Development of a Low-Cost Method for Determination of Sulfide Ions in Aluminate Solution of Bayer Process and Sulfide Removal using Nitrate from It

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ABSTRACT: *Sulfide ions in the solution of Bayer process can accelerate the corrosion of the equipment and increase impurity of the final product. In the current investigation, sulfide ions concentration of the aluminate solution during the Bayer process was determined using an indirect and inexpensive method. The method did not require any advanced apparatus, which made it suitable for sulfide concentrations over the range of 0.001-1 g/L. To investigate the source of sulfide ions in the aluminate solution, the chemical composition and crystalline structure of the bauxite used to produce alumina were characterized via XRF, XRD, and SEM analyses. The results demonstrated that the main source of sulfide ions was pyrite in bauxite. The advantages and disadvantages of sulfide removal method by nitrate from aluminate solution were investigated. Thermodynamically, the spontaneity of different half-reactions during the reduction of NO_3^- and oxidation of S^{2-} was studied. Finally, a technique was proposed for the removal of sulfide ions in the aluminate solution by adding nitrate. Moreover, the effect of nitrate concentration on lowering of sulfide ions concentration was evaluated in practical conditions of the bauxite digestion during the Bayer process. The results demonstrated that in conditions of bauxite digestion (at 270 °C, 52 bar and 60 minutes) by adding 2.5 g/L nitrate ions, the majority of sulfide ions (more than 96%) were eliminated and their undesirable effects were prevented.*

KEYWORDS: *Determination; Sulfide removal; Nitrate; Aluminate; Bayer process*

INTRODUCTION

The Bayer process is the most commonly-used industrial method for the production of alumina (Al_2O_3) from high-grade bauxites due to its low cost. In this process, caustic soda is used to extract aluminum oxide from diaspora bauxite at temperatures higher than 270 °C (Eq. 1).

$$Al_2O_3.H_2O \text{ (s)} + 2NaOH \text{ (aq.)} =$$
$$2NaAlO_2 \text{ (aq.)} + 2H_2O \text{ (l)} \qquad (1)$$
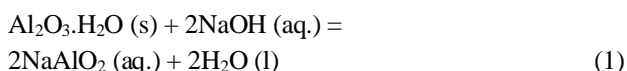
The iron oxide and other caustic insoluble impurities remain in suspension and are separated by decantation and filtration. The filtrate is cooled and aluminum hydroxide seed introduced to the liquid sodium aluminate ($NaAlO_2$) causes precipitation of solid phase aluminum hydroxide. The alumina tri-hydrate crystals formed are washed and calcined to produce high-purity crystalline alumina

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and the caustic alkaline liquor is recycled [1].

In recent years, the fast development of the alumina industry has attracted a great deal of attention to the sulfide removal methods and its negative effects on this industry. Although only a few studies were allocated to sulfide removal techniques during the alumina production process, many studies were focused on sulfide removal in other industries such as Oil, Gas, Wastewater, etc. [2-7].

The most important negative effects of sulfide presence in the Bayer process solution are as follows: (1) sulfide ions accelerate the corrosion of the equipment in addition to increasing the maintenance costs and cause serious human safety problems, (2) increase the iron content of the alumina and reduce the quality of the final product, (3) disturb the sedimentation of red mud and evaporation of spent liquor, and (4) increase the caustic soda consumption and production costs [8-11].

Among the sulfur-containing minerals in bauxite, pyrite (FeS_2) is the most detrimental mineral to alumina production. The pyrite in bauxite can easily react with alkaline aluminate liquor during the digestion step of the Bayer process. As a result, S^{2-} ions enter and accumulate in the Bayer liquor [12-14].

Desulfurization in the alumina industry can be divided into two categories; pretreatment of high-sulfur bauxite and removal of sulfide from sodium aluminate solution. The former mainly includes flotation [15,16], bioleaching [17,18], and roasting desulfurization [19, 20]. These methods present poor performance and high costs. Although they can control the sulfur content of the bauxite, deep desulfurization is necessary afterward.

In the Bayer process, the main effort is focused on the desulfurization of the sodium aluminate solution. Wet oxidation is one of the desulfurization methods. In this method, gaseous oxygen or air is employed to remove sulfide ions and decompose complex organic materials into carbonate and water. Complete oxidation is only possible at high pressures and temperatures using high-performance catalysts. During this technique, hydrogen is produced, which poses inherent safety risks and is costly [21, 22].

