
SYNTHESIS REPORT

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RECOVERY OF MAJOR ELEMENTS FROM COAL FLY ASHES (SILEX)

Project co-ordinator: KEMA

Dr.Ir. M. Janssen-Jurkovicová

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SUMMARY

Key words: combustion residues, fly ash, zeolite, synthesis, adsorption.

About 60 Mt of glassy combustion residues are produced annually within the EU by electric power generation and waste incineration. An average of 50% of these residues is utilised, with a large variation from country to country (15-100%). The coal combustion residues have been produced for more than 80 years, but in the last 40 years only the constructional (cement) industry has been a large user worldwide.

As these residues contain more than 70% aluminium-silicate glass, there is the possibility of other, more attractive, potential applications. Among the most promising of those products are the **fly ash based zeolitic materials** (obtained by the direct conversion of fly ashes into zeolites) or **pure fly ash based zeolites** (obtained by conversion of silicium extracted from fly ashes).

The main objective of the SILEX project was to build up the scientific and technical bases for the recovery of silicium from the coal ash either by extraction or conversion in order to indicate their suitability for the production of high-quality marketable products which would be interesting from both the environmental (as substitutes of virgin raw materials) and the economical point of view.

Work has been done to investigate the technical properties of fly ashes suitable for the conversion into a zeolitic product or for the production of pure zeolites. For this purpose 23 fly ashes differing in their chemical composition and or physical properties have been studied. From the results obtained in this study it could be derived that the following technical parameters should be met for the production of:

- 1 **zeolitic products:** glass content > 80%, mullite < 10%, quartz < 10%, content of $\text{Al}_2\text{O}_3 + \text{SiO}_2 > 65\%$. The ratio of $\text{SiO}_2 / \text{Al}_2\text{O}_3$ in the glass matrix varies between 1,8 to 2,4
- 2 **pure zeolites (through Si-extraction):** bulk SiO_2 content in fly ash > 50%. SiO_2 in glass + SiO_2 as opal > 50%. The ratio of $\text{SiO}_2 / \text{Al}_2\text{O}_3$ in the glass matrix should be > 2,4.

As concerns the conversion technology there are two possibilities there: a continuous and a discontinuous process. Both of them depending on the desired type of zeolite and the technical parameters of a fly ash can be carried out at a temperature of 80-150 °C. The conversion costs of 1 ton of fly ash into zeolite (product) vary between EUR 70-140. The costs are mainly determined by the costs of NaOH. Using lower grade purity NaOH or a

residue of aluminium anodising industry (available for the transport costs only) can decrease the process costs considerably.

From the preliminary data of a study carried out by KEMA (confidential) it has been indicated that the potential market for fly ash conversion products to be used mainly in the environmental technology (treatment of wastewater, geo-barriers for the landfill sites etc) would vary between 15-20% of the annual fly ash production. This in case that the fly ashes suitable for the production of zeolites would really be available. The technical specifications to be met are given in Scheme 1 of this report.

Fly ash derived zeolites are unknown at the moment on the market. Looking at the potential these zeolites have there is an urgent need to champion them by an individual or other suitable organisation as strong marketing is required in order to penetrate suitable markets.

1 CONSORTIUM

The partners cited here below have taken part in the Consortium of the SILEX project.



KEMA, NL. KEMA employs more than 1600 researches, consultants and technicians. Synergy between all disciplines and fields of application is one of KEMA's greatest assets and it results in tailor made solutions for clients requirements. KEMA Power Generation & Sustainables is the part of KEMA which is committed to support the research and consultancy needs of energy companies, municipal and industrial waste treatment companies, other type of industries and public authorities in the field of sustainability issues. Activities range from (contract) research, policy studies, project management services, consultancy and engineering focused on renewable energy sources, sustainable materials, environmental health and safety. More information on KEMA can be found on <http://www.kema-kps.nl>.

Data contact person:

Dr. Ir. M. Janssen-Jurkovicová
KEMA Nederland B.V.
Utrechtseweg 310
P.O. Box 9035
NL-6800 ET ARNHEM
The Netherlands
Phone: +31 26 3 56 30 04
Fax: +31 26 4 45 16 43
E-mail: m.janssen@mta6.kema.nl



Delft University of Technology, NL. It is the oldest and most famous of the three technical universities in the Netherlands. The new University research portfolio focuses among others on the sustainable technology concerning subjects such as supercritical extraction of heavy metals from MSWI ashes harbour sludge, quality improvement of gypsum residues from the fertiliser industry. The Department of Resource Engineering of the Faculty of Civil Engineering and Geosciences is specifically active in the field of industrial minerals, waste treatment, and recycling and separation techniques for wastes applying mineral processing principles. Further there is a long experience in the use of residues and wastes in cement, concrete and other building materials, as well as recycling of construction wastes.

