The study on determination of Fluoride in Aluminum Ash Leachate

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Abstract. The content of fluoride ion in aluminum ash leaching solution was measured by using the ion selective electrode method accurately. The measure conditions were also studied. Theoretical and experimental results show that pH, temperature, instrument performance and coexisting ions have an important influence on the measure of fluoride ions in aluminum ash leaching solution. Hydrochloric acid was added to adjust pH closing to the neutral and adding 10 mL total ionic strength adjustment buffer solution, Controlling the pH between 5 –6. The temperature was consistent with the standard solution, and the measurement result was the most accurate. The fluoride ion content in the aluminum ash leaching solution reaches 446mg/L, far exceeding the national standard.

1. Introduction

Since the beginning of the 21st century, the output of aluminum has increased dramatically, becoming a metal which is second only to steel [1]. At present, most of the production of aluminum is through cryolite-alumina molten salt electrolysis. During the electrolysis process, the molten aluminum inevitably generates a large amount of aluminum when it comes into contact with the atmosphere inside the furnace due to the aluminum metal is easily oxidized [2].

Aluminum ash can be divided into white aluminum ash and black aluminum ash depending on the different source. White aluminum ash: It is also called primary aluminum ash, the color is white. It is mainly derived from the process of electrolytic aluminum without adding a salt solvent. The main components are aluminum metal and aluminum oxide, and it can be treated as a raw material for secondary production of the aluminum industry. Black aluminum ash: It is called secondary aluminum ash and its color is black. In addition to containing aluminum and aluminum oxide, it also contains a large number of salts [3], including some fluorides, which are very harmful to the environment. At present, the treatment of aluminum ash is mainly to recover aluminum and alumina therein. The main methods are tilting rotary furnace method, plasma instant dissolution method, modified MRM method and ALUREC method [4-7]. The process of preparing refractory brick material, calcium aluminate cement, mullite-zirconia, hexagonal mesoporous aluminum phosphate and the like by using aluminum ash is also realized in the laboratory [8-15]. A large amount of aluminum ash is still directly stacked or landfilled every year. According to statistics, 95% of the aluminum ash is not harmlessly handled when it is landfilled [16], which will result in the toxic fluorination flowing into the groundwater, causing great harm to the environment. Therefore, it is urgent to dispose fluoride in aluminum ash.

The nature of fluorine is very active, and there is no free fluorine in nature. Fluorine is mainly present in the form of fluoride in minerals such as fluorite and cryolite. At present, methods for
detecting fluoride ions include fluorine ion selective electrode method [17], fluorine reagent colorimetry[18], spectrophotometry and high performance liquid chromatography. The fluoride ion electrode method is simple in operation and wide in measurement range. In this paper, the concentration of fluoride ion in aluminum ash and aluminum ash leaching solution was accurately determined by X Ray Fluorescence(XRF) and fluoride ion selective electrode method.

2. Experiment

2.1. Materials
Aluminum ash: Jiayuguan Chengyu Metal Materials Company Limited; NaOH: Tianjin Binhai Cody Chemical Reagent Company Limited; anhydrous sodium acetate (CH3COONa): Sinopharm Chemical Reagent Company Limited; glacial acetic acid :Tianjin Sailboat Chemical Reagent Technology Company Limited; Sodium Chloride (NaCl): Tianjin Dingshengxin Chemical Company Limited; Sodium Fluoride (NaF): Tianjin BASF Chemical Company Limited; cyclohexanediaminetetraacetic acid (CDTA): Coo Chemical Technology Company Limited; the above reagents are of analytical grade.
Electronic balance: FA1004, Shanghai Anting Electronic Instrument Factory; speed control oscillator: HY-8, Changzhou Guohua Electric Company Limited; vacuum drying oven: D29-6020, Shanghai Jinghong Experimental Equipment Company Limited; circulating water multi-purpose vacuum pump : SHB-III, Zhengzhou Changcheng Branch Industry and Trade Company Limited; X-ray fluorescence spectrometer (XRF): 1800, Japan Shimadzu Company; pH acidity meter:PHS-3C, Shanghai INESA Scientific Instrument Company Limited; pH composite electrode:E-201F,Shanghai INESA Scientific Instrument Company Limited; Reference electrode:232-01, Shanghai INESA Scientific Instrument Company Limited; Fluoride ion electrode: PF-2-01,Shanghai INESA Scientific Instrument Company Limited.