Another method to remove sulfide ions from sodium aluminate solution is by adding a precipitating or oxidizing chemical agent. The precipitating agent is used to precipitate S^{2-} or SO_4^{2-} (caused by sulfide oxidation) [9]. Barium salts or lime are used to remove SO_4^{2-} ions by the formation of $BaSO_4$ or $3CaO.Al_2O_3.CaSO_4.nH_2O$ precipitates

in the solution. It has been reported that zinc oxide removes S^{2-} ions by forming insoluble ZnS salt [11]. It has also been reported that desulfurization can be also performed by sodium ferrite by precipitation of $NaFeS_2.2H_2O$ through the reaction of $Fe(OH)_4^-$ and S^{2-} ions in aluminate solution. However, these desulfurization methods have insurmountable disadvantages such as the high cost of materials (barium salts and zinc oxide) and the low efficiency of lime. Another purpose of adding a chemical agent is removing sulfide by oxidation. Via this method, S^{2-} ions are first oxidized by a chemical agent such as H_2O_2 to produce sulfate and finally, sulfate ions are eliminated by adding the precipitating chemical agent [9].

On the other hand, there are standard methods 4500-S^{2-} to determine the concentration of sulfide in water and wastewater. In these standard methods, while categorizing the types of sulfides in water, wastewater, and sediment, different methods suitable for the determination of sulfides under various conditions and with different precision are described [23]. Also, other various methods have been developed for the determination of sulfide ions. These methods include spectrophotometry [24, 25], fluorescence [26], chemiluminescence [27], Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) [28,29], Atomic Absorption Spectrometry (AAS) [30], Flow Injection Analysis (FIA) [31], ion chromatography [32], electrochemical methods [33,34], etc. All the mentioned methods require expensive instruments and specific chemicals such as N, N-dimethylphenylene 1, 4-diamine [35], N, N-diphenylene-P-phenylenediamine [36], and so on. Hence, it is important to employ a facile and inexpensive method without the need for high-tech instruments to detect sulfide ions in the aluminate solution of the Bayer process.

In the current study, an indirect facile method was investigated for the determination of sulfide ions in the aluminate solution of Iran Alumina Company. This method can be applied in any industrial factory laboratory without the need for high-tech instruments and costly materials. On the other hand, because one of the sulfide removal methods in aluminate solution is the addition of oxidizing agents and it has been reported that the use of nitrate can control sulfide generation in oily waste [2], in the current investigation, the effect of nitrate was investigated as an oxidizing chemical agent to remove sulfide ions in aluminate solution.

EXPERIMENTAL SECTION

Chemicals and instrumentation

The bauxite used in the Bayer process was analyzed by X-Ray Fluorescence (XRF) (Siemens model SRS 3000) and the crystalline phases of bauxite minerals were studied using X-Ray Diffraction (XRD) (Siemens model D5000) and Scanning Electron Microscope (SEM) (LEO model 1450VP). To investigate the effect of nitrate ions on decreasing the sulfide content of aluminate solution, Hoffer autoclave, analytical balance with an accuracy of $\pm$ 0.0001 g, and $NaNO_3$ (Merck Co., Germany) were used. Analysis of the aluminate liquor was carried out by the titration method to determine the concentrations of Al_2O_3, Na_2O. The aluminate solution used in all experiments was obtained from evaporation spent liqueur in Iran Alumina Company (Jajarm, North Khorasan, Iran) and its chemical components are listed in Table 1.

To separate and determine sulfide ions from the aluminate solution concentrated HCl, $CuSO_4$, cadmium acetate ($Cd(AC)_2.2H_2O$), acetic acid (HAC), $Na_2S.9H_2O$, $Na_2S_2O_3.5H_2O$, Na_2CO_3, $K_2Cr_2O_7$, KI, I_2, H_2SO_4 (all chemicals produced by Merck Co., Germany), glassware (Fig. 1), a nitrogen cylinder, and an iodine flask were used. All aqueous solutions were prepared using double distilled water (DDW). The 1 g/L sulfide stock solution for calibration was prepared from sodium sulfide nonahydrate crystals by diluting 3.75 g $Na_2S.9H_2O$ to a final volume of 500 mL. The decomposition solution was prepared by adding 670 mL concentrated HCl (37%) to 330 mL DDW. The absorption solutions were attained by dissolving 15 g $Cd(AC)_2.2H_2O$ in DDW, 200 mL HAC, and diluting to 1L. The solution of 0.01 M sodium hyposulfite was prepared and standardized using potassium dichromate and potassium iodide in the presence of a starch indicator to obtain a green color after blue. The solution of 0.02 M iodine was prepared and standardized by standard sodium hyposulfite solution in the presence of a starch indicator until the blue color disappeared.

