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Corrosion Study of A516 Grade 70 Steel in Sodium Aluminate Solution of Bayer Process Containing Sulfide and Determination of Sulfide by a Practical Method

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Abstract

Sulfide ions in the Bayer process solution can accelerate the corrosion of steel equipment. In the present research, after determining the concentration of sulfide ions in sodium aluminate solution of Bayer process by a developed method and investigating the source of sulfide in the aluminate solution, the corrosion rate of A516 grade70 steel pieces in the presence of S^{2-} ion was investigated. For this purpose, the corrosion of pieces of A516 grade70 steel in dimensions (5x15x25 mm) in concentrations of 0.2 to 0.6 g/L of sulfide ions was investigated for 5 days inside the autoclave under conditions similar to the Bayer process. The corrosion rate was calculated using the method of measuring the weight loss of steel samples. In addition, the corrosion rate of steel pieces in the pure sulfide solution and in the aluminate solution whose sulfide was neutralized by nitrate was investigated and compared. The results demonstrated that steel corrosion rate in the presence of pure sulfide is very insignificant. However, steel corrosion rate in aluminate solution containing sulfide, even with small quantities, is significant.

Keywords: Corrosion, A516 steel, Sulfide, Aluminate solution, Bayer process.

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Introduction

All over the world, one of the following two main processes does the industrial production of alumina (Al2O3): (1) Bayer process (2) Sintering process. Nowadays, the Bayer process is the most common and economical industrial method of producing alumina from bauxite due to its low cost [1]. In the Bayer process, caustic soda is used at a temperature of more than 270 ^{o}C to dissolve hydrated aluminum oxide from diasporic bauxite (Eq. 1).

$$Al_2O_3.H_2O\ (s) + 2NaOH\ (aq.) = 2NaAlO_2\ (aq.) + 2H_2O \qquad (1)$$

The presence of sulfide ions in the Bayer process solution, even in small quantities, causes many problems for the alumina production industry. To reduce harmful effects of the presence of sulfide ions in aluminate solution and to remove sulfide in this solution, various methods have been studied and investigated [2, 3].

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 [4-7].

Corrosion is an electrochemical reaction between a substance (usually a metal) and its surrounding environment, which will lead to a change in the properties of the substance. Because thermodynamically oxidized materials are at a lower level of energy compared to materials in a normal state, so the tendency to reach a lower energy level causes the metal to corrode. The most common method to study corrosion is to express the amount of corrosion as a corrosion rate. Corrosion rates are usually expressed in millimetres per year (mm/yr.) [8, 9].

The studies carried out to investigate the corrosion of steel in sodium aluminate solution or Bayer process liquor demonstrate that in alumina production factories due to special operating conditions such as: high temperature and pressure, the use of concentrated caustic soda and the presence of species such as OH^-, AlO_2^- and S^{2-}, the phenomenon of corrosion occurs frequently. In addition, these studies show the effect of sulfide on the corrosion of steel in two alumina production plants in Russia. In a factory where the amount of sulfide in its process liquor was 0.02 g/L, equipment corrosion occurred in the early years of operation, while in another factory where there was no sulfide ions in its liquor, corrosion occurred after 12 to 20 years [10]. Hui Fu *et al* [11] studied the effect of Na_2S on the corrosion behaviour of Q345 steel in sodium aluminate solution and they showed that the corrosion of steel is accelerated by increasing the concentration of S^{2-}. The obtained results indicated that corrosion products mainly include FeO, FeS and FeOOH. Hazlewood *et al* [12, 13] found that the corrosion resistance of carbon steels in caustic soda solution containing sulfide depends on the formation of a stable passive film on the metal surface. By changing processes in chemical concentrations and temperature parameters, the corrosion rate of the system also changes. They also found that the corrosion rate of carbon steel increases by increasing concentration of Na_2S in hot sodium hydroxide solution. Some other studies indicate that S^{2-} and NaOH accelerate metal corrosion due to their inhibition of passive protective film formation [14, 15]. In addition, Chasse *et al* [16] found that the surface films that formed in the caustic solution containing sodium sulfide were defective due to sulfide adsorption, which causes the instability of the passive film and leads to the formation of insoluble metal sulfide compounds. Su'E Liu *et al* [17] studied the stress corrosion cracking (SCC) of pressure vessel steels in caustic aluminate solutions. While studying the SCC behaviour of three types of pressure vessel steel at high temperature (200-300^{o}C) in aluminate solution, they showed that stress corrosion cracking increases with increasing temperature. Huy Ha Le *et al* [18] have evaluated the effect of Bayer Liquor impurities on stress cracking of steel used in alumina industry by the slow strain rate tests. They proved that among different species, AlO_2^- ions have the greatest effect on SCC of steel and increase the brittleness of steel by 25%.