2.2. Theory of ion selective electrode measurement
When the fluorine electrode is in contact with the fluorine-containing test solution, the electromotive force E of the electrode changes as the fluoride ion activity in the solution changes (observing the Nernst equation). When the total ionic strength in the solution is constant and sufficient, the relationship is obeyed: 

$$E = E_0 - \frac{2.303RT}{F} \log{\alpha_F}.$$ 

$E$ is linear with $\log{\alpha_F}$. \( \frac{2.303RT}{F} \) is the slope of the line and also the slope of the electrode.

2.3. Drawing of fluoride ion standard curve
A 0.2210-g standard sodium fluoride (NaF) (It is dried at 105-110 °C for 2 h previously, then cooled in a desiccator) was weighed and dissolved in the water, and then transferred to a 1000 mL volumetric flask, diluted to the mark and shook well, Storing it in a polyethylene bottle in the end. Pipette 10.00 mL of sodium fluoride standard stock solution with a non-fractional pipette, injected into a 100 mL volumetric flask, diluted to the mark and shook well, and then set aside. Pipette 1.00, 3.00, 5.00, 10.0, 20.0 mL of fluoride standard solution into the 50mL polyethylene cup respectively, adding 10mL total ionic strength adjustment buffer solution, diluted to the mark and shook well, and injecting 100mL respectively. In the polyethylene cup, insert the electrode in order of concentration from high to low, and stirring the solution continuously. After the potential is stabilized, reading the potential value $E$ while continuing to stir. rinse the electrode with water and then using it before each measurement. A standard curve is drawn on semi-logarithmic paper, the concentration is indicated on the logarithmic grid, and the lowest concentration is indicated on the start of the abscissa.

2.4. Preparation of total ionic strength adjustment buffer solution
Approximately 500mL of water was weighed into a 1 L beaker, and 57 mL of glacial acetic acid, 58 g of sodium chloride and 4.0-g cyclohexanediaminetetraacetic acid (CDTA) were added and stirred to
dissolve. Place the beaker in a cold water bath, adding 6 mol/L NaOH slowly with stirring to adjust the pH to 5-5.5 constant, transferred to a 1000 mL volumetric flask, diluted to the mark and shook well.

2.5. Determination of 100mg/L sodium fluoride solution after adjusting pH by sodium acetate/hydrochloric acid

A 0.0552-g standard sodium fluoride (NaF) was weighed and dissolved in the water, and then transferred to a 250 mL volumetric flask, diluted to the mark and shook well, stored in a polyethylene bottle. Pipette 10 mL of 100 mg/L sodium fluoride solution into the 50 mL polyethylene cups No. 1 and No. 2 respectively with a non-dividing pipette. Add 10mL total ionic strength adjustment buffer solution to No. 1, adjusting the pH to near neutral with saturated sodium acetate solution, diluted to the mark and shook well, and then injected into 100mL polyethylene cup. In the No. 2, the pH was adjusted to near neutral with 1 mol/L hydrochloric acid, then 10 mL total ionic strength adjustment buffer solution was added, diluted to the mark and shook well, and poured into a 100 mL polyethylene cup. Insert the electrodes separately, and stirring the solution continuously. After the potential is stabilized, reading the potential value E while continuing to stir. Rinse the electrode with water and blot dry with filter paper before each measurement.

2.6. Preparation of aluminum ash leaching solution

A 100.00-g aluminum ash was weighed accurately and transferred to a 2500mL jar, and then adding 1000 mL of distilled water. Place the jar on the speed control oscillator, adjusting the oscillation frequency to 110 times/min, shaking it at room temperature for 8 hours, letting it stand for 16 hours, then filtering it immediately, storing the test solution in a polyethylene bottle, and testing the sample immediately . The Buchner funnel and red mud were placed in an oven, the temperature was adjusted to 120 °C, and baked for 24 h until it is dried completely. Remove the red mud from the funnel and stored in a sealed bag.

