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Research progress on desulfurization technology of high-sulfur bauxite

Gan CHENG[1,2,3], Yu-long LI[1], Meng-ni ZHANG[1]

1. College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo 454000, China;
2. Henan Key Laboratory of Coal Green Transformation, Henan Polytechnic University, Jiaozuo 454000, China;
3. Collaborative Innovation Center of Coal Work Safety and Clean High Efficiency Utilization, Henan Polytechnic University, Jiaozuo 454000, China

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Abstract: Bauxite is the main raw material of the alumina industry. However, high-sulfur bauxite constitutes a relatively large proportion of bauxite resource in China. Excessive sulfur impurities in bauxite have significant impact on the Bayer process, such as corrosion of equipment and pipelines, increased consumption of alkali, and difficulties in sedimentation of red mud particles after digestion. As the mainstreams of bauxite desulfurization technologies, the bauxite pre-desulfurization (roasting, electrochemistry, biology, flotation, etc) and Bayer process desulfurization (oxidation and precipitation) need to be fully understood for the further improvement of desulfurization performance. Here, an in-depth review on their mechanisms and advantages/disadvantages is presented.

Key words: bauxite; sulfur; desulfurization; flotation

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1 Introduction

Aluminium is the third most abundant element in the Earth's crust [1], the second highly produced metal next to iron and the most produced non-ferrous metal [2]. It has been widely used in the building, packaging, automotive, aerospace, electrical distribution industries, etc. In 2020 alone, China's alumina and electrolytic aluminum productions reached up to 73.13 million tons and 37.08 million tons, accounting for 54.03% and 56.13% of the world's total productions, respectively.

Bauxite is the main raw material of the alumina industry [3]. More than 90% of alumina is acquired from bauxite around the world. According to the 2021 USGS (United States Geological Survey) Mineral Commodity Summary, there are currently 55 to 75 billion tons of bauxite resources globally (Fig. 1 [4,5]), distributing across Africa (32%), Oceania (23%), South America and the Caribbean (21%), Asia (18%), and elsewhere (6%). Although China supplies more than 50% of the world's aluminum production, only 16.17% of the world's total bauxite resource reserves is utilized. The bauxite resource in China is mostly diasporic-type ore with complex mineral composition characteristics [6], low A/S ratio (mass ratio of Al_2O_3 to SiO_2), and is refractory. In 2020, China imported about 111.5366 million tons of bauxite [7]. Although the sub-limit of A/S for bauxites is generally kept around 7, some researchers suggest that the A/S ratio should be more than 8 for Bayer technology. If the A/S ratio of bauxite is below 8 (which is defined as low- grade bauxite), sintering process or combination of sintering and Bayer process can be typically applied in the industry. This sintering process is an energy-intensive process which increases alumina production cost and may also result in environmental pollution due to its gas emissions [8].

Corresponding author: Gan CHENG, E-mail: chenggan464@126.com

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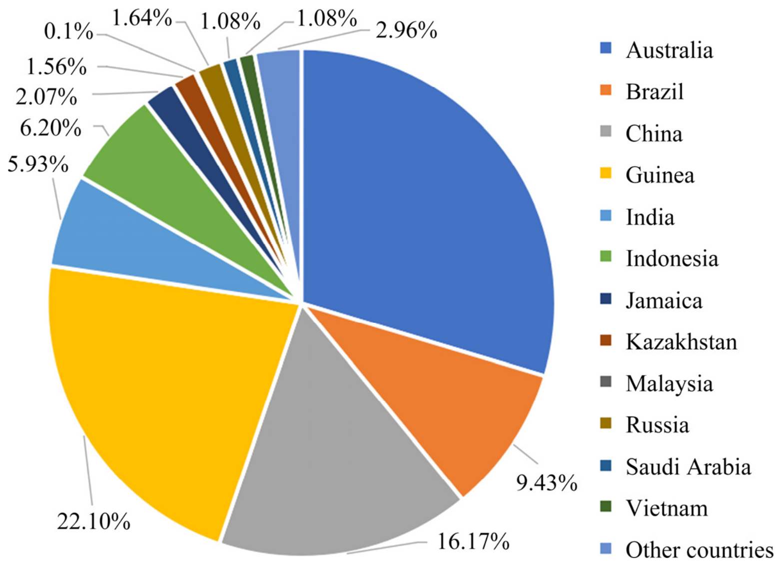

Fig. 1 Global distribution of bauxite resources

To reduce the need for this import, researchers are looking into the effective utilization of diasporic high-sulfur bauxite (sulfur content >0.7%) currently available in China, which are mainly distributed in Henan Province, Chongqing City, Guizhou Province, Guangxi Zhuang Autonomous Region, etc. Therefore, this work aims to review the progress on bauxite desulfurization, while also focusing on the origin and hazards of sulfur in bauxite.

2 Origin and hazards of sulfur in bauxite

2.1 Origin of sulfur in bauxite

In China, sulfur in bauxite exists mainly in the form of pyrite (FeS_2), which is the most common iron sulfide mineral and often viewed as a gangue mineral [9]. In addition, sulfur also exists in bauxite in the forms of pyrite isomers, such as marcasite, meteorite (FeS) and pyrrhotite ($Fe_{1-n}S$), sulfate minerals, such as alumite ($FeSO_4 \cdot 7H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$) and barite ($BaSO_4$), and sulfides of copper and zinc, such as chalcopyrite ($CuFeS_2$) and sphalerite (ZnS). Their intercalation with diasporic bauxite is complex and the removal of sulfur impurities in high-sulfur bauxite is, therefore, a great challenge.

