Reaction Kinetics of Fly Ash in Al_2O_3 -NaOH Solution Systems

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Reaction kinetics of fly ash in Al_2O_3 -NaOH solution system were analyzed by a modified “Jander” equation. After kinetics analysis, only two reaction stages could be found during the reaction process. Stage 1, the reaction process was limited by diffusion through a porous layer. Stage 2, the reaction process was controlled by diffusion through a dense layer. The rate constants of stage 2 were in the order of 7.5 M NaOH (0.00609), $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0 > 7.5 \text{ M NaOH}$, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.0066 > (0.00404) > 7.5 \text{ M NaOH}$, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.013$ (0.00301) $> 7.5 \text{ M NaOH}$, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.033$ (0.00128).

Keywords: Fly ash, Kinetics, Alkaline solution.

INTRODUCTION

Fly ash is a solid waste formed in power plants. As the fastest developing country, China produced about 400 million tons every year and the utilization ratio of fly ash is not more than 30 %. Most of them were disposed of in landfills and ash ponds which lead to cover huge areas of cultivated land as well other pollutions for atmosphere and groundwater¹⁻³. Nowadays, synthesizing zeolite and new geopolymer material⁴⁻⁷ are two important new developing way to recycle fly ash. The identical basic mechanism of two synthesizing processes is the alkaline-activator. Van Deventer and Provis⁸ have analyzed the synthesis process of zeolite and geopolymer and advices that their reaction process could be divided into 3 stages: the dissolution of solid reactants in alkaline environment, transferring of the dissolved species from the solid surface into a gel phase, nucleation and condensation of the gel phase⁸. In order to improve fly ash as a major component for zeolite and new geopolymer formulations, the reaction kinetics of fly ash and alkaline systems must be understand. The objective of this paper is focusing on the understanding of reaction kinetics of fly ash in Al_2O_3 -NaOH solution system. The alkaline environment is (7.5 NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ from 0.0066-0.013). The reaction kinetics was analyzed by a modified “Jander” equation.

EXPERIMENTAL

The original fly ash is gained from Taicang harbour golden concord electric-power generation Co. Ltd (Taicang, Jiangsu province). The main chemical composition is given in Table-1. All chemicals used in present experiment are analytical reagent and bought from China National Pharmaceutical Group Corporation. Alkaline solutions used for experiment were sodium hydroxide and sodium aluminum solutions. The molarities of NaOH were all 7.5M and $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ was from 0.0066-0.033. Experiments were conducted with 2.5 g fly ash with 100 g alkaline solution. The reaction time was from 1 to 72 h and temperature was 75 °C. After reaction, the mixture solutions were filtered with 0.45 μm filter membrane with a vacuum pump. The filter residue were washed and put in 100 % absolute ethanol to stop further hydration, then dried at 105 °C and stored in a dry box.

RESULTS AND DISCUSSION

The method used to calculate reaction progress was improved from Fernández-Jiménez *et al.*⁹. Typically, the reaction progress could be given by:

$$\partial_t = \frac{\Delta m(t)}{m_0} = \frac{m_0 - m_t}{m_0} \quad (1)$$

TABLE-1
CHEMICAL COMPOSITION OF FLY ASH (%)

Oxides	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	K_2O	TiO_2	P_2O_5	LOI*
F-Fly ash	56.71	28.9	2.34	4.02	0.46	0.04	1.32	1.07	0.12	4.81

*LOI = loss on ignition at 960 °C.

here, m_0 is the initial mass of fly ash and m_t is the residual mass of fly ash after reaction with alkaline solutions.

Considering that frequently many precipitations could form on the fly ash particles, the m_t gained from weighting the products should not really represent the residual mass of fly ash and must be corrected. So we modified the eqns. 2 and 3:

$$\partial'_t = \frac{\Delta m(t)}{m_0} = \frac{m_0 - m'_t}{m_0} \quad (2)$$

here, ∂'_t is the apparent reaction progress and m'_t is the mass of reaction products after alkaline leaching.

The real residual mass of fly ash was gained from dissolving the reaction products with HCl solution ($\text{HCl}/\text{H}_2\text{O}$, 1:20). 0.5 g reaction product was mixed with 150 mL HCl solution at room temperature and reaction time was 3 h. The mixture solutions were filtered with 0.45 μm filter membrane and then dried at 105 $^\circ\text{C}$ and weighed.

So, the overall reaction progress could be given by:

$$\partial_t = \partial'_t + \beta_t = \frac{m_0 - m_t}{m_0} \quad (3)$$

here, m_t is the mass after dissolution of all surface precipitates in HCl solution. The kinetics model used was first suggested by Jander¹⁰ and then modified by Kondo *et al.*¹¹ to broad its application for solid/liquid reaction. The equations were as follow:

$$[1 - (1 - \partial)^{1/3}]^N = K_N t \quad (4)$$

or in linear form

$$\ln[1 - (1 - \partial)^{1/3}] = \frac{1}{N} \ln K_N + \frac{1}{N} \ln t \quad (5)$$

K_N is the rate constant and t is the reaction time. N is the reaction grade which has the following meaning:

(a) $N \leq 1$: The process is controlled by a chemical reaction at surface or by dissolution of reactants or precipitation of reaction products.

(b) $1 < N \leq 2$: The process is controlled by diffusion of reactants through a porous layer of reaction products.

(c) $N > 2$: The process is controlled by diffusion of reactants through a dense layer of reaction products.

Fig. 1 shows how $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ in original solutions affects the reaction progress. As Fig. 1, the reaction rate reduces with $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ increasing. For example, reaction progress reaches 70.7 and 75.7 % after 24 and 72 h in solution 1 (pure 7.5 M NaOH) while in solution 4 (7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.033$), reaction progress only could reach 49.8 % (24 h) and 53.3 % (72 h). The similar results could be observed from the curves of solution 2 (7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.0066$) and 3 (7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.013$).

The data of Fig. 1 was plotted by kinetics equations mentioned above and results were showed in Fig. 2. The results of four alkaline solutions were similar and it could be seen that only the slope $N = 2$ and $N > 2$ which represents the diffusion-control could be found for data up to 72 h. The results why slope $N = 1$ could not be found should due to the high reaction temperature (75 $^\circ\text{C}$). It was clear that rate constant of stage 2 was in the order of pure 7.5 M NaOH (0.00609) > 7.5 M

Fig. 1. Reaction progress with a function of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$

Fig 2. Analysis of reaction kinetics

NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.0066$ (0.00404) > 7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.013$ (0.00301) > 7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.033$ (0.00182) and a great linear relation could be gained between $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and rate constant (Fig. 3). The linear relation equation is as below and the R^2 is 0.9583.

$$\text{Reaction constant} = \frac{-0.1316 \cdot \text{Al}_2\text{O}_3}{\text{Na}_2\text{O}} + 0.0057 \quad (6)$$

Conclusion

The paper studied how $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ in original solutions affects the reaction kinetics of fly ash. The results show that the total reaction process of fly ash in Al_2O_3 -NaOH solution at 75 $^\circ\text{C}$ is diffusion control. Two kinetics stages could be found after analyzing the data by a modified "Jander" equation¹⁰. First, the process is controlled by diffusion of reactants through a porous layer of reaction products and then controlled by diffusion of reactants through a dense layer of reaction products. The rate constants of stage 2 are in the order of 7.5 M NaOH

Fig. 3. Reaction constants as a function of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$

(0.00609) > 7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.0066$ (0.00404) > 7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.013$ (0.00301) > 7.5 M NaOH, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 0.033$ (0.00182). There is a great linear relation between $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and rate constants.

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