On the other hand, various methods have been developed for determination of sulfide ions. These methods include spectrophotometry [19, 20], fluorescence [21], chemiluminescence [22], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [23, 24], atomic absorption spectrometry (AAS) [25], flow injection analysis (FIA) [26], ion chromatography [27], electrochemical methods [28, 29], etc. In addition, 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 determination sulfides under various conditions and with different precision are described [30].

All the mentioned methods require expensive instruments and specific chemicals such as N, N-dimethylphenylene 1, 4-diamine [31], N, N-diphenylene-P-phenylenediamine [32], etc. 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 need for high-tech instruments and costly materials.

On the other hand, field investigation of caustic soda liquor transmission pipelines, caustic soda storage tanks and equipment used in Jajarm alumina factory by the authors showed that a significant number of factory equipment were corroded. Therefore, investigating the causes of steel corrosion used in most of the equipment of this industry seemed necessary. As a result, by providing conditions similar to the Bayer process (in terms of temperature, pressure and time), the effect of sulfide ion on the corrosion rate of A516 grade 70 steel pieces was investigated. Finally, by removing sulfide in the aluminate solution of the Bayer process using a completely effective method, in order to prevent corrosion, the corrosion rate of A516 grade 70 steel was investigated again.

Experimental

Chemicals and instrumentation

The bauxite used in the Bayer process was analysed 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 also, an analytical balance with an accuracy of ±0.0001 g was used to weigh materials. Sodium aluminate solution samples were obtained from the process of Iran Alumina Company (Jajarm, North Khorasan, Iran) and were analysed by titration method to determine the concentration of Al_2O_3 and Na_2O.

To separate and determine sulfide ions from the aluminate solution $Na_2S.9H_2O$, $Na_2S_2O_3.5H_2O$, Na_2CO_3, $K_2Cr_2O_7$, KI, I_2, H_2SO_4, $CuSO_4$, concentrated HCl, cadmium acetate ($Cd(Ac)_2.2H_2O$), acetic acid (HAc), (all chemicals produced by Merck Co., Germany), glassware (Figure 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 0.01M sodium thiosulfate 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 thiosulfate solution in the presence of a starch indicator until the blue color was disappeared.

To investigate the effect of sulfide on steel corrosion, carbon steel pieces (A516 grade 70) with dimensions (5x15x25 mm), Hofer autoclave made in Germany (to provide the necessary conditions: 150 bar and 300 ^{o}C), analytical balance with accuracy ±0.0001 g, desiccator, $Na_2S.9H_2O$ and $NaNO_3$ (both produced by Merck co.), and sodium aluminate liquor (prepared by Bayer process of Iran Alumina Company) were used.

The chemical composition of A516 grade 70-carbon steel used to investigate the effect of sulfide on steel corrosion is shown in Table 1.

Table 1. Chemical composition of A516 grade 70 steel (%)

C	**Mn**	**P**	**S**	**Si**	**Cu**	**Ni**	**Cr**	**Mo**	**Fe**
0.31	0.85-1.20	0.035	0.040	0.15-0.40	0.044	0.025	0.033	0.004	Rest

Development new methods for 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 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 Figure 1.

