The Research on Sodium in Fly Ash Red Mud was Removed by Using Magnesium Salt

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Abstract—Fly ash red mud occupied a great quantity of soils and polluted water source because of it has a very high sodium content. In the present work, the magnesium salts were used to remove sodium from fly ash red mud. The Mg2+ replaced Na+ from the compounds in the fly ash red mud and then the new created compounds dissolved in water to remove Na+. The reaction time, reaction temperature, liquid-solid ratio and magnesium salt/Na2O ration were studied. The optimal reaction conditions are: reaction time is 80 min, reaction temperature is 80℃, liquid-solid ratio is 5 and magnesium salt- Na2O ratio is 2 for Mg(NO3)2 and MgSO4, respectively. Mg(NO3)2 have a better property for removing sodium from fly ash red mud than MgSO4. Both of them can achieve the requirement that make the sodium content below 2w%. The treated red can be used as raw materials in cement industry.

Keywords— Fly ash red mud; Magnesium salt; Sodium; Cement; Environment protection.

Ⅰ. INTRODUCTION

Red mud is the solid waste which comes from the process of separating alumina from after-mentioning-silicon fly ash by using soda lime sintering method in alumina smelting industry [1,2]. Nowadays, there are more than 45 million tons of red mud were discharged per year all over the world. The solid waste seriously pollutes the environment, occupies a great quantity of soils [3]. In addition, the pH value of red mud is up to 12 to 14 [4] because of the red mud has a very high sodium content, which limit the reuse of red mud in the industries where limit the sodium content. Therefore the comprehensive utilization of red mud is imperative.

With the rapid development of industry, there is an increasing demand for cement. The main row materials for the traditional cement industry are limestone and clay [5]. The exploitation of these materials will consume the soil resources and damage the environment. So expanding cement raw material resources is a way to solve the sustainable development of cement industry.

Red mud contains necessary substance [6,7,8], CaO、SiO2、Al2O3、Fe2O3 and silicate minerals, to produce cement. In addition, the red mud contains a certain amount of β-C2S and amorphous aluminosilicate material which can react with water and make the red mud has activity, so that red mud can be used in cement production [9]. But the sodium components of red mud has restricted the adding proportion of red mud in cement and then limit the large-scale application of red mud as raw materials for the production of cement. This shortage can be solved if the sodium content of red mud is lowered to 2w% by a simple way.

In the present work, the magnesium salts were used to remove sodium from fly ash red mud. The reaction time, reaction temperature, liquid-solid ratio and magnesium salt/Na2O ration were studied.

Ⅱ. EXPERIMENTAL

The fly ash red mud was obtained from Inner Mongolia Datang International Renewable Resources Development co., LTD. The silicon and aluminum were distilled from fly ash by soda lime sintering method to get red mud. This production process is ongoing industrialized. A.R. grade chemicals of MgSO4、Mg(NO3)2 were used as sodium remover. A typical route for the experimental process as follows: weight a certain amount of MgSO4 or Mg(NO3)2 in a beaker and dissolved by adding appropriate amount of deionized water. Then the red mud, dried at 110℃ for 24 h, were added into the solution with magnetic stirrer on constant heat. After reaction, the solution was filtered and washed the filter cake several times with deionized water. The filter cake was dried at 110℃ for 24 h for further analysis.

The method of analysis sodium content in fly ash red mud as follows: weight 0.1000g red mud in platinum crucible, adding some drops deionized water, 2~3 mL HF and 10 drops dilute H2SO4. Put the solution on electric hot plate until the liquid evaporated. Then 20 mL hot water and 1 drop methyl red were added into the platinum crucible. After that, using dilute ammonium hydroxide to neutralize the solution to yellow and then 5 mL ammonium carbonate solution was added into the solution. Filter the solution after boiling 20 min. The liquid was collected into 100 mL volumetric flask and cooling down to room temperature. Using hydrochloric acid neutralize the liquid to reddish, then dilute with water to 100 mL. The sodium in as-prepared liquid was measured by flame photometer (6400). The sodium standard solution purchased from Sinopharm Chemical Reagent co., Ltd. The standard solution was diluted to different concentration to create standard curve. The linear correlation R=0.9997.