Experimental method for removal of sulfide ions

Sulfide removal experiments by adding sodium nitrate to the aluminate solution were carried out in the Hoffer autoclave at the digestion temperature of the Bayer process (270 °C). This autoclave is heated by an electric element and the experiment temperature can be controlled within the variation range of 1 °C. The aluminate solution prepared from the Jajarm alumina refinery (Table 1)

Table 1: Chemical components of sodium aluminate solution (concentration, g/L).

Na_2O_T	Na_2O_k	Al_2O_3
306	266	138

Note: Na_2O_T= Total soda (as Na_2O), Na_2O_K= Caustic soda (as Na_2O)

Was poured into a 2-liter, stainless steel chamber of this autoclave. The chamber was completely sealed during the experiment and its contents were stirred with a mechanical stirrer. The autoclave chamber pressure was about 52 bar corresponding to its temperature. The duration of the experiment was 60 minutes. The concentration of sulfide ions in aluminate solution before and after the experiment was determined by the methods developed in this research.

Development the new methods for the separation and determination of sulfide ions in aluminate solution

5.00 mL of aluminate liquor sample obtained from the Bayer process together with 30 mL DDW were poured into a three-necked balloon. 50 mL of decomposition liquor was poured into a separating funnel and 20 mL of DDW was poured into a bottle washer. 40 mL of absorption liquor was poured into the two absorption bottle separately and the testing apparatus was coupled according to Fig. 1.

First, the nitrogen gas stream was inserted the system to purge the oxygen. After 5 min, the nitrogen stream was stopped and the decomposition solution was inserted into the three-necked balloon through the separating funnel. The nitrogen stream was reopened and the bottom of the balloon was heated by an electric heater or alcohol burner to accelerate the reaction. After 20 min of heating and absorption, the heating of the bottom of the bottle washer was continued by another alcohol burner until partial boiling of the solution to avoid the dissolution of H_2S in the water. The heating was then stopped and the air was allowed into the system for 5 min to complete the absorption. The absorption bottles were separated, the absorption solutions of the two bottle washers were mixed, and the connecting tubes were washed with DDW and added to the absorption solution. An appropriate amount of iodine was added accurately to the absorption bottle according to the quantity of sedimentation. After 3 min of storage in a dark place, 25 mL DDW was added to it and it was titrated by standard sodium hyposulfite solution until the pale yellow color appeared. Afterward, 3 mL starch solution was added to it was continued until it became colorless. The concentration of sulfide ions (g/L) was calculated from Eq. (2).
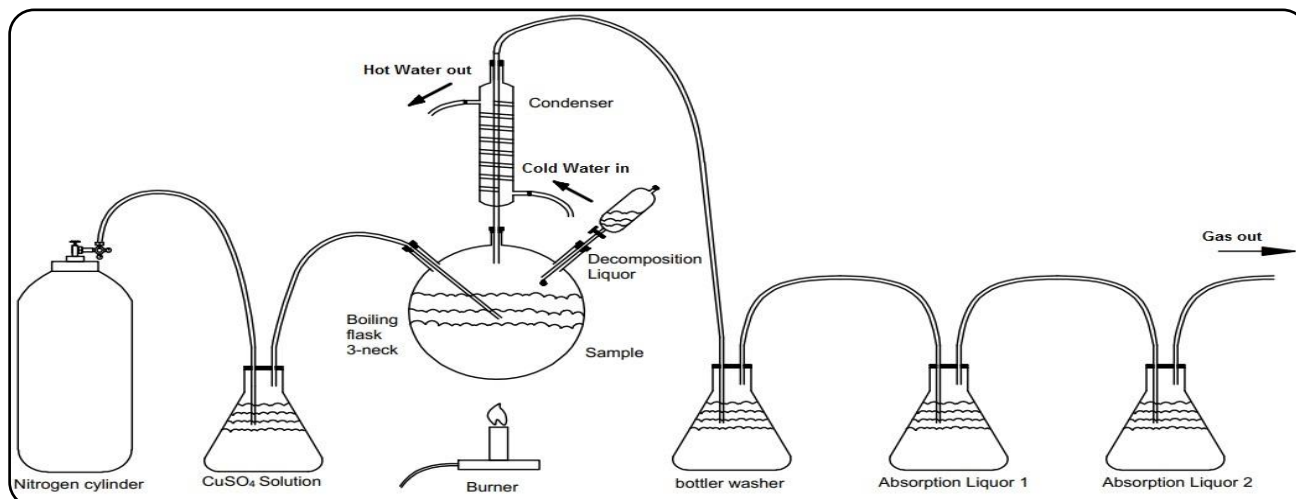
Fig. 1: Schematic of the apparatus required for the separation of sulfide ions from the Bayer process aluminate solution.
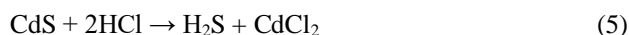
$$C(S^{2-}) = \frac{C_1 V_1 - C_2 V_2}{2V_0} \times 32 \tag{2}$$

