

Determination of the Available Si and Al from Coal Fly Ashes under Alkaline Conditions with the Aim of Synthesizing Zeolite Products

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ABSTRACT

Pure zeolites can be synthesized from silica extracts obtained from fly ash by alkaline leaching. The extraction potential of various types of European fly ashes was investigated under realistic process conditions (2 M NaOH; 90°C; L/S=3; 6h.) and found to vary from 1 to 130 g of SiO₂ per kg ash, using a single step process. However, during extraction zeolites are formed in the ash and this limits the amount of SiO₂ liberated, and thus the yield of pure zeolites to be produced from the extracts. The Al content in the extracts is almost negligible, showing that the liberated Al in the process is all used for crystallizing zeolites and hence consumption of Si. As zeolites form on the ash particles, this also makes the dissolution reactions to cease before completion. In order to avoid zeolite formation at an early stage and to determine the availability of SiO₂, experiments were done at 50°C, 2.5 M NaOH, L/S=20 and reaction times up to 72h. In this way the maximum extraction found increased up to 280 g/kg but still zeolites were found in the residues, showing that the maximum available amount of SiO₂ could not be maintained in the solution. Although the amount of available SiO₂ and Al₂O₃ will be related to fly ash characteristics, it turned out to be difficult to generalize this relation as for different ashes different assumptions were required to fit a model. The formation of zeolites is mainly influenced by the build-up of Al in the liquid phase. Therefore, Al-complexants were added to the solutions with the aim of suppressing the crystallization of zeolites. Zeolites were not detected in the residues, and although the extracted Al₂O₃ increased significantly, the amount of extracted SiO₂ was hardly affected. It is believed that with further development of those experiments and more insight in the glass fraction of the ashes, availability of Si and Al may be determined as a function of ash properties.

INTRODUCTION

The conversion of fly ash into zeolitic materials has been reported for more than 25 years and literature has been accumulated since. The pioneering work of Höller and Wirsching¹, Kolousek et al.² and Singer and Berggaut³ deserve to be mentioned as well

as more recent work from Querol and co-workers.⁴⁻⁶ This conversion is usually carried out through a hydrothermal treatment of the fly ash with an alkaline solution. The type and amount of zeolite that is synthesized depend on the experimental conditions, the most important ones are the composition of the ash, the reaction solution, the liquid/solid ratio, the temperature, the reaction time and the intensity of mixing. Methods of direct conversion combine the liberation of Si and Al and the crystallization of zeolites in one single process. It normally results in a mixed final product with a zeolite content of 40-60%. The type of zeolite formed may be influenced by the prevailing conditions but this is rather limited. These facts can be attributed to:

- Incomplete conversion. As the crystallization process is generally faster than the dissolution process, once crystallization starts it will quickly consume all available Al in the solution. Moreover, fly ash particles will act as support for crystallization and thus the available ash surface for dissolution will decrease until finally locking up the remaining ash particles.
- The presence of non-reactive components of ash in the final product, such as iron oxides, calcite, lime, gypsum, mullite, non-reactive glass and trace minerals.
- The fixed Si/Al ratio in the extractable fraction of the fly ash. Therefore, the Si/Al ratio in the solution can only be influenced slightly by the conditions applied (T, L/S, strength and nature of solution). Since this is one of the factors that largely determine the species of zeolite to be formed, consequently there is little room to play with it. Prior introduction of Al into the solution is not successful because of the effect of decreasing the incubation time.

By trying to separate the dissolution process from the crystallization process, Hollman et al.⁷ proposed to synthesize zeolites from filtrates obtained from the mixture at the end of the incubation time. Al and Si concentrations in the solutions are at their maximum and the Si/Al ratio can be adjusted by adding Al from an external source. This avoids the presence of non-reactive and residual glass in the final product. Pure zeolites A and X were obtained but yields were low, in the order of 100 g per kg of ash used.

