

Zeolitisation of Coal Fly Ashes using Microwaves. Process Optimization

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Introduction

Ion exchangers like zeolites have been considered for soil remediation and heavy metal removal. The required cheap absorbents can be obtained by hydrothermal treatment of fly ash¹⁻⁵, which is a suitable material for zeolite synthesis given the high content of reactive phases as well as the high specific surface area of the particles. Usually, fly ashes have low Si/Al ratios, allowing the synthesis of low-Si zeolites with high ion exchange capacity.

The zeolite formation by alkaline activation of fly ash has been studied by Höller and Wirsching¹, showing that yield and type of zeolite obtained depend on temperature, solution composition and concentration. Other workers used sodium melting prior to hydrothermal treatment for conversion of fly ash to Na-X zeolites. In recent studies high efficiencies in synthesizing Na and K zeolites have been obtained by alkaline activation in closed systems. Activation periods in these works range from few hours to several days. Our previous work on this subject⁶⁻⁷ demonstrated that different zeolites can be synthesized from the same coal fly ash depending on reaction parameters like temperature, alkali concentration, reaction time,... The main problem for the industrial application of this process are the long times required for synthesizing useful zeolite phases like NaP1 or Herschelite. In a later study⁸, we investigated the application of microwaves for accelerating the zeolite synthesis. Results showed that while the zeolite phases obtained were of the same type of those obtained by conventional heating, reaction times were drastically reduced, requiring about 30 minutes for most zeolite syntheses.

Among the zeolite phases obtained by alkaline activation with microwaves, just two were of interest due to their high ion-exchange capacity, NaP1 and Herschelite, while other obtained phases like analcime, tobermorite, hydroxysodalite or hydroxycancrinite were useless for our purposes, as shown by ion-exchange experiments with ammonium and heavy metals. In this paper, process optimization for obtaining NaP1 or Herschelite zeolites using closed systems in a microwave oven is presented.

Experimental

Material and Methods: Eight different fly ashes from different coal-based power stations in Spain were collected and used in this work. Their detailed analysis, as determined by ICP-AES, ICP-

MS and XRD, is given in Table I, reflecting the different coals used at each power station as well as the different type of boilers in use.

	Andorra	La Ro bla	Com postilla	Meira ma	Narcea	Puerto llano	Espiel	Barrios
SiO ₂	472	401	498	519	543	584	520	451
Al ₂ O ₃	256	233	261	264	23	293	342	376
Fe ₂ O ₃	166	143	84	48	7	75	61	28
CaO	56	89	27	75	42	9	21	90
MgO	12	2	24	23	27	10	16	22
Na ₂ O	2	3	8	4	8	4	6	4
K ₂ O	16	26	43	8	39	24	41	7
P ₂ O ₅	2	8	5	4	2	1	4	17
TiO ₂	8	9	10	15	11	7	9	15
MnO	4	1	8	5	9	1	1	1
SO ₃	6	4	3	2	1	2	1	7
SiO ₂ / Al ₂ O ₃	18	17	19	2	24	20	15	12

Table I. Fly ash characterization

Microwave equipment: The reactions were carried out in a laboratory microwave oven (Milestone MLS-1200 MEGA). This oven is controlled by microprocessor allowing temperature control with an grounded K-type thermocouple immersed in one of the vessels. The reactors used for this work have 90mL capacity and consist in an inner PTFE vessel with PTFE cap inside a PEEK cylinder which gives the ensemble the capacity to withstand pressures up to 100bar. A PEEK spring for safety relief is located in the upper part of the reactor. For the experiments, seven or eight reactors were simultaneously used, depending on the number of fly ashes used.

Reaction procedure: The corresponding amount of coal fly ashes were weighed and poured into the reactor vessel. The adequate volume of freshly prepared sodium hydroxide solution of the required concentration was added and the reactor closed using the tool provided by the manufacturer. The whole set of used reactors was placed in a rotary placeholder inside the microwave oven. Computer control of the operation through an internal microprocessor controller was used. Microwave power was set at 1000 W for all experiments and 180° rotating switching movement of the place holder around the center of the oven was allowed to homogenize the amount of microwave radiation received by each reactor. The reaction was maintained at the adequate temperature a given time and let cool inside the oven. After cooling, the reactors were opened and their content filtered through filter paper. Distilled water washing

was continued until neutral pH of the filtrate. The zeolitized materials were vacuum-dried and stored before XRD analysis.