Where, C_1 is the concentration of the standard iodine solution (mol/L), C_2 is $Na_2S_2O_3$ concentration (mol/L), V_1 is the volume of the standard iodine solution (mL), V_2 is the volume of the standard $Na_2S_2O_3$ solution (mL) and V_0 is the sample volume (mL).

RESULTS AND DISCUSSION

Sulfide determination in aluminate solution

When the decomposition solution was added to the sodium aluminate solution, sulfide ions in the liquor were converted to H_2S. Then it flowed on the $Cd(AC)_2$ absorption solution, which CdS sediment was obtained. By adding proper amounts of HCl and iodine, another sediment was obtained. Excess iodine was then titrated by the standard sodium hyposulfite solution and the concentration of sulfide ions (S^{2-}) in the sodium aluminate solution was calculated.

$$S^{2-} + HCl \rightarrow H_2S + 2Cl^- \tag{3}$$

$$H_2S + Cd(AC)_2 \rightarrow CdS + 2HAC \tag{4}$$

$$CdS + 2HCl \rightarrow H_2S + CdCl_2 \tag{5}$$

$$H_2S + I_2 \rightarrow 2HI + S \tag{6}$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \tag{7}$$

Accuracy and precision evaluation of the method

Since titration is an absolute method, the linearity can be obtained directly. For this, five different concentrations of sulfide solution were titrated in the range of 0.001 to 1 g/L and a linear regression of the sulfide concentration versus the consumed titrant volume at the equivalence point was established. The coefficient of determination (R^2) was used to evaluate linearity. R^2 equal to 0.9997 was obtained, which indicates that the determination method is highly linear in this range.

Also, by standard addition method and adding standard sodium sulfide to the sodium aluminate solution of Bayer process, the recovery rate and the interference of other impurities were investigated. The results showed that in aluminate solution samples (n=6), more than 98% of the sulfide added was recovered by this method and it was found that impurities and other compounds in the aluminate solution did not create a significant error in this method. The reproducibility of this determination method was investigated in 10 samples of sodium aluminate solution by calculating the standard deviation and relative standard deviation. S=0.012 and RSD=5.46% were obtained, indicating that this determination method of sulfide has good precision. Finally, the concentration average of sulfide ions in 10 different samples prepared from Bayer process of Iran Alumina Company was 0.224 g/L.
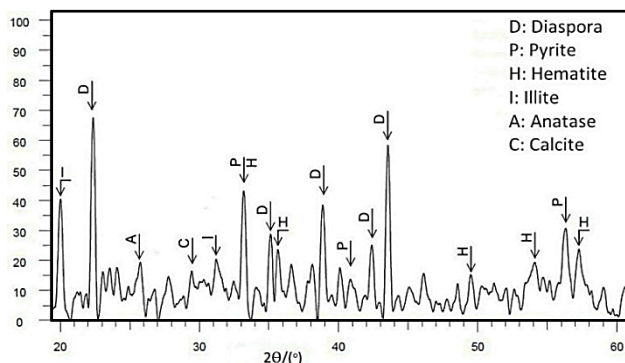
Chemical composition of the bauxite

To investigate the source of sulfide ions in the aluminate solution of the Bayer process, Jajarm bauxite was analyzed by XRF. The results are shown in Table 2.