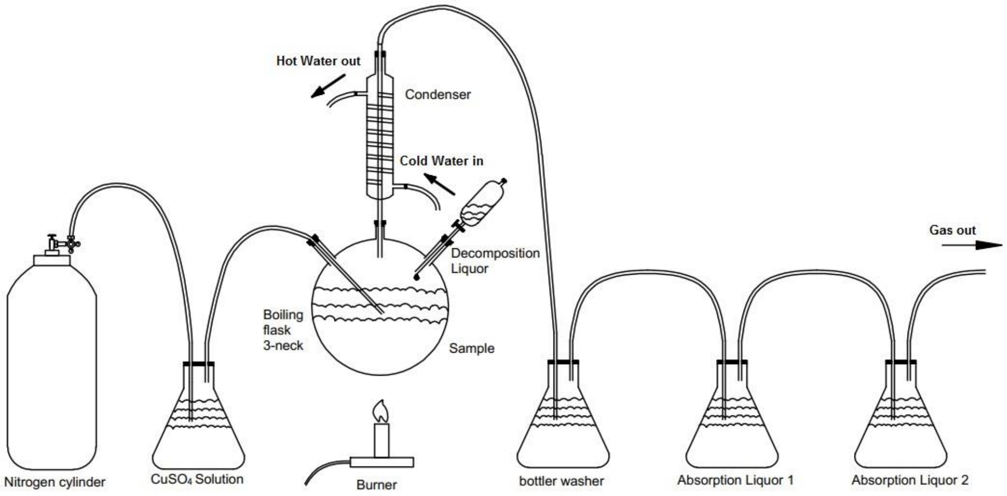

Figure 1. Schematic of the apparatus required for the separation of sulfide ions from the Bayer process aluminate solution.

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 an electric heater or alcohol burner to accelerate the reaction heated the bottom of the balloon. After 20 min of heating and absorption, another alcohol burner continued the heating of the bottom of the bottle washer 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 to 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 thiosulfate solution until the pale yellow colour appeared. Afterward, 3 mL starch solution was added to it was continued until it became colourless. The concentration of sulfide ions (g/L) was calculated from Eq. (2).

$$C_{S^{2-}} = \frac{C_1V_1 - C_2V_2}{2V_0} \times 32 \qquad (2)$$

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).

Preparation of aluminate solution with different concentrations of added sulfide

In order to provide conditions similar to Bayer process (alumina production) for testing steel corrosion, sodium aluminate liquor was prepared in the required quantity of Jajarm alumina production plant. The aluminate solution was prepared with different concentrations of added sulfide (0.2, 0.4 and 0.6 g/L). For this purpose, precise amounts of sodium sulfide salt ($Na_2S.\ 9H_2O$) were weighed and added to volumetric flasks and its volume was filled to the mark. After stirring the solution inside the balloon, the solution was placed in a suitable place to completely dissolve the sulfide in the aluminate solution.

Preparation of carbon steel samples for corrosion test

A516 grade 70 carbon steel samples were cut in specific dimensions (5mm x 15mm x 25mm) and with the same area. Before the test, the samples were washed with distilled water and polished with silicon carbide paper 180, 240, 360 and 600, respectively. All steel samples were degreased with acetone and thoroughly cleaned with distilled water and dried with cold air and kept in a desiccator. Then each one was weighed with an analytical balance with an accuracy of ±0.0001 grams.

Corrosion test conditions of carbon steel in aluminate solution containing sulfide

All corrosion tests were performed at 150±1 °C for 5 days (120 hours) in an autoclave with a stainless steel tank and with external temperature control (Figure 2). It took approximately 1 hour for the autoclave to reach the test temperature. After the specified time for the corrosion test, the autoclave was cooled and turned off, and then the sample was taken out of the autoclave. After the corrosion process, the samples were washed with the prepared solution (500 ml hydrochloric acid + 500 ml deionized water + 10 g hexamethylene tetramine), finally washed with distilled water, and dried by cold air.