The aim of an EC sponsored research project (SILEX) is to increase the yield considerably so that at least most of the Si from the fly ash is used. Al can be added if required through the use of waste etching solutions from Al anodizing plants. It is tried in this study to get insight into the maximum amount of Si and Al that is available for extraction and how this depends upon the characteristics of the fly ash.

METHODOLOGY

Materials

Initially 23 pulverized coal combustion fly ashes were selected by the project. The ashes originated from power plants in Spain (11), the Netherlands (8), Italy (3) and Greece (1). In Table 1 the names, their location and the major chemical components (SiO_2 and Al_2O_3) as well as the main mineralogical components (glass, quartz and mullite) are given. More detailed chemical, mineralogical and physical characterization is given by other members of the project.^{8,9}

Si-extraction

The initial extraction experiments at 90°C were carried out in 60 ml Savillex PFA reactors. Later tests at lower temperatures were done in PP erlemeyers in a hot water shaking bath (Nickel-Electro Ltd Type NE5-28D) and in a hot water bath equipped with magnetic stirrers (IKAMAG RO 15 POWER).

Analyses

The bulk SiO₂ contents in fly ashes were determined by XRF and the other elements by ICP-MS and ICP-AES. The analyses of Si, Al and Na in the leachates were done with ICP-AES and for SiO₂ partly with flame AAS. The mineral compositions of the fly ashes and the residues were determined by XRD, in case of the major components of the ashes using the Reference Intensity Method with CaF₂ as an internal standard.

RESULTS AND DISCUSSION

Initially for all 23 ashes a single step extraction test was carried out in 2 M NaOH at 90°C for 6 hours with an L/S ratio of 3. The amounts of SiO₂ retained in the solutions are given in Table 1 in g/kg of ash. There is a large variation of SiO₂ extraction from almost nothing for the Lignite ash up to 120 and 126 g/kg for Meirama and CCB. The latter figures in theory represent the synthesis of almost 400 g of zeolite A per kg ash, a considerable improvement compared to the results of Hollman, but it still means only slightly more than 20% of the SiO₂ present in the ash as actually recovered. Further, during all of those extractions the amounts of Al₂O₃ in the solutions were found to be very low, in the order of 0-2 g/kg ash. This means that virtually all Al for the synthesis of pure zeolites from the extracts will have to be supplied from external sources. On the other hand, XRD scans of the residues show the presence of zeolites (NaP1, A and Herschelite) in almost all experiments. Thus, the conditions were such that the Al liberated was used up together with part of the Si to form zeolites. This, as pointed out earlier, will have hindered the further liberation of Si and Al from the ash particles. So, even if the amounts present in the zeolites can be quantified, this still will not give the upper limit of potentially available SiO₂ and Al₂O₃ in the ashes. Further, no clear relation between the extracted SiO₂ and the ash characteristics could be found, probably due to the role zeolite crystallization is playing.

As a consequence, it was then tried to rule out zeolite crystallization during extraction tests by carrying out experiments at 50°C. The required amount of OH⁻ to bring all Si and Al into solution was calculated. Twice the average amount for the ashes was used for all experiments. To avoid high NaOH concentrations a high L/S ratio of 20.8 was required at 2.5 M NaOH (2.4 g of ash in 50 ml solution). To make the particles more accessible, ashes were first ground but this had only effect on the reaction speed and not on the maximum obtained dissolution result.

Table 1. Extraction yields for all 23 selected fly ashes at 2 M NaOH, 90°C, L/S=3 and 6 hours given in g/kg of ash. The zeolite contents of the residue are given as A (zeolite A), P (zeolite NaP1) and H (Herschelite) for their presence, with a + when significant and with ++ when abundant. Fly ashes are identified by their power plant name and country location (Loc.) and characterized by the contents of major chemical and mineralogical constituents.