The values in Table 2 indicate that SO_3 was present in significant amounts (0.16%) in the bauxite. As previously mentioned sulfide ions produced from the digestion of

Table 2: Chemical composition of Jajarm bauxite (mass fraction, (%)).

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	SO_3	CaO	MgO
48.38	12.07	19.77	3.70	0.16	2.51	0.40
K_2O	P_2O_5	Na_2O	V_2O_5	Cr_2O_3	MnO	L.O.I
0.36	0.05	0.06	0.16	0.10	0.22	12.04

D: Diaspora
P: Pyrite
H: Hematite
I: Illite
A: Anatase
C: Calcite

Fig. 2: X-ray diffraction pattern of Jajarm Bauxite.

bauxite can accumulate in the aluminate solution of the Bayer process and show negative effects on the alumina production process.

Bauxite mineralogy analysis

In addition to analyzing the chemical composition of Jajarm bauxite, it was necessary to determine the mineralogy of the source of sulfide production in aluminate solution. Thus, the bauxite was analyzed for the presence of sulfide-containing minerals (pyrite) by XRD. Fig. 2 shows the XRD pattern of the bauxite.

For this, first, a standard quartz sample was used to calibrate the device. After ensuring the calibration of the device, the target sample was analyzed. "Evaluation" software, which was installed on the device by the manufacturer, was then used to search for mineral peaks.

This process is completely systematic and automatic. As shown in Fig. 2, diaspora, illite, hematite, anatase, calcite and pyrite were present in the bauxite sample of Jajarm. As can be seen in the figure, the pyrite crystals were detected at 2-Theta ~ 56.4°, 40.8°and 33.2°. Consequently, pyrite was considered the main source of sulfide ions in the solution.
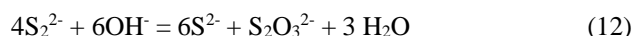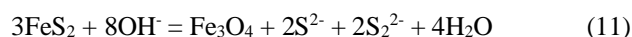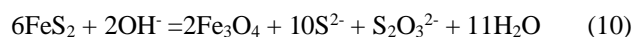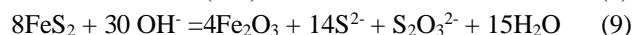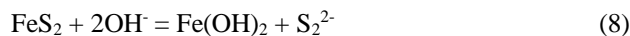
SEM observations

To accurately investigate the presence of sulfide-containing minerals in Jajarm bauxite, this sample was studied by SEM, which is shown in Fig. 3.
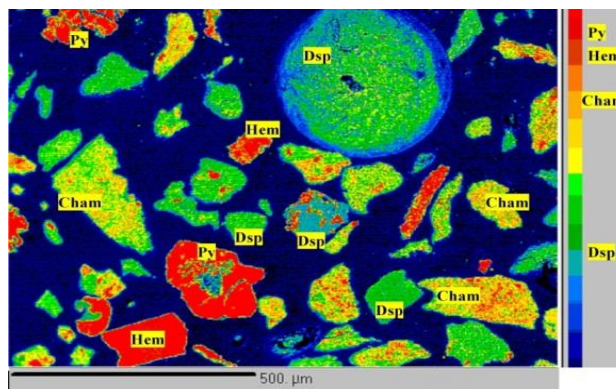
Fig. 3: SEM micrograph of Jajarm bauxite.

SEM images obtained for minerals are usually black and white. The device used in the research has ability to display it in color. For this, the various phases were painted from low density (cold color like blue) to high density (warm color like red). The blue color (background) in the image is related to an adhesive (a type of polymer) which was used to hold minerals that were crushed to degrees of freedom. As shown in Fig. 3, pyrite (Py) was detected along with other minerals such as diaspora (Dsp), hematite (Hem), chamosite (Cham). Thus, the XRD pattern and SEM micrograph confirmed that the main source of sulfide ions in the aluminate solution was pyrite.