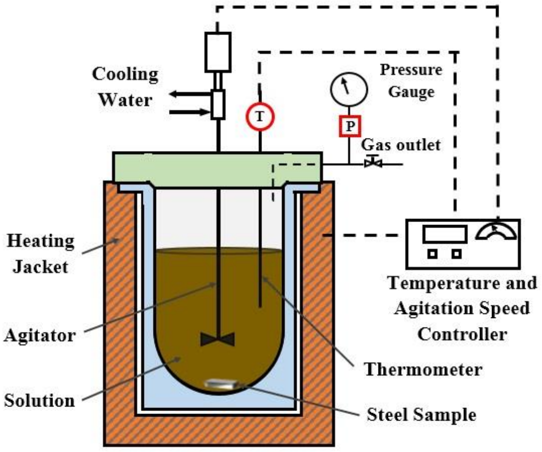

Figure 2. Schematic of autoclave used for corrosion test.

This experiment was performed to investigate the corrosion of carbon steel samples in normal sodium aluminate solution (without adding sulfide ions) and aluminate solution with specific amounts of sulfide. After each experiment, the carbon steel samples were weighed by an analytical balance with an accuracy of ±0.0001 g. The average corrosion rate was calculated from the weight change of the samples during the test. The values reported in this research are the average of two measurements.

Calculation of carbon steel corrosion rate

The corrosion rate was calculated by measuring the weight loss of the steel sample and using equation number 3.

$$R = \frac{W_1 - W_2}{A.t.d} \times 8.76 \times 10^4 \qquad (3)$$

Where, "R" is corrosion rate (mm/yr), W_1 is sample weight before corrosion test (g), W_2 is sample weight after corrosion test (g), "A" is surface area of steel sample (cm^2), "t" is Corrosion time (h) and "d" is the density of tested steel (g/cm^3).

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 was 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 thiosulfate solution and the concentration of sulfide ions (S^{2-}) in the sodium aluminate solution was calculated.

$$S^{2-} + HCl \rightarrow H_2S + 2Cl^- \qquad (4)$$

$$H_2S + Cd(AC)_2 \rightarrow CdS + 2HAC \qquad (5)$$

$$CdS + 2HCl \rightarrow H_2S + CdCl_2 \qquad (6)$$

$$H_2S + I_2 \rightarrow 2HI + S \qquad (7)$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \qquad (8)$$

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 linear in this range.

In addition, by standard addition method and adding standard sodium sulfide to 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 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.

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

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

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 bauxite can accumulate in the aluminate solution of the Bayer process and show the 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 in aluminate solution. Thus, the bauxite was analyzed for the presence of sulfide-containing minerals (pyrite) by XRD. Figure 3 shows the XRD pattern of the bauxite.

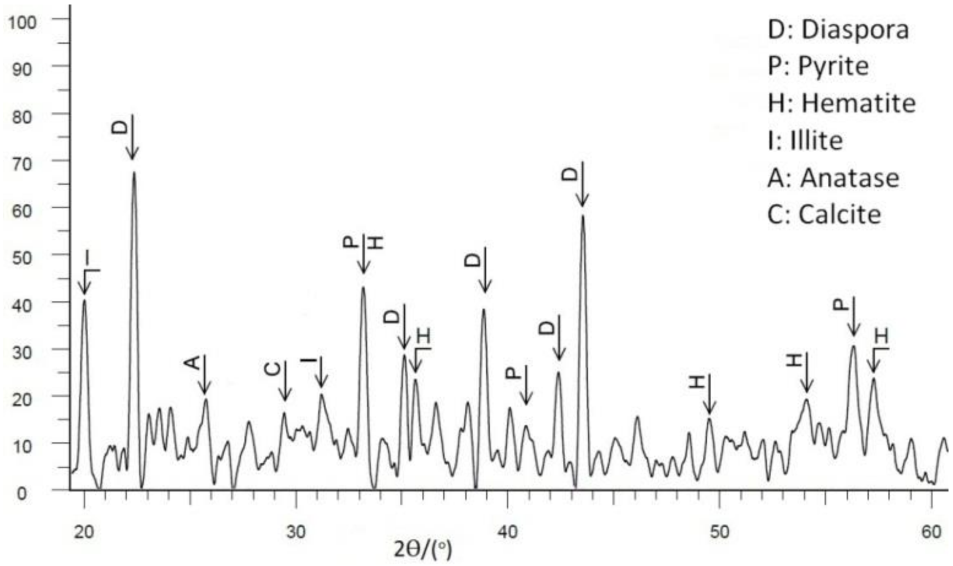

Figure 3. X-ray diffraction pattern of Jajarm Bauxite.