	Loc.	Chemical (wt%)		Mineralogical (wt%)			Extraction yield	
		SiO ₂	Al ₂ O ₃	Glass	Quartz	Mullite	SiO ₂ (g/kg)	Residue
Acid	NL	51.3	28.9	83.1	6.0	9.1	47	P++ A
Alkaline	NL	46.8	24.8	63.1	11.2	20.1	48	P++
Amer-8	NL	45.2	26.5	77.8	6.9	8.2	61	P+
Amer-9	NL	52.4	25.8	77.4	12.5	9.1	76	P++ A
As Pontes	ES	41.5	30.1	51.8	6.2	29.4	40	P+
Barrios	ES	42.6	35.6	48.4	3.4	40.4	42	P++
CCB	NL	59.6	27.0	80.1	9.4	9.8	126	
Compostilla	ES	51.2	25.5	88.8	3.1	3.2	38	A
Escucha	ES	49.5	26.7	55.5	9.6	24.4	62	P+
Espiel	ES	52.3	28.5	85.7	2.7	7.4	27	A H
Fusina	IT	48.2	25.9	71.6	6.4	17.4	61	P++
Hemweg-8	NL	53.2	26.0	83.9	7.8	6.6	56	P+
La Robla	ES	44.1	23.2	84.9	1.7	4.2	13	P+
Lignite	GR	28.5	17.9	61.5	9.2	---	1	
Meirama	ES	49.2	17.6	62.5	6.9	19.6	120	P+
Monfalcone	IT	50.8	33.4	73.1	3.2	25.9	98	P++
Narcea	ES	55.2	23.3	85.6	6.6	3.8	34	P+ A
Neutral	NL	53.3	26.1	80.1	7.1	10.9	80	P++ A
Nijmegen	NL	45.3	25.0	82.2	6.1	4.9	38	P++ A
Puertollano	ES	58.6	27.4	64.7	10.4	20.7	82	
Sardegna	IT	41.7	29.0	74.0	4.0	14.5	21	P++
Soto Ribera	ES	48.9	30.6	74.4	5.0	18.4	42	P++
Teruel	ES	48.3	23.9	62.7	8.6	19.4	40	P+

Eight ashes were selected for those experiments (Table 2) and the time evolution of the extracts was monitored for up to 72 hours reaction time. The two time profiles shown in Figure 1 illustrate the behavior found. The form of the Al curves is for all eight tested ashes the same although the absolute values vary a bit. Up to 24 hours the Al concentration increases to a maximum after which it drops back to almost nil. The Si concentration reaches a maximum constant value between 24 and 48 hours and remains at that value (fig. 1a) for Acid, Neutral, Compostilla and Monfalcone or decreases slightly (Alkaline and Meirama). However, for Puertollano (fig. 1b) and CCB a different behavior is found in that the Si concentration keeps increasing up to 72 hours even though the Al decreases.

The decrease in Al should be attributed to the formation of zeolites since for all four residues, for which XRD scans were made, zeolites appeared at 72 hours. Although in the experiments at 90°C no zeolites were found in the Puertollano ash residue, in the 50°C experiments small peaks of zeolite type minerals do occur in the 72 hours scan. This is in agreement with the decreasing Al content of the solution. So it is consistently found that the highest release of SiO₂ and lowest zeolite formation appears for the Puertollano and CCB ashes. However, the maximum SiO₂ extraction for these two ashes is always found together with almost no Al₂O₃ in the solution. The maximum SiO₂