The chemical composition content was measured by X-ray fluorescence spectrometer (XRF, S4 PIONEER). The powder XRD pattern was recorded with a RIGAKU D/MAX2200 X-ray diffracmeter.

Ⅲ. RESULTS AND DISCUSSION

A. Experimental principle

When the MgSO4 or Mg(NO3)2 mixed with red mud under hydrothermal condition, the Mg2+ ions would replace sodium from the component of the red mud and created new component which undissolved. The sodium was released to the water. The reaction formulas are as follows:

MgSO4＋Na2O·Al2O3＋aq → MgO·Al2O3·6H2O＋2NaNO3＋aq

MgSO4＋Na2CO3＋aq → MgCO3＋2NaNO3＋aq

MgSO4＋Na2SiO3＋aq → MgSiO3＋2NaNO3＋aq

Mg(NO3)2＋Na2O·Al2O3＋aq → CaO·Al2O3·6H2O＋2NaNO3＋aq

Mg(NO3)2＋Na2CO3＋aq → MgCO3＋2NaNO3＋aq

Mg(NO3)2＋Na2SO4＋aq → MgSO4＋2NaNO3＋aq

Mg(NO3)2＋Na2SiO3＋aq → MgSiO3＋2NaNO3＋aq

B. Chemical composition and phase composition of fly ash red mud

TABLE 1. The Chemical Composition of Fly Ash Red Mud.

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO
Percentage composition	22.72	7.965	5.169	1.26	2.015
Chemical composition	CaO	Na_2O	K_2O	other	
Percentage composition	47.07	3.44	0.845	9.516	

Table. 1 shown the chemical composition of fly ash red mud which was measured by XRF. According to the quantitative analysis, the main composition of fly ash red mud were CaO, SiO_2, Fe_2O_3 and Al_2O_3. Additionally, small amount of TiO_2 and MgO existed in the red mud. However the sodium content reached up to 3.44% which was too high to act as raw materials in the cement industry.

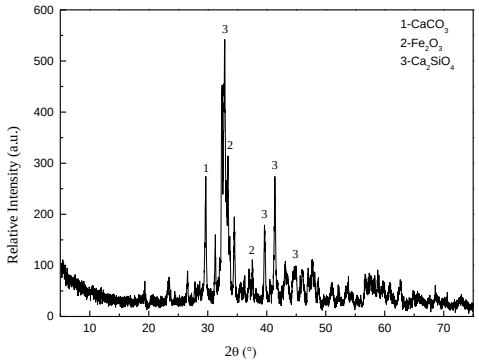

Figure 1. The XRD pattern of fly ash red mud

The XRD pattern of fly ash red mud was showed in Fig .1. Three phases of fly ash red mud can be seen, as shown in Fig .1. The composition of CaCO3, Fe2O3, Ca2SiO4 in fly ash red mud were suitable for which was used in the cement industry as raw materials.

C. The removing of sodium at different conditions

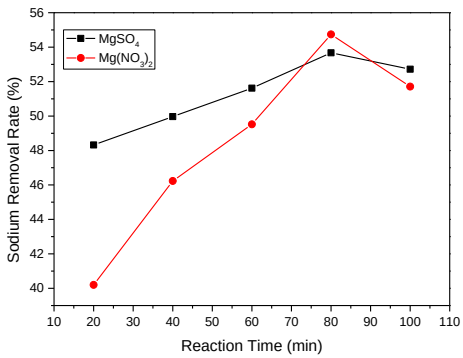

Figure 2. The sodium removal rate of red mud under different reaction time.

Fig .2. shown the sodium removal rate of red mud under different reaction time. As can be seen, with the increasing of reaction time, the sodium removal rate increased and reached the maximum when the reaction time was 80 min. The best sodium removal rate of $MgSO_4$ and $Mg(NO_3)_2$ were 53.67% and 54.74%, respectively. When the reaction time more than 80 min, sodium removal rate decreased. That may due to the replacement of Na^+ had secondary reaction in solution. Therefore the best reaction time was 80 min.