Investigation of pyrite reactions in alkaline medium

The pyrite in bauxite can easily react with alkaline aluminate liquor during the Bayer process. First, iron-hydroxyl complexes are formed by the reaction of Fe^{2+} with OH^- on the surface of pyrite in sodium aluminate solution, then the complexes detach from the surface of pyrite and sulfur enter the solution in the form of S^{2-}. Pyrite can also be converted to sulfide ion through reactions 8-12 in an alkaline medium [12].

$$FeS_2 + 2OH^- = Fe(OH)_2 + S_2^{2-} \tag{8}$$

$$8FeS_2 + 30\,OH^- = 4Fe_2O_3 + 14S^{2-} + S_2O_3^{2-} + 15H_2O \tag{9}$$

$$6FeS_2 + 2OH^- = 2Fe_3O_4 + 10S^{2-} + S_2O_3^{2-} + 11H_2O \tag{10}$$

$$3FeS_2 + 8OH^- = Fe_3O_4 + 2S^{2-} + 2S_2^{2-} + 4H_2O \tag{11}$$

$$4S_2^{2-} + 6OH^- = 6S^{2-} + S_2O_3^{2-} + 3\,H_2O \tag{12}$$

The rationalization for the selection of nitrate as a sulfide removal agent

In this study, a substance must be selected to remove sulfide ions from the alumina production process liquor, which did not have adverse effects on the process and final

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products. Nitrate was selected as a sulfide ion removal agent from the Bayer process after careful rationalizations. The major advantages and disadvantages of selecting nitrate as a desulfurization agent are presented below.

Advantages
• Nitrate has a high solubility in the aluminate solution.
• Nitrate has no adverse effect on the quality and chemical properties (purity) of alumina.
• Nitrate has no negative effect on the physical properties of alumina (grain size, angle of depose, etc.) due to its solubility, which does not interfere with the granulation of aluminum hydroxide.
• Nitrate does not adversely affect any of the stages of the Bayer process including precipitation and calcination.
• Products of nitrate reaction with sulfide ions are not in the form of sediment or colloid.
• Products of nitrate reaction with sulfide ions (sulfates and nitrites) are stable and not corrosive to metals.
• The use of nitrate on an industrial scale is economical.
• Transportation, storage, and use of nitrate on an industrial scale are convenient and safe.
• The use of nitrate does not lead to environmental pollution.
• Nitrate salts (such as sodium nitrate, potassium nitrate, and calcium nitrate) are easily accessible.
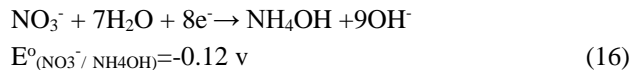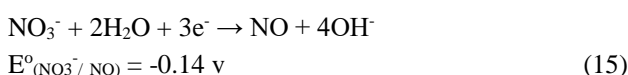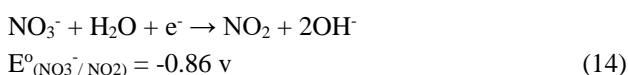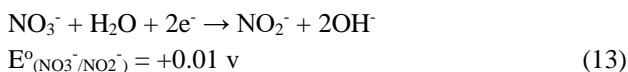
Disadvantages
• Nitrate is a weak oxidant.
• To complete the sulfide ion removal reaction and prevent the production of colloidal products, nitrate should be used higher than its stoichiometric ratio.
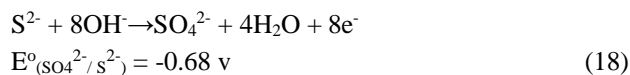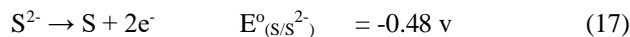
Thermodynamics of nitrate and sulfide reactions

To predict the spontaneity of oxidation-reduction reactions of nitrate and sulfide, the potential of standard electrodes of possible reactions in an alkaline medium (pH=14) was investigated [37].
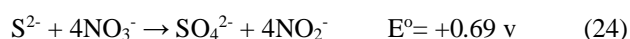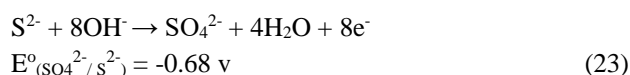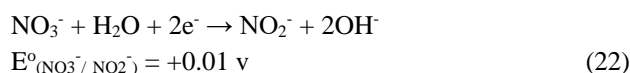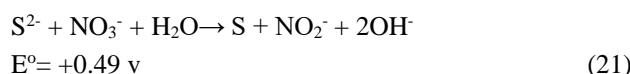
Nitrate Reduction

