

Improving reactivity of fly ashes towards zeolite synthesis by using alkaline fusion pretreatments

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1. Introduction

The increased demand for electricity has created the need to build large thermoelectric power plants where coal is the primary fuel used. This fact suggests the generation of significant amount of solid combustion residue. Fly ashes represent almost 70% of all coal combustion products. For this reason, different investigations are focused on developing new recycling techniques for coal fly ash [1].

This paper analyzes the effects of different pretreatments conditions, different synthesis mixture compositions and reaction times on the fly ash conversion to NaA zeolite by hydrothermal synthesis. A residual fly ash (Thermoelectric Central of San Nicolás, Buenos Aires, Argentina) with or without pretreatment (calcination and/or fusion with Na₂CO₃) was alkaline-treated and reacted under controlled conditions of temperature and autogenous pressure. The zeolitic phases conversion was evaluated at different reaction times by XRD and Rietveld method.

2. Experimental Part

Fly ash was subjected to different pretreatments which could include calcination with or without sodium carbonate. Alkaline fusion was carried out in an oven at 800°C for 2 or 12h with or without Na₂CO₃ (ash/Na₂CO₃=50 or 75/25%w/w). Subsequently, each of the pretreated samples was placed in contact with the activation mixture in a polypropylene reactor of 250ml. The original fly ash was used as reference. The activation mixture was formed by appropriate amounts of NaOH deionized water and NaAlO₂ (optionally

added as extra aluminum source). Each sample was mixed with magnetic stirrer for 180s and aged at room temperature for 48 or 72h. Then the mixture was placed in a stove at 100°C. The course of the reaction was followed by taking aliquots at different times. The solid products obtained were washed and dried at 110°C. The pretreatments and the compositions of the activation mixtures are detailed in Table 1. Structural and crystallographical characterization of crystalline materials was carried out by XRD. The Rietveld method was used for quantitative determination of the crystalline phases.

3. Results and discussion

The solid products obtained using different activation treatments can be seen in Fig.1 and Fig.2. In Fig.1, the diffractograms corresponding to the original fly ash (a), solid obtained after calcination of the starting fly ash after 2h at 800°C (b), and after 12h at 800°C (c) are compared. It can be observed that there is no change in the diffractograms, showing that this heating step no introduce any change in the crystalline structure of the ash. On the contrary, important changes in the ash structure were produced by calcination of ash/Na₂CO₃ mixtures (50%w/w), Fig. 2. Using as reference the (a) diffractogram, after a heating treatment of 2h, new crystalline phases appear, identified as nepheline, carnegite and minor components (b). The increase in the activation time produces a notorious increase in the crystallization percentage of the nepheline phase (c). Changes in the ash/Na₂CO₃ ratio in the starting mixture were also analyzed. Small nepheline crystallization level after heat treatment was observed for samples of ash/sodium carbonate mixtures (75/25 % w/w) and the results obtained for (25/75% w/w) were similar to those obtained using (50% w/w). The results obtained for the different synthesis conditions are presented in Table 1. From reactions D7-D14 and D17-D21, fly ash underwent calcination pretreatment with 50% w/w of Na₂CO₃. The maximum conversion in zeolite NaA was 39% at 23h of reaction in the test D7 and the same conversion level was obtained at 5h in the test D10. The variation of NaOH percentage (tests D8 and D11) showed that the

maximum conversion in zeolite NaA at higher alkalinities is reached at shorter times.