2.2 Hazards of sulfur in bauxite

During the dissolution process of the Bayer process, sulfur exists in bauxite in the form of SO_3^{2-}, SO_4^{2-}, S^{2-}, $S_2O_3^{2-}$, etc, which will cause iron pollution in sodium aluminate solution, damage the passivation film on steel surfaces, and accelerate steel corrosion [10]. The sintering and Bayer are the two basic processes of alumina extraction from bauxite. The disadvantage of the sintering is its low efficiency (33% or lower) [11]. Nonetheless, the lower cost makes the Bayer process the more commonly-used method.

As known, the Bayer process in the aluminum industry was developed by Carl Josef Bayer in 1887 [12] and is an essential intermediate step in the production of aluminum metal. Bayer process involves leaching at 100−250 °C by a caustic soda solution (sodium hydroxide) followed by solid−liquid separation, cooling, precipitation, filtration, and calcination [13]. During the Bayer process, the pyrite dissolves into the solution in the form of S^{2-}, which then gets oxidized into $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}. These sulfur complexes increase the sulfur and iron contents in aluminum hydroxide and alumina products, decrease the digestibility of the alumina, accelerate the corrosion of steel equipment, increase alkali consumption, decrease the particle size of aluminum hydroxide and alumina products, and scale up the evaporators and digesters [14].

At present, the pre-desulfurization and desulfurization in the Bayer process are the two main methods of bauxite desulfurization [15].

3 Pre-desulfurization

Pre-desulfurization refers to the removal of sulfur impurities before the Bayer process. Roasting, electrochemical, flotation and biological desulfurizations are the commonly-used methods of pre-desulfurization.

3.1 Roasting desulfurization

In the 1840s, the Lauta plant in Germany treated high-silica bauxite via roasting method. The method was as follows: bauxite was roasted at 700−1000 °C, and then dissolved at 90 °C using 10% caustic solution. The optimal temperature for roasting and desilication was 900−1000 °C, and the desiliconization rate was up to 80% [16]. During roasting desulfurization, pyrite is converted to SO_2 at a certain temperature. A series of complex reactions such as dehydration, decomposition, and crystal transformation during the heating process lead to the destruction of the mineral structure. While new crystals have no time to form or have a low degree of order, the specific surface area of the ore and the chemical activity increase. After $Al_2O_3\cdot H_2O$ is roasted, the number of pores in the ore increases, which increases the reaction ability of each component significantly, further accelerating the dissolution and improving the dissolution rate [17]. The reaction of pyrite under oxidative roasting is as follows [18]:

$$(1-x)FeS_2+(1-2x)O_2=Fe_{1-x}S+(1-2x)SO_2 \quad (1)$$

$$2Fe_{1-x}S+(3-x)O_2=2(1-x)FeO+2SO_2 \quad (2)$$

$$3FeO+1/2O_2=Fe_3O_4 \quad (3)$$

$$2FeS_2=2FeS+S_2 \quad (4)$$

$$S_2+2O_2=2SO_2 \quad (5)$$

$$4FeS+7O_2=2Fe_2O_3+4SO_2 \quad (6)$$

The total reaction is

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2 \quad (7)$$

The muffle furnaces, rotary tube furnaces, and fluidized beds are used in roasting desulfurization. LÜ et al [19] found that the suitable conditions for pretreatment of muffle furnaces and rotary tube furnaces were roasting temperature of 750 °C and roasting time of 30 min; while the suitable conditions for fluidized bed are roasting temperature of 800 °C and roasting time of 10 min. YIN et al [18] studied the roasting and desulfurization of low−medium grade high-sulfur bauxite. The optimum roasting conditions were 750 °C, 60 min, surface density of 7.6 kg/m^2, and particle size of 147−177 μm. The sulfur content was found to decrease from 2.70% to below 0.40%. WU et al [20] adopted suspension−roasting and muffle furnace roasting to increase digestion properties of low-grade high-sulfur bauxite. The optimal digestion conditions were as follows: t=70 min, T=280 °C, w(CaO)=8% and N_k (caustic soda concentration, in the form of Na_2O) =245 g/L, in which the digestion ratios were 94.45% and 92.08% for the suspension-roasting and muffle furnace roasting, respectively.

At present, roasting can not only effectively remove sulfur and improve the dissolution performance, but also eliminate the detrimental effects of organic matter, which has gradually attracted widespread attention. The conventional roasting desulfurization, however, requires high temperatures, long duration, etc. Microwave heating which uses electromagnetic wave with wavelengths of 0.1−100.0 cm and frequencies of 0.3−300.0 GHz has been studied to accelerate the reaction rate and heat minerals selectively. The relative permittivity of pyrite (FeS_2) is as high as 33.7−81.0 which is close to that of hematite (Fe_2O_3). During microwave heating, the wave absorption performance of pyrite is observed to be better than that of diaspore (relative permittivity of 6.5) and kaolinite (relative permittivity of 11.8) due to its higher dielectric constant. Most silicate minerals (illite, mica), carbonate minerals (dolomite, calcite), and titanium-containing minerals (anatase, rutile) have poor microwave absorbing properties. Based on the difference of the wave absorption performance among pyrite and other minerals, the rapid heating and desulfurization were achieved [21]. The desulfurization mechanism of pyrite in the microwave field is shown in Fig. 2. During microwave heating, the breakage of Fe—S bond in pyrite is induced under the action of dipole orientation polarization, and the rapid increase in internal temperature of pyrite particles. While the sulfide ions continuously diffuse into the mineral surface layer, SO_2 gas is generated with the help of air. Since the accumulated heat in the pyrite particles cannot be quickly dissipated, a local temperature difference occurs between the inside