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$E^o_{(NO3^-/NO2^-)} = +0.01 \text{ v} \tag{13}$$

$$NO_3^- + H_2O + e^- \rightarrow NO_2 + 2OH^-$$
$$E^o_{(NO3^-/NO2)} = -0.86 \text{ v} \tag{14}$$

$$NO_3^- + 2H_2O + 3e^- \rightarrow NO + 4OH^-$$
$$E^o_{(NO3^-/NO)} = -0.14 \text{ v} \tag{15}$$

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4OH + 9OH^-$$
$$E^o_{(NO3^-/NH4OH)} = -0.12 \text{ v} \tag{16}$$

Sulfide Oxidation

$$S^{2-} \rightarrow S + 2e^- \qquad E^o_{(S/S^{2-})} = -0.48 \text{ v} \tag{17}$$

$$S^{2-} + 8OH^- \rightarrow SO_4^{2-} + 4H_2O + 8e^-$$
$$E^o_{(SO4^{2-}/S^{2-})} = -0.68 \text{ v} \tag{18}$$

Since the total reaction potential is obtained from the equation $E = E_{Red} - E_{Ox}$, E must be positive for spontaneous (galvanic) reactions. A comparison between the standard electrode potentials of nitrate and sulfide half-reactions showed that in an alkaline medium (pH=14) the reduction of NO_3^- to NO_2 (nitrogen dioxide) thermodynamically was impossible, while the probability of reduction of NO_3^- to NO and NH_4OH was very low. The only possible reaction (with a high percentage) was the reduction of NO_3^- to NO_2^- (nitrite). However, oxidation of S^{2-} to either S or SO_4^{2-} was thermodynamically possible. Therefore, possible reactions were:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$E^o_{(NO3^-/NO2^-)} = +0.01 \text{ v} \tag{19}$$

$$S^{2-} \rightarrow S + 2e^- \qquad E^o_{(S/S^{2-})} = -0.48 \text{ v} \tag{20}$$

$$S^{2-} + NO_3^- + H_2O \rightarrow S + NO_2^- + 2OH^-$$
$$E^o = +0.49 \text{ v} \tag{21}$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$E^o_{(NO3^-/NO2^-)} = +0.01 \text{ v} \tag{22}$$

$$S^{2-} + 8OH^- \rightarrow SO_4^{2-} + 4H_2O + 8e^-$$
$$E^o_{(SO4^{2-}/S^{2-})} = -0.68 \text{ v} \tag{23}$$

$$S^{2-} + 4NO_3^- \rightarrow SO_4^{2-} + 4NO_2^- \qquad E^o = +0.69 \text{ v} \tag{24}$$
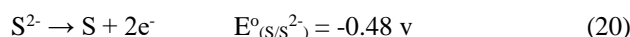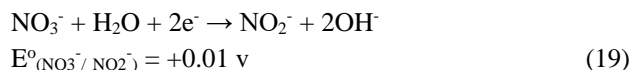
Due to the positive value of E^o for reactions 21 and 24, it was concluded that these reactions were spontaneous (galvanic). Also, because nitrate was not a strong oxidant, it was predicted that for significant sulfide oxidation, the amount of nitrate required should be higher than the stoichiometric ratio.

Effect of nitrate concentration on sulfide removal in aluminate solution

To study the effect of nitrate concentrations on the elimination of sulfide ions and optimizing the efficiency factors, several experiments were designed and performed. First, a sample with the proper volume of sodium aluminate solution of Bayer process was prepared (Table 1).
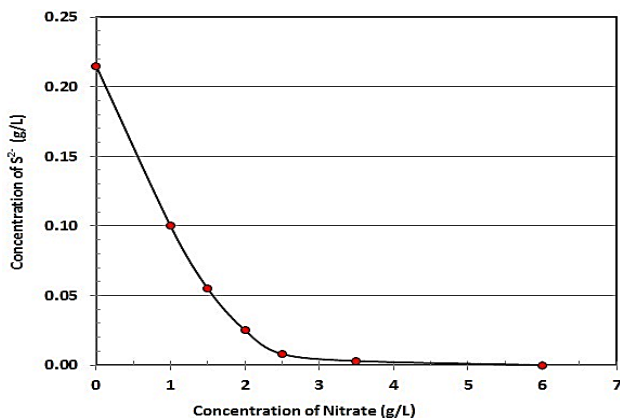
Fig. 4: Effect of different concentrations of nitrate on sulfide removal in aluminate solution (at 270 ºC under the pressure of 52 bar for 1 h)