An initial factorial design using Statgraphics was used for establishing initial conditions for optimization. Modified Simplex (MultiSimplex software) was used for optimization.

Results and Discussion

Based on previous knowledge about significant parameters, an initial factorial design was used for establishing the significant effects and the best starting points for the optimization process. Four variables were selected: sodium hydroxide concentration (2-5M), reaction time (10-30min), temperature (150-200°C) and weight of ash (10-20g). A constant 50mL volume of alkali solution was used. The half fractional design with two centered points required 10 experiments whose results (XRD counts) are shown in Table II, where NaP stands for NaP1 type and Her. for Herschelite type zeolites.

[NaOH]	M	5	2	2	5	2	2	5	5	35	35
time	min	10	30	10	30	10	30	30	10	20	20
Temperature	°C	200	200	150	150	200	150	200	150	175	175
Ash weight	g	10	10	10	10	20	20	20	20	15	15
Puertollano	NaP		96					16			27
	Her.										
Compostilla	NaP		59								
	Her.										
La Robla	NaP		2								
	Her.							12			
Los Barrios	NaP		18								
	Her.										
Andorra	NaP		23								
	Her.							13			
Meirama	NaP	4	92	23	12	21	25	7	24	24	9
	Her.										
Espiel	NaP										
	Her.							12			

Table II. Results for the initial factorial design.

Cancrinite and sodalite type zeolites were also obtained, generally in higher yields, but their ion-exchange capacity is very low and useless for our purposes. However, they are important as they represent competition amongst different zeolite types, being these ones the easiest to obtain in our system. Very fine tuning of the system will be required to obtain high NaP1 or Herschelite yields.

The results clearly show that the yields of NaP1 or Herschelite strongly depend on the type of ash used, Meirama being the most adequate for the synthesis of NaP1 type. There is one experiment with appreciable yield for nearly all ashes, using 2M NaOH, 30 min., 200°C and high liquid to solid ratio (10 g ash, 50mL solution). This one was selected as the basis for the optimization process. Herschelite proved to be more elusive to synthesize as just 3 ashes yielded detectable amounts of it, using rather hard conditions: 5M NaOH, 30 min., 200°C and 20g (low liquid to solid ratio). This conditions were selected for further optimization. Experiments in conventional Parr bombs had shown that good results can be obtained with very low liquid to solid ratio, but this is not applicable to microwave heating as water evaporates and causes partial sodium hydroxide melting with uncontrollable results. In view of the different conditions and results obtained for both zeolites, optimization for each type was started separately with different set of initial conditions.

NaP1 optimization

From the above results, initial simplex was chosen at the following conditions: 2.0 ± 0.25 M NaOH, 30 ± 10 min., 200 ± 25 °C and 10 ± 2.5 g of ash. Experiments with two ashes placed in two different positions of the carousel were used to determine reproducibility of the procedure. We found that results are significantly different and reproducibility is poor. We are considering two possible explanations to this behavior: non-uniform distribution of microwaves in the oven (but twist of the carousel is allowed to compensate the effect) or problems in the analytical methodology due to coarse particles obtained by alkaline activation. As we could neither determine nor solve the problem we decided to go on trying a global optimization using the sum of XRD counts obtained for every ash at each experiment.

The evolution of the zeolite distribution obtained for the first experiments is shown in Fig. 1. The optimization algorithm leads to improved NaP1 content from a good initial set of conditions (NAP 1 to 5). The results showed that competition among different zeolites can drive the reaction to different NaP1 yields. The best results obtained so far make partial use of quartz and little or no use of mullite, the vitreous phase of the fly ash being the main supply of silica and alumina. The optimization direction shifts slightly from the starting conditions to 1.69M NaOH, 46min, 213°C and 11.3g of ash in exp. 10 There is a deep interaction among the four parameters that required fine tuning of the reaction parameters to obtain maximum NaP1 yields.

Herschelite optimization

The starting conditions for the optimization, as obtained from the initial factorial design were chosen as follows: 5 ± 2.5 M NaOH, 50 ± 15 min., 200 ± 25 °C and 20 ± 5 g of ash. The reaction time was lengthened due to other evidences obtained in conventional synthesis. As happened with

NaP1 optimization, the sum of XRD counts obtained for every ash at each experiment was used as response for optimization.