For this purpose, 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 automatic. As shown in Figure 3, 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 as the main source of sulfide ions in the solution.

The chemical composition of aluminate solution to investigate the effect of sulfide on steel corrosion

The sodium aluminate solution used in all the tests to investigate the effect of sulfide on steel corrosion was obtained from the evaporated spent liquor at Iran Alumina Company and its chemical composition is given in Table 3.

Table 3. Chemical components of sodium aluminate solution (concentration, g/L).

Na_2O_T	Na_2O_k	Al_2O_3	S^{2-}
306	266	138	**0.215**

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

Measuring the corrosion rate of carbon steel in sodium aluminate solution containing sulfide

The average results of two times of corrosion testing of carbon steel samples in sodium aluminate solution prepared from the Bayer process of Jajarm alumina factory, which contains different amounts of sulfide, are given in Table 4 and Figure 4.

Table 4. Weight loss of steel piece (corroded) in sodium aluminate solution with different concentrations of sulfide added

Test No	**1**	**2**	**3**	**4**
Sulfide concentration added to sodium aluminate solution (g/L)	0	0.2	0.4	0.6
Weight loss of steel piece after corrosion test (g)	0.0627	0.0690	0.0712	0.0763

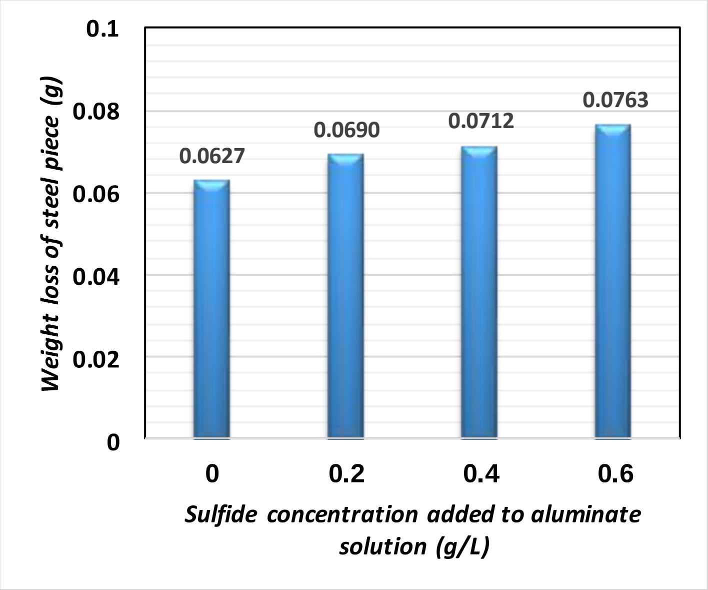

Figure 4. Weight loss of steel piece (corroded) in sodium aluminate solution with different concentrations of sulfide added.

Based on the weight loss values of the steel pieces obtained in the corrosion test and using the formula (Eq. 3), the corrosion rate of these pieces in the sodium aluminate solution of the Bayer process in the conditions of "without adding sulfide" and "with different concentrations of sulfide added" can be calculated. The corrosion rate of these pieces is shown in Figure 5.

