ball milling, the particles are tighter, more uniform, and have smaller pores. The collision of steel balls in the ball mill, which transmits more mechanical energy to the particles, can crush and refine the particles.

3 Results And Discussion

3.1 The effect of red mud slurry concentration on desulfurization

The influence of slurry concentration on the desulfurization process was characterized by the change in slurry pH value. As shown in Fig. 4, in the red mud slurry desulfurization process, the pH value changes over time into three stages: a rapid decline stage, a slow decline stage, and a basically unchanged stage. When the concentration of red mud slurry increases from 7 g/L to 10 g/L, the time of pH drop is prolonged. This means that an increase in concentration can prolong the absorption reaction time and absorb and process more SO_2 . When the slurry concentration of red mud increases from 10 g/L to 15 g/L, the increase in slurry concentration does not prolong the absorption reaction time in the first 10 min. With the increase in slurry concentration, the free alkali in red mud and other substances that react with SO_2 cannot be dissolved in a short time. With increasing time, 15 g/L red mud can have a longer absorption reaction time. However, as its absorption reaction time is not much different from that of 10 g/L red mud, the red mud slurry concentration is selected as 10 g/L in the following experiments after comprehensive consideration.

3.2 The effect on desulfurization under the strengthening of the external field

3.2.1 Changes in slurry pH and desulfurization efficiency during red mud desulfurization

As shown in Fig. 5, the change trend of the red mud after ball milling is the same as that of the raw red mud. The raw red mud can completely absorb low-concentration SO_2 in the first 25 min, and the desulfurization rate is maintained at 100%. After 25 min, the absorption of SO_2 in red mud gradually

reaches saturation, and the concentration of SO₂ in tail gas increases continuously. After ball milling, red mud desulfurization uses mechanical energy to refine the red mud particles, promote the decomposition of the red mud particles, and prolong the desulfurization time. It can completely absorb low concentrations of SO₂ in the first 33 min, and the desulfurization rate is maintained at 100%. After 33 min, the absorption capacity of SO₂ decreases gradually, and the concentration of SO₂ in the tail gas increases continuously.

As a kind of high-frequency mechanical wave, ultrasonication provides a cavitation effect, thermal effect and mechanical effect, which can accelerate desulfurization efficiency. Under the effect of an ultrasonic field, the desulfurization rate of raw red mud reached 100% in the first 23 min, and the desulfurization ability gradually decreased after 23 min. Under the action of an ultrasonic field, the desulfurization rate of ball milled red mud was 100% in the first 29 min, and the desulfurization capacity decreased gradually after 29 min. The SO₂ in the exhaust gas was detected earlier in the presence of an ultrasonic field, considering that cavitation of the ultrasonic frequency can accelerate the gas–liquid-solid three-phase reaction rate. At the same reaction time, the pH of the slurry in the presence of ultrasound is significantly higher than that in the absence of ultrasound, which indicates that ultrasonic frequency accelerates the reaction rate and the escape of SO₂ gas from the slurry. The existence of ball mills and ultrasonic fields can refine the red mud particles better and can make full use of the field to achieve a better desulfurization effect.

3.2.2 Changes in red mud composition during red mud desulfurization

XRF was used to detect the composition changes of red mud in the desulfurization process under various conditions, and the detection results are shown in Table 2.

Table 2 XRF results of the compositions of red mud in the desulfurization process (%) (raw red mud desulfurization (RR), ball mill red mud desulfurization (BR), raw red mud desulfurization under an ultrasonic external field (RU), ball mill red mud desulfurization under ultrasonic external field (BU))

	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	Na ₂ O	CaO	SO ₃
RR t=20 min	19.24	12.23	42.13	7.39	5.02	0.69	0.82
RR t=40 min	18.89	6.41	47.94	8.58	1.07	0.11	2.32
RR t=60 min	16.63	4.91	52.73	9.53	0.8	0.07	1.55
RR t=80 min	14.44	3.75	55.25	10.31	0.45	-	1.01
BR t=20 min	19.33	12.72	42.08	7.63	4.02	0.36	0.9
BR t=40 min	18.03	4.6	49.98	9.25	0.42	-	2.24
BR t=60 min	14.95	3.66	54.77	10.45	0.4	-	1.49
BR t=80 min	13.56	3.31	56.42	10.94	0.39	-	0.97
RU t=20 min	19.76	12.29	41.5	7.34	4.29	0.57	0.86
RU t=40 min	21.12	7.26	43.89	7.66	1.16	-	3.2
RU t=60 min	16.95	4.41	52.25	9.43	0.41	-	1.54
BU t=20 min	19.56	12.71	40.94	7.32	4.27	0.75	0.91
BU t=40 min	20.76	8.11	43.6	7.78	1.19	-	2.58
BU t=60 min	17.42	5.19	47.27	8.71	0.41	-	3.14