2.7. Determination of fluoride ion content in aluminum ash leaching solution after adjusting pH with sodium acetate/hydrochloric acid

Pipette 10 mL of aluminum ash leaching solution into the No. 1 and No. 250 mL polyethylene cups with a non-dividing pipette. Add 10mL total ionic strength adjustment buffer solution to No. 1 firstly, and then adjusting the pH to near neutral with saturated sodium acetate solution, diluted to the mark and shook well, and injected into 100mL polyethylene cup. In the No. 2, adjust the pH to near neutral with 1mol/L hydrochloric acid firstly, and then adding 10mL total ionic strength adjustment buffer solution, diluted to the mark and shook well, and injected into 100mL polyethylene cup. Insert the electrodes separately, and stirring the solution continuously. After the potential is stabilized, reading the potential value E while continuing to stir. Rinse the electrode with water and blot dry with filter paper before each measurement.

3. Result and discussion

3.1. Fluoride standard working curve

| logCF (mg/L) | 0  | 0.477 | 0.699 | 1   | 1.301 |
|-------------|----|-------|-------|-----|-------|
| Potential (mv) | 277 | 254  | 240  | 223 | 205   |
It can be seen from Table 1 and Figure 1 that the potential and \( \log \text{C}\text{F}^- \) are inversely proportional. The potential is larger, the \( \log \text{C}\text{F}^- \) and the \( \text{C}\text{F}^- \) is smaller. The linear correlation equation is \( y = -55.672x + 278.51 \), and the correlation coefficient is 0.9975. The correlation is well.

3.2. Determination of 100mg/L sodium fluoride solution after adjusting the pH value of sodium acetate/hydrochloric acid.

| sample | Potential (mV) | concentration (mg/L) | Relative error (%) |
|--------|----------------|-----------------------|--------------------|
| 1      | 165            | 109.3721              | 9.37%              |
| 2      | 168            | 96.6094               | -3.39%             |

As the Table 2 shows, the concentration of sample No. 2 was 96.6094 mg/L, the measurement error was -3.39%, and the concentration of sample No. 1 was 109.3721 mg/L, and the measurement error was 9.37%. The relative error of sample No. 2 is less than the relative error of sample No. 1. That is to say, the relative error of the measured value of the pH value adjusted with hydrochloric acid is smaller than the relative error when the pH is adjusted with sodium acetate. Therefore, the pH should be adjusted to be close to neutral with hydrochloric acid for the sodium fluoride solution, and then a buffer solution is added to control the pH between 5 and 6 to make the measurement result is more accurate. This is because if the concentration of hydroxide ions is greater than \( 10^{-6} \) mol/L in an alkaline solution, the hydroxide ions are likely to react with lanthanum fluoride (LaF\(_3\)) on the surface of the fluorine electrode film: \( \text{LaF}_3 + 3\text{OH}^- \rightarrow \text{La(OH)}_3 + 3\text{F}^- \), the reaction product F\(^-\) is a positive interference caused by the response of the electrode itself. In an acidic solution, hydrogen ions and fluoride ions form HF\(_2^+\) to reduce the concentration of fluoride ions and cause negative interference. Therefore, it is necessary to control the pH of the test solution between 5–6.
3.3. Fluorine content in aluminum ash, red mud and aluminum ash leaching solution

Table 3. Fluorine content in aluminum ash and red mud

| sample       | XRF(%) |
|--------------|--------|
| Aluminum ash | 1.741  |
| Red mud      | 1.263  |

Table 4. Determination of fluoride ion content in aluminum ash leaching solution

| sample | Potential (mV) | concentration (mg/L) | Relative error (%) |
|--------|----------------|----------------------|--------------------|
| 1      | 127            | 526.5939             | 10.04%             |
| 2      | 131            | 446.2995             | -6.69%             |

It can be seen from Table 3. The total fluorine content in the aluminum ash was 17.41 mg/g, and the total fluorine content in the red mud was 12.63 mg/g. So the fluorine content dissolved in water should be 478 mg/L. As the Table 4 shows, when the pH was adjusted to neutral with sodium acetate, the fluorine content measured by the fluoride ion electrode method was 526.5939 mg/L, and the relative error was 10.04%. When the pH was adjusted to neutral with hydrochloric acid and the pH was measured between 5 and 6, the fluorine content measured by the fluoride ion electrode method was 446.2995 mg/L, and the relative error was -6.69%. Therefore, the fluoride ion selective electrode method measures the fluorine content in the aluminum ash leaching solution, that is, the content of soluble fluorine. And the pH is adjusted with hydrochloric acid, the pH is controlled between 5 and 6 during the measurement, the error is small, and the result of measurement result is more accurate. This is consistent with the results of measuring sodium fluoride solution.