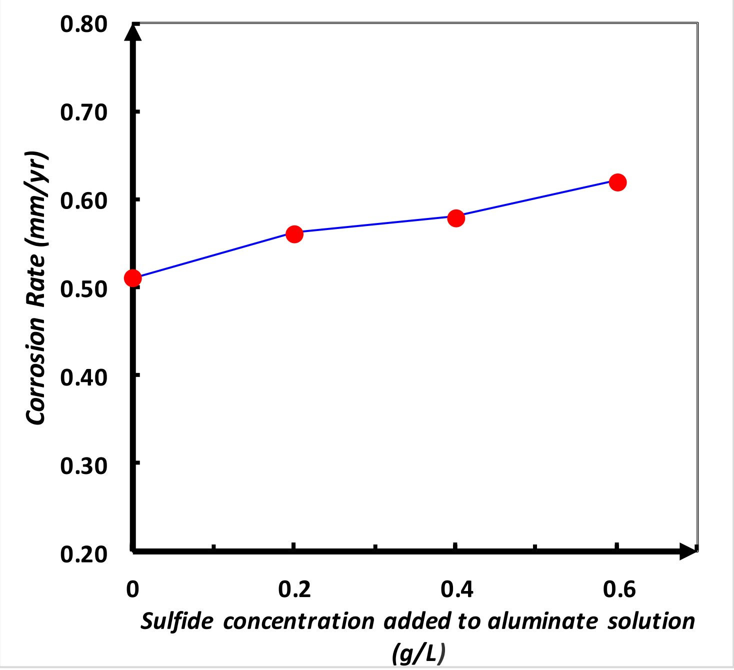

Figure 5. Corrosion rate of carbon steel piece in aluminate solution with different concentrations of added sulfide.

Interpretation of carbon steel corrosion in sodium aluminate solution containing sulfide

As figure 5 shows, the amount of weight loss of carbon steel piece (A516 grade 70) and its corrosion rate in sodium aluminate solution of Bayer process "without adding sulfide ions" (of course with natural sulfide ions of Bayer process) is about 0.51 mm per year. By increasing the concentration of sulfide added to aluminate solution from 0.2 g/L to 0.6 g/L, the corrosion rate of the steel increases. This indicates that sulfide ions have a significant effect on the corrosion of the tested steel piece, and with the increase of sulfide ions in the liquor; the corrosion process of the steel pieces increases. If the corrosion occurs in high stress areas of steel equipment, sulfide ions will increase the rate of corrosion and ultimately cause the destruction of the equipment. This test clearly demonstrates the role of sulfide in the occurrence and increase of the corrosion rate of steel pieces, and it is necessary to prevent the occurrence of corrosion and remove or reduce the corrosion-accelerating factor (sulfide).

The mechanism of steel corrosion intensification in aluminate solution in the presence of sulfide

The studies conducted on the effect of Na_2S on the corrosion behavior of steel in sodium aluminate solution show that with increasing concentration of S^{2-}, corrosion of steel accelerates and the corrosion products mainly include FeO, FeS and FeOOH. In addition, the results of these studies indicate that in sodium aluminate solution, corrosion reactions mainly occur in the interface between matrix and sodium aluminate environment. The corrosion mechanism of steel in sodium aluminate solution containing caustic soda and sulfide ions is shown in Figure 6. At first, steel corrosion starts with the absorption of OH^- on its surface (**a**). Due to the reaction of Fe and OH^-, a stable passive film is created and the protective film prevents the contact between corrosive environment and sample surface (**b**). Therefore, the rate of corrosion slows down temporarily. However, due to the continuous adsorption of S^{2-} on the interface, more FeS is produced (**c**) and damages the previously passive film, resulting in accelerated corrosion (**d**) [11].