Sulfide ions were separated and determined in the aluminate solution, which was prepared by the method mentioned in the experimental section. Different concentrations of nitrate (1, 1.5, 2, 2.5, 3.5, and 6 g/L) were added to the individual samples of aluminate solution. To simulate the Bayer process conditions, in terms of temperature, pressure, and time, the above solutions were poured into the autoclave chamber mentioned in the experimental section. In the autoclave, the solution was heated and stirred at 270 ºC under the pressure of 52 bar for 60 minutes. After the separation and determination of residual sulfide ions in aluminate solution with the method mentioned in the experimental section, the initial and residual concentrations of sulfide ions were compared. The sulfide removal efficiency was calculated at different concentrations of nitrate and the obtained results were plotted (Fig. 4).

As can be seen, in practical conditions of bauxite digestion during the Bayer process (at 270 ºC under the pressure of 52 bar for 1 h) by adding nitrate to the aluminate solution, sulfide ions could be completely eliminated. Since the majority of sulfide ions (more than 96%) were removed by adding 2.5 g/L nitrate ions, it was considered the most optimum amount of nitrate to neutralize sulfide. Due to the circulation of aluminate solution during the Bayer process and the infinite reaction time of nitrate with sulfide in the process, the sulfide removal reaction could be practically completed at this concentration. As predicted, because nitrate was a weak oxidant, its optimum amount for sulfide removal exceeded the stoichiometric ratio. Moreover, due to the high solubility of nitrate and its reaction products, it had no adverse effect on the Bayer process and the quality of the final obtained alumina. Furthermore, it was expected that the corrosion of transmission tubes and equipment significantly lowered by this method.

CONCLUSIONS

A practical and inexpensive method for the separation and determination of sulfide ions in the aluminate solution of the Bayer process was studied. This method can be applied in any industrial factory laboratory without the need for special equipment and materials. The concentration of sulfide ions in the Bayer process liquor of Iran Alumina Company (Jajarm, North Khorasan, Iran) was indirectly determined successfully. The average concentration of sulfide ions in the sodium aluminate solution was 0.224 g/L and the relative standard deviation was RSD = 5.46%. To investigate the source of sulfide ions in the aluminate solution, the bauxite used in the Bayer process was examined by XRF. Additionally, to study the presence of sulfide-containing minerals (such as pyrite) XRD and SEM analyses were carried out. It was found that pyrite was the main source of sulfide ions in the aluminate solution of the Bayer process. Various sulfide removal methods applicable in the Bayer process were studied and the advantages and disadvantages of sulfide removal method by nitrate from aluminate solution were investigated. Thermodynamically, the spontaneity of different half-reactions during the reduction of NO_3^- and oxidation of S^{2-} in aluminate solution was studied. Because of the significant advantages and low disadvantages, nitrate was selected as a sulfide ion removal agent from the solution of the Bayer process. The results demonstrated that in practical conditions of bauxite digestion during the Bayer process (at 270 °C, 52 bar, and 60 minutes), the sulfide ions could be almost completely eliminated by adding nitrate to the aluminate solution. Since the majority of sulfide ions (more than 96%) were removed by adding 2.5 g/L nitrate ions it was considered as the optimum nitrate concentration to neutralize sulfide ions.

Abbreviations

Double Distilled Water	DDW
X-Ray Fluorescence	XRF
X-Ray Diffraction	XRD
Scanning Electron Microscope	SEM
Acetic Acid	HAC

Cadmium Acetate	Cd(AC)$_2$
Relative Standard Deviation	RSD
Pyrite	Py
Diaspora	Dsp
Hematite	Hem
Chamosite	Cham

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