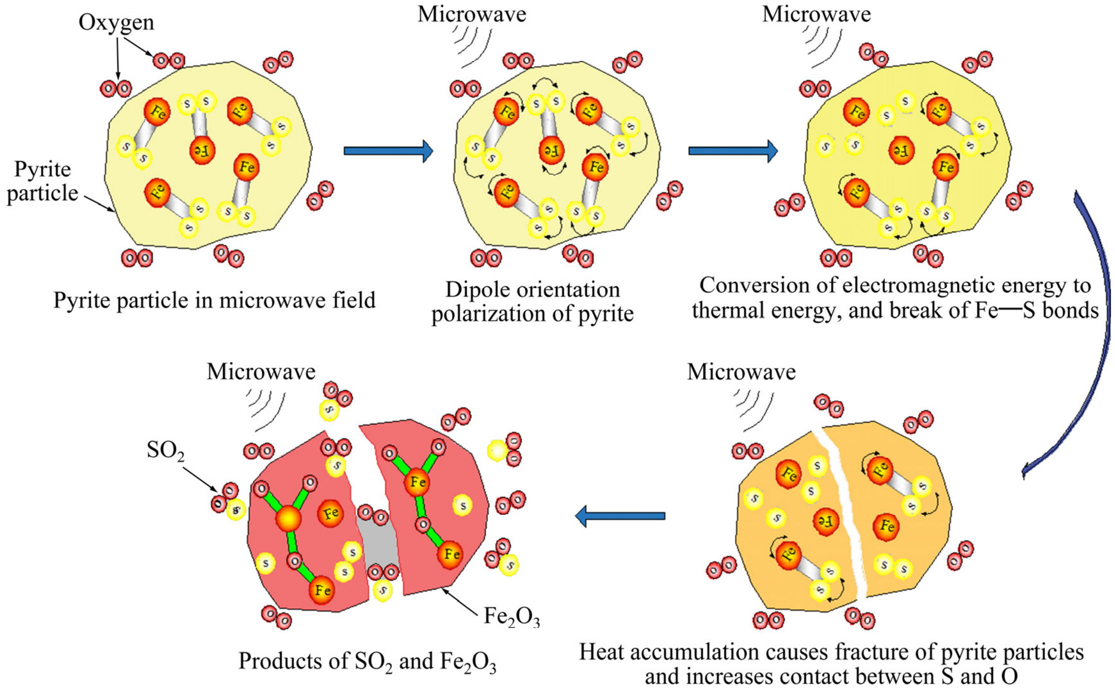

Fig. 2 Mechanism of pyrite particle desulfurization in microwave field

and outside, resulting in thermal stress and different degrees of cracks. The formation of cracks or the rupture of particles can effectively promote the dissociation of pyrite and increase effective reaction area.

During microwave roasting, pyrite in bauxite may undergo the following reactions:

$$2FeS_2=2FeS+S_2 \tag{8}$$

$$FeS_2+O_2=FeS+SO_2 \tag{9}$$

$$4FeS_2+3O_2=2Fe_2O_3+8S \tag{10}$$

$$2FeS_2+5O_2=2FeO+4SO_2 \tag{11}$$

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2 \tag{12}$$

$$4FeS+7O_2=2Fe_2O_3+4SO_2 \tag{13}$$

$$S+O_2=SO_2 \tag{14}$$

$$6FeO+O_2=2Fe_3O_4 \tag{15}$$

$$4Fe_3O_4+O_2=6Fe_2O_3 \tag{16}$$

$$4FeO+O_2=2Fe_2O_3 \tag{17}$$

ZHU et al [22] obtained the optimal microwave desulfurization conditions via orthogonal experiments as follows: microwave power of 4.5 kW, heating time of 15 min, and mineral particle size of 75−90 μm. Results showed a decrease in sulfur content from 4.15% to 0.32%, and dissolution rate was over 90%. JIN et al [21] adopted microwave roasting at 600 °C for 15 min, in which the sulfur mass fraction in bauxite was observed to decrease from 2.01% to 0.32%, and the desulfurization efficiency of approximately 85% was acquired. CHEN et al [23] adopted a self-made dispersed roaster to treat bauxite with 1.61% sulfur content. Results showed that when roasting at 650 °C for 120 s, the desulfurization efficiency was up to 76.98%, while the residual sulfur in the roasted ore was found to be 0.07%. HU et al [24] roasted high-sulfur bauxite ore at 600 °C for 60 min, and the dissolution test was performed at 240 °C and roasted for 60 min. The mass concentration of S^{2-} in the eluate of the roast ore decreased from 1.78 to 0.15 g/L.