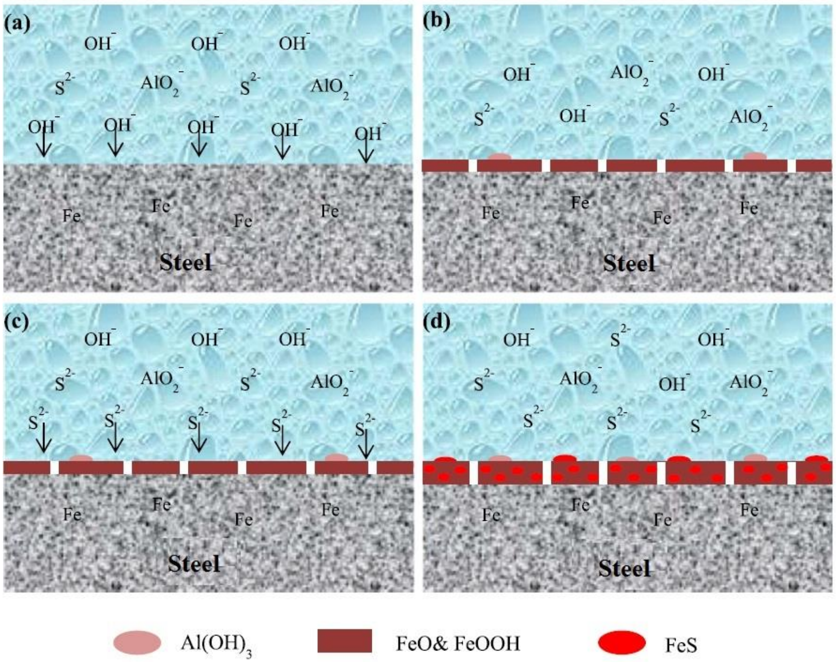

Figure 6. Corrosion mechanism of steel in sodium aluminate solution containing caustic soda and sulfide ions, **a**: Absorption of OH^- on steel surface, **b**: Passive film formation on steel surface, **c**: Adsorption of S^{2-} on the interface, **d**: Damage to the passive film and acceleration of corrosion.

Based on the physico-chemical study of corrosion products, the corrosion mechanism of steel in sodium sulfide can be concluded using equations 9 to 14. Gibbs free energy data has been calculated using FactStage thermodynamic software. Considering that the sodium aluminate solution is alkaline, the concentration of OH^- is much higher than S^{2-} and it is dominant during the competitive absorption of OH^-. Therefore, OH^- preferentially reacts with Fe matrix to form dense FeO and FeOOH. At the same time, sodium aluminate was decomposed. Therefore, the formed aluminum hydroxide adheres to the surface of the corrosion product. As the concentration of S^{2-} increases, the sulfide ion is adsorbed on the surface of the film. As a result, reaction number 14 moves further to the right. Then, more generated FeS leads to increased damage to the passive film. Therefore, steel corrosion increased with increasing S^{2-} concentration [11].

$$2Fe + 4NaOH + O_2 \rightarrow 2Fe(OH)_2 + 2Na_2O \qquad \Delta G_{323K} = -134.93 kJ/mol \quad (9)$$

$$4Fe(OH)_2 + 8NaOH + O_2 \rightarrow 4FeOOH + 6H_2O + 4Na_2O \qquad \Delta G_{323K} = -2141.71 kJ/mol \quad (10)$$

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \qquad \Delta G_{323K} = -16.18 kJ/mol \quad (11)$$

$$Fe_3O_4 \rightarrow Fe_2O_3 + FeO \qquad \Delta G_{323K} = -26.63 kJ/mol \quad (12)$$

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \qquad \Delta G_{323K} = -30.22 kJ/mol \quad (13)$$

$$2Fe + 2Na_2S + O_2 \rightarrow 2FeS + 2Na_2O \qquad \Delta G_{323K} = -127.14 kJ/mol \quad (14)$$

Investigating the corrosion rate of steel in aluminate solution after removing sulfide with nitrate

Published research shows that by adding specific amounts of sodium nitrate under conditions of temperature and pressure similar to the Bayer process, the sulfide in the aluminate solution can be completely removed and neutralized [2]. Therefore, in this research, exactly 2.5 g/L nitrate ions were added to the Bayer process liquor, which contains 0.215 g/L sulfide, and under the same conditions as the bauxite dissolution conditions in the Bayer process (temperature: 270 ^{o}C, pressure: 52 bar and time: 1 hr) the reaction Nitrate was supplemented with sulfide. Then, in order to study the corrosion rate of the steel piece (A516 grade 70) by sulfide after adding nitrate to the aluminate solution, the same corrosion test as mentioned above was performed. In addition, in order to check the corrosion rate of steel piece (A516 grade 70) by pure sulfide solution (without aluminate and caustic soda), a sulfide solution with a concentration of 0.2 g/L was prepared with double distilled water. For this, exactly 1.5 g of sodium sulfide salt ($Na_2S.\ 9H_2O$) was weighed and transferred to a 1-liter flask and diluted to the specified volume. Then, the corrosion test was carried out in this case, similar to what was mentioned above. Weight loss and corrosion rate of the carbon steel sample were measured in these tests. The results are shown in Table 5 and Figure 7.