From the XRF results of the red mud in the desulfurization process in Table 1 and Table 2, it is clear that Al and Na are more easily dissolved in the initial stage of the reaction. As the desulfurization reaction

proceeds, the slurry becomes more acidic, and the aluminum and silicon in the red mud begin to dissolve in large amounts (Nie et al. 2019). The iron minerals are relatively stable, and the Fe_2O_3 content is almost unaffected by the desulfurization reaction. With the continuous dissolution of Na, Al and Si, the mass of red mud decreases, which is also the reason for the increase in Fe_2O_3 content. CaO and TiO_2 were partially dissolved with the reaction. The dissolution rate of Fe, Ti and Ca metal substances increased with the intensification of ultrasonication (Agrawal et al. 2021). The Na_2O content in the red mud of the desulfurization process in Table 2 is represented in Fig. 6. Fig. 6 clearly shows the decreasing content of Na_2O in the red mud as desulfurization proceeds. For the red mud after 60 min of desulfurization under the above conditions, the content of Na_2O is <1%, which can meet the composition requirements of cement, brick, geopolymer and other construction materials (Wang et al. 2018). The S content in the desulfurized red mud did not increase significantly, indicating that the red mud is mainly dissolved in the liquid phase under the condition of oxidation without the addition of oxygen.

3.2.3 Changes in the morphology of desulfurized red mud

Figure 7 shows the SEM image of the red mud with desulfurization time $t = 60$ min. Compared with the undesulfurized SEM image in Fig. 3, the microscopic morphology of the red mud changed significantly after desulfurization. In red mud desulfurization, the solid phase material in the red mud is involved in the reaction, while it is continuously consumed. After desulfurization, the red mud is broken down into many small spherical particles, and the microstructure of the red mud becomes loose as a result. The microstructure of red mud is more fluffy after desulfurization by ball milling. The ultrasonically dispersed particles are more uniform, and the desulfurized red mud has more small spherical particles and smaller pores. In short, the ball mill machinery outfield is able to extend the desulfurization time by refining the red mud particles. The ultrasonic external field disperses the red mud particles, which can improve the reaction rate and promote the dissolution of metals such as Ti and Fe. However, it also accelerates the escape of SO_2 gas, resulting in no longer absorbing SO_2 at slurry $\text{pH} = 4$. Combining the ball mill and ultrasonic external field can both accelerate the reaction rate and extend the reaction time compared to generating the external field alone.

3.3 Mechanism of red mud desulfurization

As shown in Fig. 8, the diffraction peaks of sodium aluminosilicate hydrate and calcium aluminosilicate hydrate mainly change during the desulfurization of red mud. In the initial stage of the reaction, hydrated sodium aluminosilicate first decomposes and dissolves aluminum and sodium. As the desulfurization reaction proceeds, the XRD diffraction peaks of both sodium aluminosilicate hydrate and calcium aluminosilicate hydrate gradually weaken. When desulfurization was carried out for 40 minutes, the pH was approximately 4, and the phases of sodium aluminosilicate and calcium aluminosilicate hydrate were not observed in the desulfurization red mud. The raw red mud will have decomposed Al^{3+} combined with OH^- in the form of $\text{Al}(\text{OH})_3$ in the desulfurized red mud. Some of the Si is present as a stable structure of amorphous SiO_2 , which is also detected in the desulfurized red mud. After 20 min of reaction, CaCO_3 in the red mud decomposed, and the final desulfurized red mud did not contain Ca^{2+} , which was

consistent with the XRF results in Table 2. Part of the hematite (Fe_2O_3) in the red mud is reduced to Fe^{2+} by reaction with sulfur dioxide. Fe^{2+} is unstable and easily oxidized. Eventually, a part of Fe is present in the desulfurized red mud in the form of titanium iron oxide.