At present, the researches on the roasting desulfurization are mainly focused on the changes in microstructure and crystal structure of the ore after calcination. The effects of sulfur occurring in different forms in bauxite are different, particularly the divalent sulfur ions generated in the dissolution process, which are known to be the most harmful. In addition, static roasting desulfurization easily causes SO_2 gas accumulation in the ore powder, which leads to uneven heating and phenomena of “underburning” or “overburning” [25]. As a result, many other technologies, e.g. dry desulfurization, semi-dry desulfurization, and wet desulfurization, have been developed to treat roasting flue gas [26−28].

3.2 Electrochemical desulfurization

Electrochemical desulfurization is oxidation process of solid-phase sulfur in minerals into soluble sulfur. The experimental apparatus is shown in Fig. 3 [29].

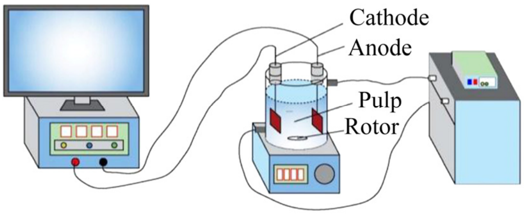

Fig. 3 Schematic diagram of electrochemical desulfurization device

The main reactions of electrochemical desulfurization bauxite in alkaline solution are as follows:

Cathode: $4H_2O+4e=2H_2+4OH^-$ (18)

Anode: $4OH^-=O_2+4e+2H_2O$ (19)

Liquid: $4FeS_2+16OH^-+15O_2=$
$4Fe(OH)_3+8SO_4^{2-}+2H_2O$ (20)

The conversion of sulfur in the liquid phase is then as follows:

$4S^-+O_2+2H_2O=4S+4OH^-$ (21)

$S+O_2+2OH^-=SO_3^{2-}+H_2O$ (22)

$S+SO_3^{2-}=S_2O_3^{2-}$ (23)

$2SO_3^{2-}+O_2=2SO_4^{2-}$ (24)

$S_2O_3^{2-}+2O_2+2OH^-=2SO_4^{2-}+H_2O$ (25)

GONG et al [30] investigated the electrochemical desulfurization kinetics of bauxite in NaCl and NaOH solution systems. The results showed that with the increase in electric current density, the desulfurization efficiency of NaCl solution increased, while the desulfurization efficiency of NaOH solution increased and then decreased with an increase in electric current density. The electrochemical desulfurization in NaCl and NaOH solutions is controlled by internal diffusion and interface chemical reactions, respectively. In another study, GONG et al [31] regenerated the electrolyte by adding anhydrous calcium chloride into the solution. Results showed that the desulfurization efficiency unexpectedly increased with an increase in the number of electrolyte cycles. The increase in cycle times led to a decrease in pH value and an increase in Fe ions concentration in the electrolyte, which therefore increased the desulfurization efficiency with the increase of electrolyte recovery. Significant change in the desulfurization efficiency and anode surface activity were both observed with an increase in Ca^{2+} concentration. In addition, ultrasound [32] and pressure [33] were also found to promote the formation and mass transfer of ROSs (reactive oxygen species) simultaneously; however, their effect on the thermodynamics of ROS formation is insignificant [34].

3.3 Biological desulfurization

Biological desulfurization adopts selected bacterial or enzyme metabolic processes to catalyze specific desulfurization reactions under mild conditions [35,36]. *Mycobacterium phlei* [37], *Thiobacillus ferrooxidans* [38], *Pleurotus flavus*, *Thiobacillus thiooxidans* [39], *Bacillus polymyxa*, etc are the frequently-used bacteria for the removal of sulfur from coal. XU et al [40] optimized the desulfurization conditions of high-sulfur coal from Datong, Shanxi, China, using *Escherichia coli* and *Phanerochaete chrysosporium*, respectively. It was found that with coal particle size of 0.075−0.125 mm, coal slurry concentration of 0.4 g/mL, inoculum volume of 5 mL, pH value of 7.0, when the corresponding culture temperatures were 30 and 28 °C, and culture time was 10 and 14 d, the desulfurization efficiencies were 50.42% and 40.17%, respectively. In study by LI et al [41], *Ochrobactrum* was shown to be able to revert dibenzothiophene to biphenyl. WANG et al [42] studied the adsorption of bacteria and yeasts on the surface of raw coal and observed that yeast was more likely to adsorb on the surface of the clean coal, which could enhance the hydrophobicity of the clean coal, thus making the gangue more hydrophobic.

The microbial desulfurization undergoes the complex reaction process at normal temperature and pressure. Besides that, the reaction effect is shown to be good, process is stable, operation is simple, and pollutant conversion efficiency is high. Nonetheless, as research studies are limited in this technology, many aspects need to be strengthened prior to its commercialization, including (1) solving the problem of slow bacterial leaching speed and long cycle time, and reducing the cost of bacterial culture; (2) taking measures to maintain high bacteria concentration in the industrial production process [43].

3.4 Flotation desulfurization

Flotation desulfurization is to use collectors to recover pyrite from bauxite [44−47]. The Ural Academy of Sciences of Soviet Union first adopted this method, in which sulfur content in the concentrate was found to drop from 2% to less than 0.41%, and the Al_2O_3 recovery was 99.17%.