Table 5. Weight loss and corrosion rate of steel piece in aluminate solution prepared by Bayer process, aluminate solution with 2.5g/L nitrate and sodium sulfide solution (without aluminate and caustic soda).

Test No	**1**	**2**	**3**
Solution type	Aluminate solution	Aluminate solution + Nitrate	Sodium sulfide solution
Weight loss of steel piece after corrosion test (g)	0.0627	0.0467	0.0013
Corrosion rate of steel piece (mm/yr)	0.51	0.38	0.01

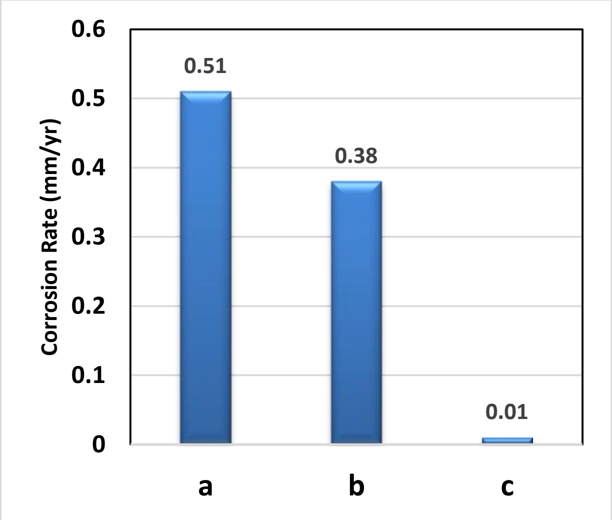

Figure 7. Comparison of carbon steel corrosion rate in: a - "Bayer process aluminate solution", b- "Bayer process aluminate solution + 2.5 g/L nitrate" and c- "0.2 g/L sulfide solution".

The initial sulfide concentration in both aluminate solutions (a, b) is 0.215 g/L. As seen in Figure 7, in the solution to which no nitrate is added, the steel corrosion rate is 0.51 mm/yr (**a**), in the solution that sulfide ions are removed or neutralized with nitrate, the steel corrosion rate is 0.38 mm/yr (**b**) And in a solution that contains only sulfide ions and has not added caustic soda or sodium aluminate, the corrosion rate of carbon steel is 0.01 mm/yr (**c**).

Therefore, it can be concluded that although the corrosion of carbon steel in pure sulfide solution (alone) is insignificant, but in the Bayer process sodium aluminate solution (Table 3), the presence of sulfide has an extraordinary effect on steel corrosion. In addition, the effect of sulfide removal from aluminate solution on steel corrosion is much higher than its removal from pure sulfide. On the other hand, it can be said that removing sulfide has a greater effect on steel corrosion than adding sulfide ions to the aluminate solution.

Conclusion

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 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 analysis was carried out. It was found that pyrite was the main source of sulfide ions in the aluminate solution of the Bayer process.

Measuring the amount of weight loss of carbon steel piece (A516 grade 70) and calculating the corrosion rate of carbon steel in Bayer process sodium aluminate solution shows that sulfide ions have a significant effect on the corrosion of steel piece and with the increase of sulfide ions in Bayer process liquor, corrosion steel also increase.

By examining the corrosion rate of the steel piece (A516 grade 70) in a pure sulfide solution (without alumina and caustic soda) and in the sulfide solution with the concentration of 0.2 g/L, it can be concluded that although the corrosion of carbon steel in the pure sulfide solution (alone) is insignificant, but in the sodium aluminate solution of the Bayer process, the presence of sulfide has a great effect on accelerating of steel corrosion.

By removing sulfide ions from the Bayer process aluminate solution, the possibility of steel corrosion (A516 grade 70) will not be eliminated. Because environmental conditions such as high temperature, pressure, and the presence of ions such as AlO^{2-} and OH^- in high concentrations will provide the basis for corrosion. However, the removal of sulfide ions will prevent the intensification of corrosion and the possibility of sudden destruction of the equipment.

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