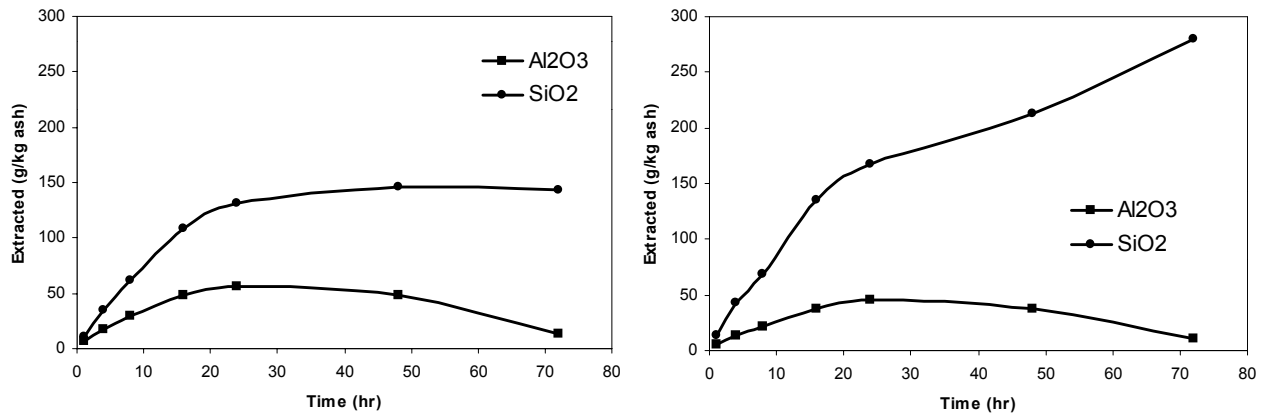


Figure 1. SiO₂ and Al₂O₃ extraction as a function of reaction time. Left is for fly ash “Acid” and right for “Puertollano”.

and Al₂O₃ extractions reached, although not obtained at the same time, are shown in Table 2. The values show that the SiO₂ extraction has in general doubled or even more than tripled in the case of Puertollano compared to the first set of experiments and that now also significant amounts of Al₂O₃ are recovered.

Table 2. Maximum obtained SiO₂ and Al₂O₃ extraction for 8 selected fly ashes in 2.5 M NaOH at 50°C and L/S=20.8 during the testing period of 72 hours.

	Extracted g/kg	
	SiO ₂	Al ₂ O ₃
Puertollano	280	45
CCB	235	44
Meirama	207	28
Monfalcone	176	40
Acid	146	56
Alkaline	142	46
Compostilla	141	57
Neutral	136	55

In general there is more SiO₂ than Al₂O₃ in the extracts than would be expected from the bulk chemistry of the ashes. For short reaction times this is attributed to below average dissolution of Al rich phases (mullite) and/or over average dissolution of Si rich phases (high Si-glass). At longer reaction times the precipitation of zeolites, for which the SiO₂/Al₂O₃ ratio is lower than for the dissolving phases, becomes the dominant factor and makes the two curves rapidly diverge. By making assumptions on the solubility of the mineralogical phases, such as for example “only glass dissolves” or “all except mullite dissolves”, the percentages of SiO₂ and Al₂O₃ at the beginning of the

extraction (up to 16-24 hours) could be made to coincide. In Figure 2 this is done for the Puertollano ash by plotting the extraction percentages of SiO_2 and Al_2O_3 relative to their presence in the glass phase. The glass composition is calculated from chemical and mineralogical data.

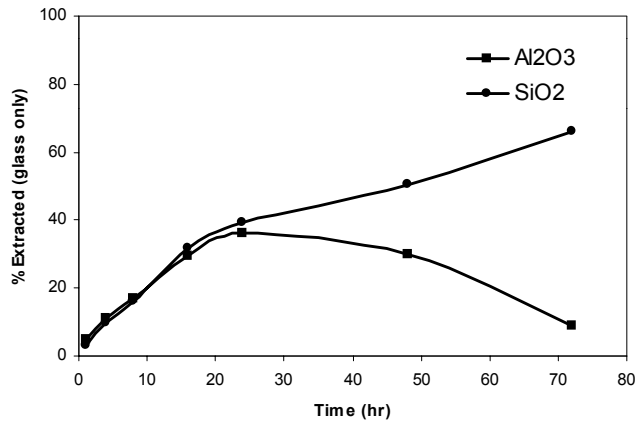


Figure 2. Percentages of SiO_2 and Al_2O_3 extraction related to the glass fraction of the Puertollano fly ash (recalculated from chemical and mineralogical data from Table 1).