3.4.1 Ultrasonic and microwave-assisted flotation desulfurization

In recent years, the cavitation effect of ultrasonic waves in liquid systems has been used to improve the flotation performance [48,49]. OUYANG et al [50] studied the effect of pre-ultrasonic, synchroultrasonic, and the combination of preultrasonic and synchroultrasonic. Results showed that the sulfur content of aluminium oxide concentrate obtained by preultrasonic of 20 kHz for 5 min was reduced by 20%; while the sulfur content of aluminium oxide concentrate obtained by synchroultrasonic treatment at 20 kHz for 4 min was reduced by 23.64%. CHENG [51] studied the enhancement of surface properties of pyrite by ultrasound. The contact angle and SEM results showed that the ultrasonic treatment enhanced the removal of impurities adhering onto the pyrite surface and peeled off some harmful minerals. Additionally, the hydrophobicity of mildly oxidized pyrite was recovered within 20 s; the hydrophobicity of partial heavy oxidation pyrite was improved within 10 s, and the contact angle of heavy oxidized pyrite decreased after 10 s.

Microwave, on the other hand, has also been widely used in coal desulfurization, and in-depth research has been conducted. However, this technology presents the disadvantage of having large energy consumptions so it has yet to be industrially applied. GE et al [52] found that microwave had a non-thermal effect on the structure of thiophene sulfur, one of the most important form of organic sulfur in coking coal. HU [53] analyzed the microwave thermal and non-thermal effects on the composition of coal, while applying quantum chemical calculation software to explore sulfur compounds. GUO [54] analyzed the properties of dibenzyl sulfide, diphenyl sulfone, dibenzothiophene, and the reaction of dibenzothiophene with peracetic acid by quantum chemical calculations, and revealed non-thermal effect of coal microwave desulfurization.

3.4.2 Development of bauxite desulfurization

Bauxite desulfurization and desiliconization processes are performed separately or jointly [55]. In a one-stage grinding, one-stage roughing and two-stage scavenging flowsheet, MA et al [56] observed that the sulfur content in the aluminium oxide concentrate was reduced from 1.87% to 0.31%, while the sulfur removal rate and the Al_2O_3 recovery were 85.34% and 97.13%, respectively. ZHENG et al [57] proposed a “three-step strategy” for desulfurization by “flotation + oxidation + precipitation”. WANG et al [58] adopted a two-step reverse flotation process to reduce the sulfur content in bauxite from 2.08% to 0.65%. Similarly, CHEN et al [59] also adopted reverse flotation to reduce sulfur content from 0.96% to 0.44%. MA et al [60] utilized the polarizing microscope, X-ray diffractometer, and quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) to conduct technological mineralogical research on high-sulfur bauxite in Zunyi city, China. TAN [61] adopted one-stage roughing, two-stage cleaning and one-stage scavenging reverse flotation flowsheet to obtain aluminium oxide concentrate with a sulfur content of 0.26% and Al_2O_3 recovery of 99.02%. TAO [62] adopted one-stage roughing, three-stage scavenging and four-stage cleaning to recover 97.60% of Al_2O_3 concentrate with sulfur content of 0.42%. YANG et al [63] adopted one-stage roughing, one-stage scavenging and one-stage cleaning reverse flotation for a high sulfur and high silicon bauxite in Guizhou, China. REN et al [64] adopted one-stage roughing, three-stage cleaning and one-stage scavenging desulfurization flotation, and the scavenging tailings were treated by two-stage roughing, four-stage cleaning and one-stage scavenging desiliconization flotation. In a study by YAN et al [65] where cetyl trimethyl ammonium bromide (CTAB) as desilication collector and butyl xanthate as desulfurization collector were used, the Al_2O_3 yield of 42.87%, Al_2O_3 grade of 63.14%, sulfur content of 0.21%, and a recovery of 49.00% were obtained.

3.4.3 Research and development of bauxite desulfurization collector

A common feature of pyrite collectors is that they contain sulfur atoms in the molecule, which can selectively capture sulfide ores, but have no effect on gangue minerals such as kaolin and quartz. According to the type of the ore-prone base, the sulfide ore collector can be divided into xanthophytes, black catching agent, thiourethanes, sulfur nitrogens, and thioureas. Their molecular formulas are shown in Fig. 4.

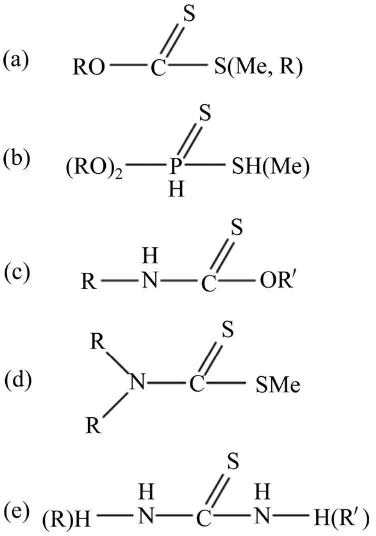

Fig. 4 Sulphide ore collector: (a) Xanthogenate type collector; (b) Dithiophosphate type collector; (c) O-alkyl-N-alkyldithiocarbamate; (d) N,N-dialkyldithiocarbamate; (e) Thioureas type collector