The synthesis of Herschelite proved to be more elusive than that of NaP1. Most of the initial experiments as well as others in the optimization process lead to low or zero yields of Herschelite, cancrinite or sodalite being the most important zeolitic phases obtained. In general, experiments at high NaOH concentration (Hers 1,3,4, 8) can dissolve most of the quartz and mullite present in fly ash, but the high alkalinity drives the reaction towards cancrinite and sodalite zeolites.

It is worthy to note that the optimization of Herschelite converges to the optimization of NaP1 as both zeolites are synthesized under similar conditions, slightly stronger for Herschelite than for NaP.

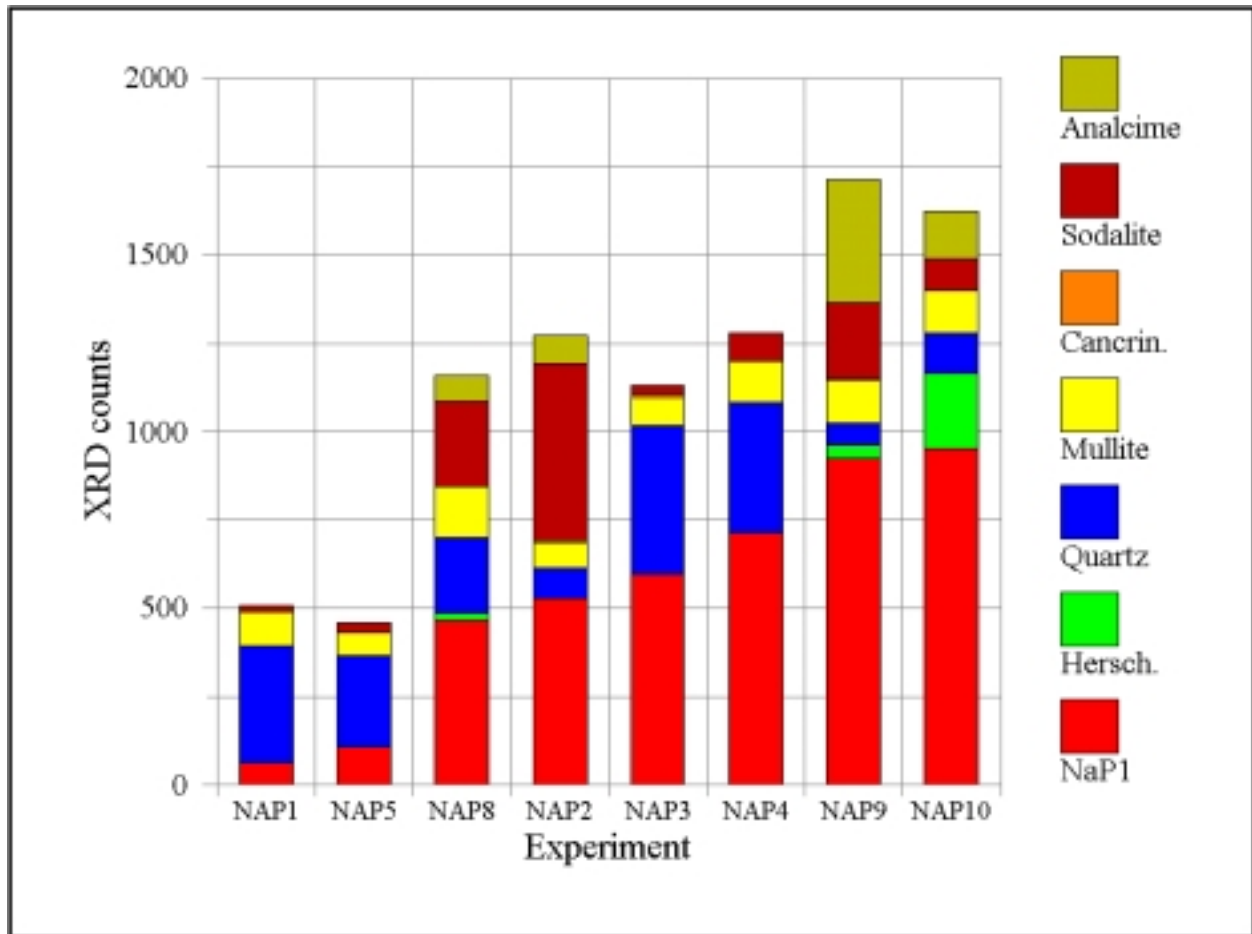


Fig. 1: Zeolite type distribution in the first optimization steps for NaP1.