From about 20 hours the precipitation of zeolite NaP1 starts. The weight ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in NaP1 is lower (1.96) than in the glass (3.4) and therefore the Al_2O_3 curve deviates faster from the initial straight line than the SiO_2 curve and the solution gets enriched in SiO_2 . Since the SiO_2 content is still increasing, dissolution continues as well. Assuming dissolution to continue along the straight line and attributing the loss of Al_2O_3 along this line to NaP1 precipitation, the calculated SiO_2 values lie slightly above the observed data points. This means that dissolution has slowed down only a little bit from 20 hours onwards. By doing the same for the Acid fly ash using the precipitation of zeolite A (as found in the experiments, Table 1, and supported by the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.9 in the glass), the slowing down of dissolution seems more rapid due to higher amounts of zeolites formed and therefore locking up the ash particles. In general the assumption that only glass dissolves fits well, but for some ashes other assumptions seem to fit better. Since there is no reason why mineral phases should behave completely different in different ashes it is suggested that, although part of the discrepancy between relative SiO_2 and Al_2O_3 extraction is due to different quartz and mullite contents, there is also part of it to be explained by the glass chemistry. The glassy component of the ashes may not be homogeneous in itself, whereby the SiO_2 rich parts are the easiest to degrade. The degree of inhomogeneity may vary between the different ashes. To get more insight in this matter the University of Limerick (Ireland) has started glass network and thermal analysis studies on the ashes^{9,10} and KEMA (Netherlands) initiated SEM element mapping on individual glass particles from those ashes.

Because zeolites are still forming during extraction at 50°C, the maximum availability of SiO₂ and Al₂O₃ was not reached and so could not be related to ash characteristics. In an attempt to avoid zeolite precipitation, Al-complexants were introduced in the extraction solution. The complexants used are the ones that are normally incorporated in additives used in etching baths in the Al anodizing industry: tartaric acid, gluconic acid, Na-gluconate and sorbitol. A mixture of gluconic and tartaric acid seems most effective. Preliminary results from the Puertollano fly ash indicate that the decreasing trend in the Al₂O₃ curves is delayed and much less pronounced. No zeolites are detected in the extraction residues. Further, the maximum amount of Al₂O₃ increased from 45 to almost 100 g/kg. However, the amount of SiO₂ extracted did not increase by adding the complexants and remained unchanged or even decreased slightly. This may be explained by lower release of both Al₂O₃ and SiO₂ at the weight ratio of 3.4 (glass) and no removal through zeolite precipitation at the ratio of 1.96 (NaP1). So, although zeolite precipitation was suppressed, the addition of the complexants also hindered the dissolution of the glass in some way. Experiments with other ashes are under way for the full understanding of the mechanisms.

CONCLUSIONS

Extraction experiments carried out under realistic process conditions (2 M NaOH; 90°C; L/S=3; 6h.) result in highly variable SiO₂ extractions depending on ash type (between 1 to 130 g SiO₂ per kg ash) and generally insignificant Al₂O₃ extraction due to the formation of zeolites in the residues. Zeolite precipitation limits the dissolution reactions and reduces the available SiO₂ and Al₂O₂ for the synthesis of pure zeolites from the extracts.

Experiments at 50°C, 2.5 M NaOH, L/S=20 and reaction times up to 72h increased SiO₂ extraction up to 280 g/kg for the most favorable ash. Although the extracted Al₂O₃ is now significant, still zeolites are found in the residues, indicating that maximum availability is not yet reached. So, it also turned out to be difficult to relate the released SiO₂ and Al₂O₃ to fly ash characteristics. The assumption that the glass fraction of ash is the only component contributing to extraction together with introducing zeolite formation at a later stage gives the best results in fitting SiO₂/Al₂O₃ ratios found in the extracts.

Adding Al-complexants did suppress the crystallization of zeolites. The extracted amount of Al₂O₃ increased significantly but SiO₂ was hardly affected.

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