The aluminum ash leaching solution and the sodium fluoride solution are both alkaline solutions. For the alkaline solution, when the ion-selective electrode method is used to measure the fluoride ion concentration, the pH should be adjusted to near-neutral with hydrochloric acid, and the buffer solution is added. The pH is controlled between 5 and 6 during the measurement, and the result of measurement is relatively accurate.

3.4. Temperature

The Nernst equation is \( E = E_0 - \frac{2.303RT}{F} \log \alpha F \) and \( E_0 \) is not the ideal true value, it depends on temperature, film characteristics, internal reference solution and liquid junction potential, and the slope of the line \( -\frac{2.303RT}{F} \) is also affected by temperature. Therefore, the temperature affects the measured potential and further affects the measured concentration. When measuring the sample, try to keep the temperature constant and the same as when measuring the standard solution.

3.5. Instrument performance

The performance of the instrument directly affects the measurement of the potential, which in turn affects the conversion of the concentration. The relationship between the electromotive force measurement error \( \Delta E \) and the concentration relative error \( \Delta c / c \) can be derived from the Nernst equation: \( \Delta E = \frac{RT}{nF} \frac{\Delta c}{c} \). When the temperature is 25°C, the potential changes by 1mV, which will produce a concentration change of about 4%. Most instruments display integer potentials directly, so choosing instruments with high sensitivity and good performance when measuring is necessary.
3.6. Coexisting ions
When Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, Al$^{3+}$, Si$^{4+}$ and hydrogen ions are present in the leachate, there is interference with the fluoride ion to form a poorly soluble compound or a complexation reaction, and the degree of interference depends on the type and concentration of the ion. The main components of aluminum ash are shown in the table 5:

| Table 5. Main element content (mass fraction) in aluminum ash. |
|------------------|----------------|----------------|----------------|----------------|
|                  | O       | F        | Na        | Mg        | Al        | Si        |
| 52.172           |         | 1.741    | 6.152     | 3.105     | 26.849    | 1.652     |
| Fe               | 0.842   | 1.361    | 0.054     | 0.596     | 0.524     | 0.286     |

It can be seen from the table 5 that aluminum ash contains a large amount of Ca, Mg, Al, Si and a small amount of Fe, which will have an impact on the measurement results. CDTA is a good complexing masking reagent, which can preferentially complex Al$^{3+}$ and mask Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$, Si$^{4+}$ plasma.

It can effectively eliminate the interference caused by these ions and has no effect on fluoride ions. The acetic acid-sodium acetate buffer pair ensures a stable pH for the control solution.

3.7. Total ionic strength
It is generally required to measure the concentration, and the ion selective electrode measures the activity according to the Nernst formula. Adding a total ionic strength adjustment buffer solution keeps the ionic strength in the solution very high and nearly uniform, so that the activity coefficients are nearly the same, and complexing the interfering ions, maintaining the proper pH of the solution.

4. Conclusions
Aluminum ash contains a large amount of fluoride, and some are dissolved in water will cause great harm to water and the environment.

Fluoride ion selective electrode method can accurately determine the content of soluble fluorine in aluminum ash accurately. pH, temperature, instrument performance and coexisting ions have an important influence on the determination of fluoride ion in aluminum ash leaching solution. The measurement conditions were as follows: hydrochloric acid was adjusted to pH to neutrality, and 10 ml of total ionic strength adjusting buffer solution was added, and the pH was determined to be between 5 and 6, and the temperature was consistent with the standard solution. The fluoride ion content in the aluminum ash leaching solution reaches 446mg/L, far exceeding the national standard.

The fluorine content in the aluminum ash and aluminum ash leaching solution exceeds the relevant national regulations, and further defluorination is required for harmless treatment.

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