In flotation desulfurization, copper sulfate is commonly used as activator, butyl xanthate or dibutyl dithiophosphate as collector, terpineol as frother, and starch as aluminium oxide inhibitor. The butyl xanthate exists in two forms of xanthanic acid and double xanthate in weakly alkaline aqueous solution, which can improve their ability to collect sulfur compounds [66]. Starch as a bio-degradable non-toxic natural polysaccharide polymer possesses strong depression effect onto diaspore. Adsorption of depressants occurs on the available Al—O bonds of diaspore particles whose surfaces have sufficient Al—O sites available and starch can be chemically adsorbed onto them. A slight decrease was observed in the recovery of kaolinite or the aluminosilicates in the presence of starch due to the minute sites of Al—O on the kaolinite surface [67]. The adsorption of copper ions on pyrite surface was observed to be pH-dependent, and whereby the adsorption magnitude of copper ions at alkaline pH was higher than that at acidic and neutral pH due to a strong interaction between O atom in $Cu(OH)_2$ and surface Fe atom except for the interaction between Cu atom and surface S atom in acidic and neutral environment [68]. Therefore, the addition of $CuSO_4$ can effectively improve the flotation performance of pyrite in weakly alkaline solution and promote the formation of double xanthate.

WANG et al [69] found 1-dodecanesulfonic acid sodium salt did not have the ability to desulfurize by flotation, while ethyl xanthate and diethyldithiocarbamate had certain desulfurization capabilities. The selectivity of isobutyl xanthate was also found to be good, and butyl xanthate had strong collecting ability. CHAI et al [70] found that 2-mercaptobenzimidazole (MBI) had better hydrophobicity on pyrite surface in acidic solution than in alkaline solution. Here, MBI and pyrite formed N — Fe — S coordination bond under electrostatic force and chelation. YU et al [71] investigated the organosilicon cationic as collector and starch as depressant which showed concentrates with A/S ratio of 9.58 and Al_2O_3 recovery of 83.34%. LI et al [72] used butyl xanthate as collector, terpineol oil as frother, $CuSO_4$, $FeSO_4$ and oxalic acid as activators, and modified starch as inhibitor and obtained concentrate with sulfur content of 0.28% and Al_2O_3 recovery of 95.47%. XIE et al [73] used sodium carbonate as pH adjuster, sodium silicate (SNS) as inhibitor, copper sulfate as activator, and butyl xanthate as collector, which resulted in aluminium oxide concentrate with sulfur content of 0.25%, yield of 83.31%, and desulfurization of 83.52%. YANG et al [74] replaced the traditional acid (sulfuric acid) activation system with a combination of small-molecule organic matter and salt compound K3 $(Fe(CN)_6)$ as an activator + butyl xanthate + No. 2 oil. The closed-circuit test resulted in aluminium oxide concentrate with sulfur content of 0.43%, and Al_2O_3 recovery of 92.71%. YUE and YANG [75] found that the collectorless sodium sulfide-induced flotation process did not require activator copper sulfate and collector xanthate, which eliminated reagent usage while reducing the effect of the flotation collector on subsequent aluminium oxide dissolution. REN et al [76] used AP-4 (hydroxamate collector) collector, which was a strong collector at low temperature, and silicate inhibitor SY-3 (inorganic salt inhibitor). "One-stage grinding−reverse flotation pre-desulfurization−direct flotation desilication" technological process was observed to improve the recovery of Al_2O_3. BULUT et al [77] found that impurities and structural differences in pyrite had little effect on its flotation behavior; while copper ions could activate pyrite flotation. The performance of the alkali metal sulfide collector was found to be dependent on the polar head group and the length of the non-polar hydrocarbon chain. TAGUTA et al [78] found that the adsorption heat was a strong predictor of hydrophobicity for the collectors with the same ligand type and different alkyl chain lengths.

At present, the kneader is commonly used in the industry to produce xanthate. In this method, alcohol and carbon disulfide are first added to a kneader, and then sodium hydroxide powder is added in batches into the knead to synthesize xanthate. The method, however, requires relatively fine particle size of alkali and high energy consumption. In addition, a small amount of carbon disulfide is volatilized during the production process. The intense exotherm and difficulty in temperature control result in incomplete reaction, many unwanted side reactions, low product purity and short shelf life. In the wet-alkali method, a small amount of water is added to wet the caustic soda during the production of sodium alkoxide, and the obtained sodium alkoxide is then reacted with carbon disulfide to form a liquid xanthate.

Although liquid xanthate has the advantages of low cost, no dissolution, being easy to operate, and controllable, its lack of stability and difficulty in storage greatly limits its application. The solvent method involves the reaction of caustic alkali, carbon disulfide and alcohol in an organic solvent, followed by the removal of the solvent via drying to obtain xanthate product. The reaction rate is fast and the amount of heat is large. A large amount of cooling water is therefore required to dissipate the generated heat while high energy input is required to remove the solvent by heating to obtain solid product. Although the product has high purity and yield, the required amount of solvent is large, the process is complicated, and the energy consumption is high.

In summary, during the roasting pretreatment desulfurization, sulfur is mainly generated in the form of SO_2, in which its direct emissions will cause pollution to the air. To prevent this, necessary exhaust gas treatment devices are required, resulting in high equipment cost. Electrochemical desulfurization provides new ideas and methods for pretreatment of high-sulfur bauxite, but further research is needed to better understand the method. In addition, sulfur inevitably enters into the hydrometallurgical process and accumulates cyclically, which may result in a negative impact on alumina production.