Table 1. Pretreatments type and products

Sample	Activation solution, g			NaA max. conversion		Nepheli ne%	Products
	NaOH	H ₂ O	NaAlO ₂	Time, h	%		
D7	3,56	87,6	1,2	23	39	100	A+ HS tr
D8	1,78	87,6	1,2	48	35	71	A+HS
D9	3,56	87,6	0,9	31	12	46	A+HS+X tr
D10	3,56	87,6	1,5	5	39	76	A+ HS tr
D11	5,34	87,6	1,2	3, 27	35	66	A+ HS tr
D12	3,56	131,4	1,2	21	34	80	A+ HS tr
D13	3,56	43,8	1,2	3	34	66	A+ HS tr
D14	3,56	153,3	1,2	48	35	75	A+ HS tr
D15*	3,56	87,6	1,2	-	-	0	HS+P
D16	3,56	87,6	1,2	24	19	0	A+P
D17	3,204	87,6	1,5	21	31	64	A+HS
D18	2,848	87,6	1,5	27	35	67	A+HS
D19	3,4	87,65	1,5	22	30	69	A+HS
D20	3,26	87,68	1,8	3	33	70	A+HS
D21	3,16	87,7	2	3	14	47	A+HS
D22*	3,56	87,6	1,2	-	-	0	P
D23*	3,56	87,6	1,2	-	-	0	P
D24*	3,56	87,6	1,2	-	-	0	P
D25*	3,204	87,6	1,5	24	21	0	A+P
D26*	3,204	87,6	1,5	-	-	0	X tr + P tr
D27	3,204	87,6	1,5	3	26	10	A+HS
D28	5,284	87,6	1,5	3	13	0	A+HS+ P tr
D29	4,724	87,6	1,5	3	19	47	A+ HS tr+P

*Without calcination. D15, D16, D22-D28 without Na₂CO₃ pretreatment. tr=traces

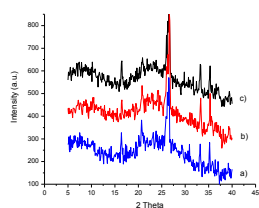


Figure 1. Fly ash subjected to calcination pretreatment

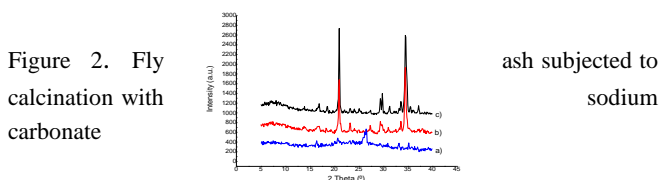


Figure 2. Fly ash subjected to calcination with sodium carbonate

On the other hand, the decrease of NaAlO₂ induces the formation of small quantities of NaA, HS and X at 3h of reaction with low conversion (12%). The NaAlO₂ increase allowed reaching maximum conversion at shorter times.

Regarding variations of water content in the selected range, its increase or decrease (D12, D13 and D14) did

not lead to substantial variations in NaA conversion with regard to sample D7. With a 50% decrease of water at 24h of reaction, the product consist of HS (main peak at 2θ=14.0). With a 75% increase of water, zeolite A crystallization is delayed, the appearance of its characteristic peaks is registered for reaction times superior to 48h. Reactions carried out without any pretreatment led to HS formation and zeolite NaP traces. In reaction D16 at 5h of reaction, zeolite NaA and traces of NaP were formed, and after 30h reaction HS traces, where quartz, mullite and albite were detected. It is observed that decreasing NaOH by 10% (D17) and 20% (D18), taking D10 as basis, a good conversion percentage between 30 and 35% is obtained. Then, increasing the percentages of NaAlO₂ by 20% (D19), 34% (D20) and 40% (D21) with a slight variation of NaOH to maintain Na₂O constant with regard to reaction D7, a peak was obtained in the conversion percentage with the increase of 34% in NaAlO₂ with 33% conversion in zeolite NaA.

4. Conclusions

It was demonstrated that the application of alkaline fusion increases the reactivity of this industrial waste considerably, favoring its conversion in different products. During the first hours, NaA zeolite crystallization takes place and then HS formation with different maximum percentages of conversion in zeolite NaA, which decrease as HS crystallization increases. It was also possible to determine synthesis conditions that allow the achievement of an evident conversion of pretreated fly ash into zeolite NaA. The crystallization reaction evolution was studied and there were determined synthesis conditions allowing conversion values in zeolite NaA close to 40% for times around 3 hours. These values represent a high improvement in conversion, if it is compared with the results of conversions obtained close to 16% when the synthesis is carried out using non-calcined fly ash or calcined fly ash without using Na₂CO₃.

References

1. Ahmaruzzaman M. Progress in Energy and Combustion Science 36 (2010) 327–363.