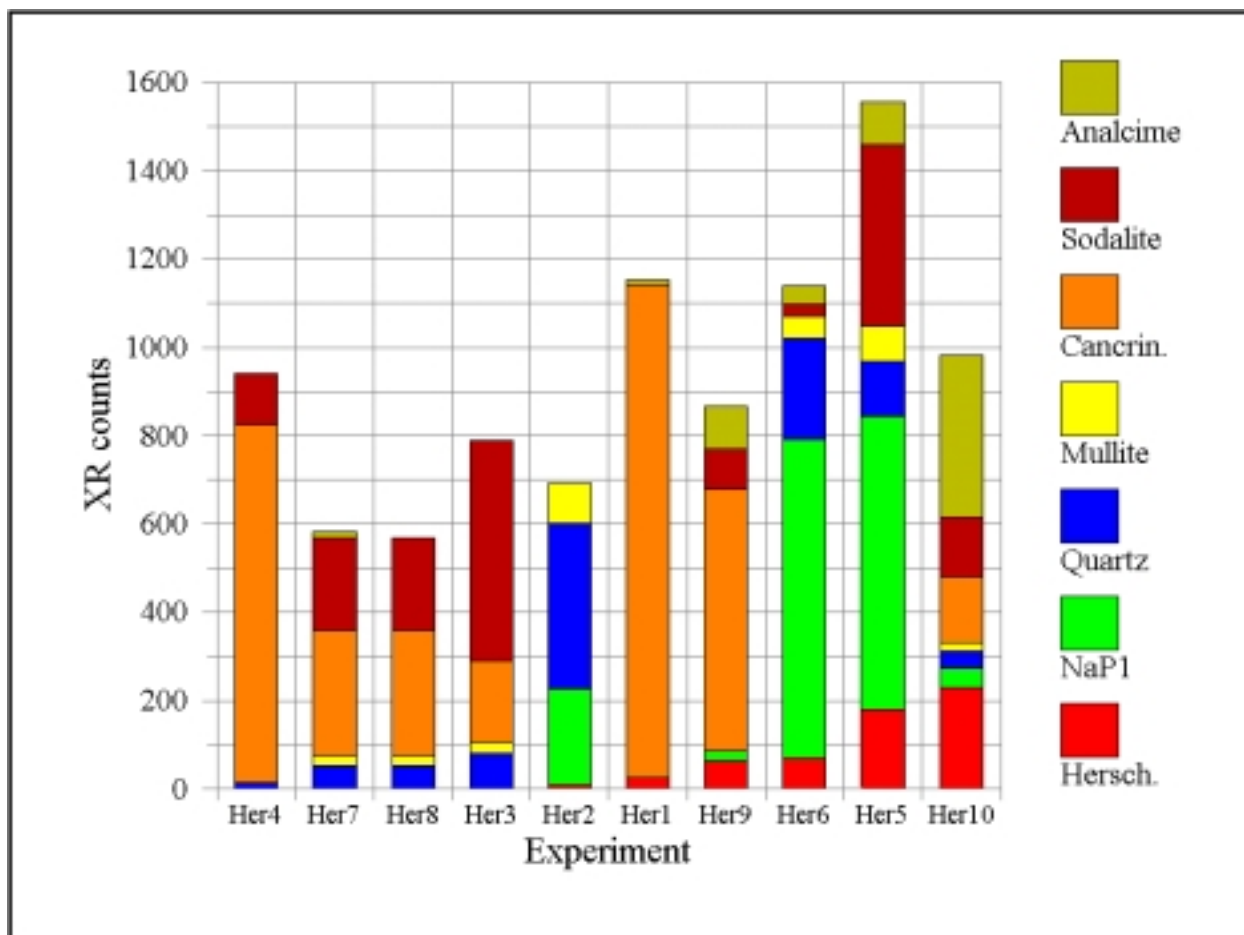


Fig 2. Zeolite type distribution in the first optimization steps for Herschelite.

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