The microwave heating method is used for roasting and pretreating high-sulfur bauxite. The produced SO_2 needs to be treated and the used civilian frequency is limited. Microbial desulfurization strains have strict environmental requirements, the strain efficiency is low and the reaction cycle is long. Wet desulfurization is a flexible and effective method, but usually requires the consumption of precipitants/oxidants, which may introduce new impurities into the digestion liquor. Additionally, the moisture due to this method may also lead to the problem of corrosion of iron and steel equipment. Flotation desulfurization is very valuable for the comprehensive utilization of minerals. Xanthate is the most widely used sulfide ore collector. However, the unstable properties of xanthate would accelerate its decomposition when exposed to heat. Other disadvantages of xanthate include its strong odour, high toxicity and easy oxidization. When adopting xanthate flotation desulfurization, lime is used to adjust the pH value to alkaline (9−12), which satisfies the alkaline conditions of xanthate and makes pyrite selective. However, the high alkalinity of the wastewater will cause pollution to the environment. Therefore, the development of highly-efficient, green, low-cost desulfurization agents is the key to desulfurization of bauxite.

4 Bayer dissolution process desulfurization

Pre-desulfurization prevents most of the sulfur in bauxite from entering the Bayer process, but sulfur in the pretreated bauxite still remains problematic. Therefore, deep desulfurization is needed in the sodium aluminate solution. The common methods for desulfurization of sodium aluminate solution include sulfur removal by oxidation and precipitation methods.

4.1 Oxidation desulfurization

Oxidation desulfurization refers to the low-valence sulfur (S^{2-}) in the sodium aluminate solution being oxidized into SO_4^{2-}. During the evaporation process, SO_4^{2-} is converted into $Na_2CO_3\cdot 2Na_2SO_4$ and precipitates. Oxidants are classified into gaseous oxidants (ozone, oxygen, etc), liquid oxidants (hydrogen peroxide, etc), and solid oxidants (sodium nitrate, sodium peroxide, etc). The sulfur in bauxite is oxidized into sodium sulfate by gaseous oxidant (ozone or air), and exogenous impurities were therefore not introduced into the sodium aluminate solution, which can avoid any adverse effects on the resultant alumina [79,80]. Nonetheless, the use of ozone or air oxidation always presents higher risks compared to liquid and solid oxidants, which are usually used for desulfurization [81].

4.2 Precipitation desulfurization

During the bauxite desulfurization process, the precipitators may be alumina or active carbon. The mechanism of sulfur removal (shown in Fig. 5) was proposed by LIU et al [82,83]. The aluminum or active carbon reacts with high-valence sulfur ($S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}) to generate low-valence sulfur (S^{2-}). The S^{2-} then reacts with $Fe(OH)_3$ and $Fe(OH)_4^-$ to generate $NaFeS_2$ which agglomerates into the red mud. Therefore, sulfur in sodium aluminate solution can be effectively removed and new impurities will not be introduced by adding aluminum in the digestion process.

Common desulfurizers are mainly CaO, ZnO and BaO.

(1) CaO

The low-valence sulfur is oxidized into the high-valence sulfate ion, which then reacts with calcium oxide and sodium aluminate to form hydrous calcium sulphoaluminate, and then settle into red mud. As a cheap desulfurizing agent, lime can increase the alumina dissolution rate, improve the sedimentation performance of red mud, reduce the alkali consumption, and adsorb organic substances such as oxalate, vanadate and chromate ions in the solution to purify the solution. The limitation to this is that it is only suitable for the treatment of solutions with a relatively low concentration of sodium aluminate, the sulfur removal rate is relatively low, and the reaction will also consume Al_2O_3, which increases the amount of red mud.

(2) BaO and $BaSO_4$

Barium ions in the desulfurizing agent and SO_4^{2-} in sodium aluminate solution form barium sulfate precipitates, which enters into the red mud to achieve sedimentation separation, while other sulfur ions, particularly divalent sulfur ions, remain in the solution. The use of barium salt as a desulfurizing agent has high utilization rate, short action time, large temperature range and can also remove carbon from the solution. However, the high price of barium salts may not be cost effective. At the same time, the quality of the product is deteriorated due to the pollution of alumina by iron, while the barium compounds are toxic.

(3) ZnO

Zn^{2+} reacts with S^{2-} in sodium aluminate solution to form insoluble zinc sulfide precipitates,

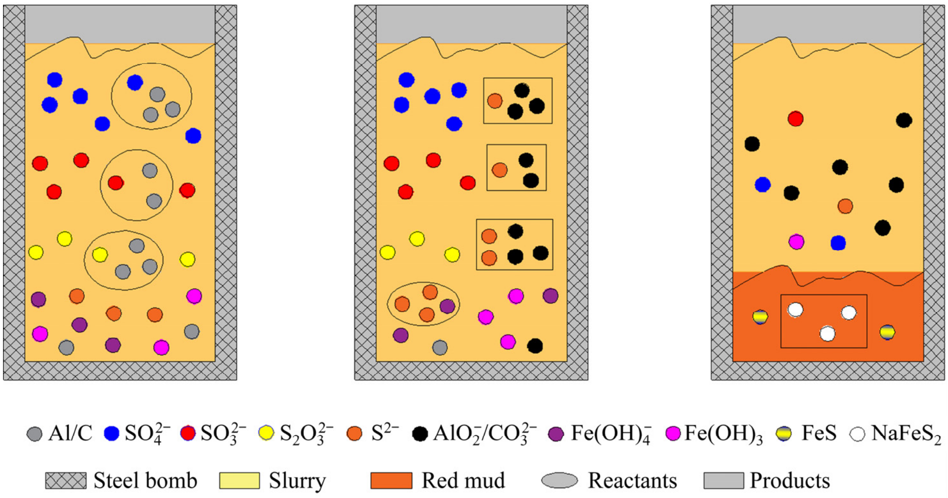

Fig. 5 Schematic illustration of sulfur removal mechanism by adding aluminum or active carbon in sodium aluminate solution