Figure 9 shows the infrared spectra of the raw red mud desulfurization process. As shown in Fig. 9, the main mid-infrared band that appears at $900\text{--}1000\text{ cm}^{-1}$ is the stretching vibration of the Si-O-Si bond (Lipinska-Kalita et al. 1990). The main mid-infrared band that appears at approximately 802 cm^{-1} is the bending vibration of the Si-O bond (He et al. 2001). The reason is that as the desulfurization reaction proceeds, a large amount of Si in sodium aluminosilicate hydrate ($1.08\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.68\text{SiO}_2\cdot 1.8\text{H}_2\text{O}$) and hydrated garnet ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$) dissolves in the aqueous solution, resulting in a weaker absorption band for the Si-O bond. The infrared band near 1410 cm^{-1} is the stretching vibration of the C-O-C bond in the CO_3^{2-} group of the red mud (Lodeiro et al. 2008; Shi et al. 2018; Brzezińska-Miecznik et al. 2017). This is consistent with the XRD results, which prove the presence of CaCO_3 in the raw red mud. The IR peak gradually decreases to disappear, and there is no CO_3^{2-} in the desulfurized red mud, indicating the participation of CaCO_3 in the desulfurization reaction. The infrared band at $1636\text{--}1640\text{ cm}^{-1}$ is the bending vibration of the H-OH bond. This indicates that there is more free water interacting with the reaction products to become bound water in the desulfurization process (Yu et al. 1999; García-Lodeiro et al. 2008). The infrared band at 2100 cm^{-1} is the stretching vibration of the Si-H bond (Maley et al. 1989; Chen et al. 1989). The broader infrared absorption band at 3140 cm^{-1} is the absorption peak of the interlayer molecule H_2O (Yu et al. 1999).

In summary, the process of red mud slurry desulfurization is divided into three steps: (1) SO_2 gas is dissolved in the slurry. At this point, the dissolution of SO_2 in water to form H_2SO_3 and the ionization of H_2SO_3 to produce SO_3^{2-} and H^+ mainly occur. The unstable H_2SO_3 decomposes to produce HSO_3^- and H^+ . (2) The free alkali in the red mud slurry reacts with H^+ to neutralize it. Neutralization and oxidation reactions of alkaline metal compounds with H^+ also occur at this time. Al^{3+} metal ions combine with OH^- to generate precipitates. (3) Dissolution of insoluble sodium salts of red mud (sodium aluminosilicate hydrate, hydrated garnet) and the physical phase transfer of reaction products. The main reactions occurring in the red mud desulfurization process are shown in equations (1)–(10), where OH^- is provided by the free base (Li et al. 2020; Tao et al. 2019; Liu et al. 2022; Zhang et al. 2021). The dissolution of the red mud desulfurization process and the reaction mechanism are shown in Fig. 10.

4 Conclusion

In this study, the use of red mud desulfurization is an economic technology to treat waste with waste. It can not only solve the industrial flue gas SO_2 pollution problem but also reduce the stockpiling of red mud. In the bottom-blown stirred reactor, the appropriate slurry concentration for red mud desulfurization is 10 g/L. The raw red mud can absorb 100% of SO_2 in the first 25 min, and the ability of red mud to absorb SO_2 decreases as the reaction time increases. The red mud is mainly free alkali involved in the reaction at the beginning stage. Sodium aluminosilicate hydrate ($1.08 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.68 \text{SiO}_2 \cdot 1.8 \text{H}_2\text{O}$), hydrated garnet ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$), and part of the Fe^{3+} in Fe_2O_3 dissolved into the liquid phase in the solid phase. The metal oxides react with H^+ to form metal ions. Al^{3+} metal ions combine with OH^- to generate precipitates. Under the present experimental conditions, S is mainly present in the liquid phase after the reaction. After 60 min of red mud desulfurization, the Na_2O in red mud is < 1%. This can meet the highly stringent requirements for the production of cement, geopolymers, etc. The use of a ball mill external field can prolong the desulfurization reaction time. An ultrasonic external field can accelerate the reaction rate.

Declarations

Ethics approval and consent to participate

Ethics approval was not required for this research.

Consent for publication

Not applicable.

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Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

All authors (Xueke Li (doctoral student), Yan Liu (Professor), Ting-an Zhang (Professor)) contributed to the study conception and design. Material preparation, data collection and analysis were performed by Xueke Li. The first draft of the manuscript was written by Xueke Li, and all authors commented on previous versions of the manuscript.

Availability of data and material

All data generated or analysed during this study are included in this published article.

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Figures

Figure 1

Experimental setup diagram

Figure 2

Adsorption-desorption isotherms before and after ball milling

Figure 3

10K magnification SEM images of raw red mud and red mud after ball milling ((a) raw red mud, (b) red mud after ball milling)

Figure 4

Changes in pH with red mud slurry concentration

Figure 5

Slurry pH and SO_2 concentration in tail gas during red mud desulfurization

Figure 6

Changes in Na₂O content in red mud during desulfurization

Figure 7

10k SEM image of desulfurized red mud ((a) raw red mud desulfurization, (b) ball mill red mud desulfurization, (c) desulfurization of raw red mud under ultrasonication, (d) desulfurization of ball-milled red mud under ultrasonication)

Figure 8

XRD of raw red mud desulfurization process

Figure 9

Infrared spectrum of the raw red mud desulfurization process

Figure 10

Mechanism of red mud desulfurization in the reactor