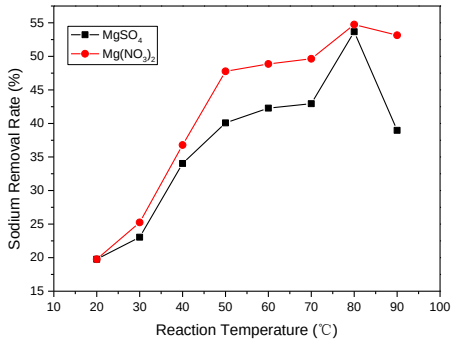

Figure 3. The sodium removal rate of red mud under different temperature.

The sodium removal rate of red mud under different temperature were showed in Fig .3. With the increasing of reaction temperature, the sodium removal rate increaced gradually and then decreased. The sodium removal rate reached the maximum when the reaction temperature was 80℃. The activity and solubility of the compound was low in the reaction solution when the reaction temperature was low. With the increasing of reaction temperature, the activity and solubility increased which resulted in the increasing of sodium removal rate. However, the solubility of MgSO4 reached the maximum at 80℃, so that the sodium removal rate of MgSO4 decreased rapidly when the reaction temperature exceeded 80℃.

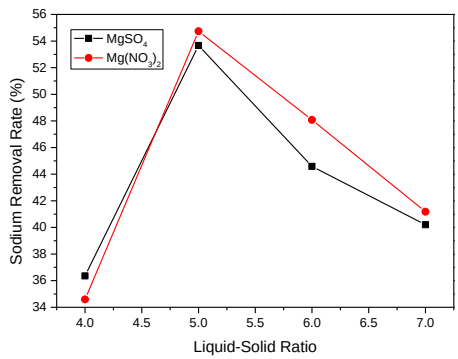

Figure 4. The sodium removal rate of red mud under different liquid-solid ratio.

Fig .4. shown the sodium removal rate of red mud under different liquid-solid ratio. According to Fig .4, the sodium removal rate increased with the increasing of liquid-solid ratio and was up to the top when liquid-solid ratio was 5. When the liquid-solid ratio was low, the

generated sodium compound were hardly dissolved in the solution. However, when the liquid-solid ratio was too high, the concentration of the compounds were low which limited the reaction between them, so that suitable liquid-solid ratio was 5.

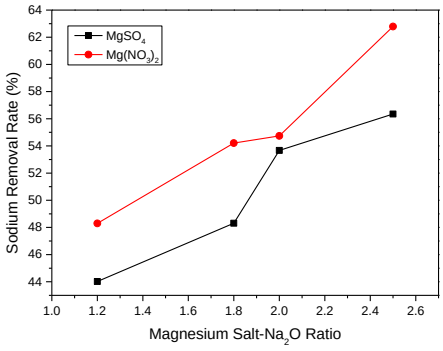

Figure 5. The sodium removal rate of red mud under different magnesium salt-Na2O ratio.

The sodium removal rate of red mud under different magnesium salt- Na2O ratio were shown in Fig .5. As can be seen in Fig .5, the sodium removal rate increased rapidly with the increasing of magnesium salt. In this system, the replacement reaction occured between liquid-liquid and liquid-solid phase. The more magnesium salt in the system, the more chance they reacted. Therefore the sodium removal rate increased rapidly with the increasing of magnesium salt. However, the sodium removal rate curve of Mg(NO3)2 was more sharp than MgSO4. That was because of the different solubility [10] between Mg(NO3)2 and MgSO4. So if there are somewhere need a better sodium removal rate, the Mg(NO3)2 is a better choice. 41.86% sodium should be removed when the content of sodium was below 2w% in the red mud. The sodium removal rate met requirement when the magnesium salt-Na2O ratio was 2, In order to make no waste, the magnesium salt- Na2O ratio should not be exceed 2.

Ⅳ. SUMARRY

In conclusion, the magnesium salt, Mg(NO3)2 and MgSO4, can be used as sodium remover in fly ash red mud which produced by using soda lime sintering method in alumina smelting industry. The sodium content can be removed more that 54.74% and 53.67% under the condition that reaction time was 80 min, reaction temperature was 80℃, liquid-solid ratio was 5 and magnesium salt-Na2O ratio was 2 for Mg(NO3)2 and MgSO4, respectively. The sodium content was below 2% after reaction which met the requirement of red mud act as raw materials in cement industry.

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