which enter into the red mud to achieve sedimentation separation. This method has high desulfurization efficiency, simple and easy operation, short time, and can reduce the iron content in the solution. However, the price of zinc is relatively high, resulting in high desulfurization cost, and it is only applicable to the treatment of bauxite in which sulfur is mainly present as divalent ions after dissolution. Although zinc oxide dust collected by blast furnace gas purification can be used as desulfurizing agent, the pollution caused by impurities therein must be avoided [84]. The main reactions of pyrite in sodium aluminate solution are as follows [85]:

$$8FeS_2+30NaOH=4Fe_2O_3+14Na_2S+Na_2S_2O_3+15H_2O \quad (26)$$

$$6FeS_2+22NaOH=2Fe_3O_4+10Na_2S+Na_2S_2O_3+11H_2O \quad (27)$$

$$3FeS_2+8NaOH=Fe_3O_4+2Na_2S+2Na_2S_2+4H_2O \quad (28)$$

As the valences of S^{2-} and $S_2O_3^{2-}$ in sodium aluminate solution are unstable, these sulfur compounds are therefore called active sulfide. SO_3^{2-} and SO_4^{2-}, on the other hand, are called inert sulfur. Under the oxidation of air, Na_2S further reacts as follows:

$$Na_2S+Na_2SO_3+0.5O_2+H_2O=Na_2S_2O_3+2NaOH \quad (29)$$

The decomposition reaction of Na_2S_2 is

$$4Na_2S_2+6NaOH=6Na_2S+Na_2S_2O_3+3H_2O \quad (30)$$

The stability of $Na_2S_2O_3$ in solution decreases with increasing temperature, and $Na_2S_2O_3$ will undergo the following decomposition reactions:

$$3Na_2S_2O_3+6NaOH=2Na_2S+4Na_2SO_3+3H_2O \quad (31)$$

$$Na_2S_2O_3+2NaOH=Na_2S+Na_2SO_4+H_2O \quad (32)$$

To sum up, the sulfur in the fermentation broth mainly exists in the form of S^{2-} and $S_2O_3^{2-}$, while SO_4^{2-} mainly exists in evaporation (concentrated) broth. The valence change of sulfur in sodium aluminate solution is complicated. S^{2-} and S_2^{2-} must be rapidly oxidized to SO_3^{2-} and SO_4^{2-}, in order to avoid the formation of $S_2O_3^{2-}$. Finally, the sulfur in the sodium aluminate solution is removed by causticization or discarded in the form of sodium sulfate. HU et al [86] selected homemade barium aluminate for the desulfurization of sodium aluminate solution, where $BaSO_4$, $BaCO_3$ and $BaSiO_3$ precipitation were formed. The sodium aluminate solution was then separated and purified. The desulfurization process is simple, cost effective, and the desulfurization efficiency was as high as 95%.

The Bayer process desulfurization can select the desulfurization site based on the distribution of sulfur during the alumina production process. Its main disadvantage, however, is that the requirement for desulfurizing agent is relatively high, and the desulfurization performance is greatly affected by the composition of the sodium aluminate solution.

5 Conclusions

The high sulfur content of bauxite limits its application. The common desulfurization methods are reviewed. During the pre-desulfurization, the microstructure, crystal structure and dissolution properties of the ore will be affected by roasting, while SO_2 emission is inevitable. It is imperative to explore green and cheap reagents for flotation method. In addition, microwave is an important auxiliary method for roasting and flotation desulfurization. During the Bayer desulfurization, wet air oxidation method has higher requirements for safety control; precipitation method provides better efficiency, while the purity of alumina may be affected by impurities.

In the future, the mechanism of the aforementioned methods needs to be further understood. In addition, cost-effective technology needs to be developed through adopting their advantages. It is recommended to select appropriate method or integrating different methods to suit the type and existing characteristics of sulfur, which may help to achieve desired desulfurization performances.

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高硫铝土矿的脱硫技术研究进展

程 敢 [1,2,3]，李玉龙 [1]，张梦妮 [1]

1. 河南理工大学 化学化工学院，焦作 454000；
2. 河南理工大学 河南省煤炭绿色转化重点实验室，焦作 454000；
3. 河南理工大学 煤炭安全生产与清洁高效利用省部共建协同创新中心，焦作 454000

摘 要：铝土矿是氧化铝工业的主要原料。然而，高硫铝土矿在我国铝土矿中所占比例较大。铝土矿中过多的硫杂质对拜耳法工艺产生不可忽视的影响，如腐蚀设备和管道、增加碱耗、溶出后赤泥颗粒难以沉淀等。预处理脱硫(焙烧、电化学、生物和浮选等)和拜耳法脱硫(氧化和沉淀)是目前铝土矿脱硫的主要技术，分析这些技术各自的机理和优缺点，以进一步提高高硫铝土矿的脱硫性能。

关键词：铝土矿；硫；脱硫；浮选

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