Data contact person:

Drs. H.W. Nugteren
Delft University of Technology
Faculty of Applied Sciences
TNW/STM/CPT/Particle Technology
P.O. Box 5045
NL-2600 GA DELFT
The Netherlands
Phone: +31 15 2 78 43 76
Fax: +31 15 2 78 44 52
E-mail: h.w.nugteren@tnw.tudelft.nl

**RESEARCH CENTRE
CONTENTO TRADE SRL**

CONTENTO, IT. CONTENTO Trade is a SME operating in the sector of the development of new technologies for recycling and valorisation of industrial wastes in various industrial sectors. The main research experience in the field of fly ashes until now has been obtained on the application of fly ashes in expanded aggregates, as rubber fillers, fibrous materials and on ettringite based materials.

Except the research on the application of fly ashes in the marketable products CONTENTO Trade is also interested in solving the environmental issues as concerns the wastes of metallurgical, agro- and construction industry.

Recently CONTENTO Trade has carried out extended research on the restoration of the archaeological waterlogged wood finds in Italy. At this moment a new restoration technique is being under development.

Data contact person:

Dr. F. Cioffi

Contento Trade SRL

Via Zorutti 84

Campoformido (UD)

IT-33030 Udine

Italy

Phone: +39 0432 66 25 55

Fax: +39 0432 66 28 89

E-mail: contento@ud.nettuno.it



University of Limerick, IE. The strengths of the University of Limerick are in the Science and Engineering sectors, the Department of Material Science and Technology being one of the strongest departments. The Materials Characterisation and Development Group specialises in the design and synthesis of novel cements and ceramics. The Group contributed to the SILEX project through the characterisation of the glass fraction in fly ash and the study of its reactivity.

Data contact person:

Dr. M. Towler
Department of Materials Science & Technology
University of Limerick
Plassey Park
IE-Limerick
Ireland
Phone: +353 61 21 30 55
Fax: +353 61 33 81 72
E-mail: Mark.Towler@UL.IE



Consejo Superior de Investigaciones Científicas, SP. The CSIC is an autonomous multisectorial, multidisciplinary public research body affiliated to the Ministry of Science and Technology, with its own legal personality, its own assets and a presence throughout the national territory. It has more than 4453 employees.

As an institution, it is open to collaboration with national, regional and local authorities, with other research institutions (universities, public and private research bodies) and social and economic agents both within the country and abroad. To all those CSIC supplies research capacity and or human and material resources to undertake research projects or it provides advisory and scientific and technical support. The CSIC has 122 research centres through the country. The ICTJA (Institute of Earth Sciences Jaume Almera (ICTJA) based in Barcelona, partner of the SILEX project is specialised in geo- (chemical) sciences.

Data contact person:

Dr. X. Querol

Consejo Superior de Investigaciones Científicas (CSIC)

Institute of Earth Sciences "Jaume Almera"

Lluís Solé Sabarís s/n

ES-08028 Barcelona

Spain

Phone: +34 93 4 09 54 10

Fax: +34 93 4 11 00 12

E-mail: xavier.querol@ija.csic.es

2 INTRODUCTION TO THE RESULTS PRESENTED IN THIS REPORT

In the SILEX project 23 fly ashes varying in their chemical composition and or physical parameters have been studied for their suitability as a source of silicium for the production of (fly ash based) zeolites under realistic process conditions.

In this report (mostly) the results obtained on a selected group of the representative fly ashes will be presented. For a more extended information on this research the reader is kindly referred to the Final Technical Report of the SILEX project (report no. 98560236-KPS/MEC 02-6132). An overview of fly ashes studied in the SILEX project is given in table 1.

Table 1 Overview of fly ashes used in studies on their suitability for the extraction of silica in the SILEX project

| fly ash name | country | collected at coal-fired power station |
|-----------------|-----------------|---------------------------------------|
| Narcea | N Spain | Unión FENOSA |
| Los Barrios | S Spain | SE |
| Escucha | EN Spain | FECSA |
| Meirama | N Spain | Unión FENOSA |
| Teruel | EN Spain | ENDESA |
| Espiel | S Spain | ENECO |
| Compostilla | N Spain | ENDESA |
| La Robla | N Spain | Unión FENOSA |
| As Pontes | NW Spain | ENDESA |
| Soto Ribera | N Spain | IBERDROLA/E.Bierzo |
| Puertollano | Central Spain | ENECO |
| Amer (Alkaline) | The Netherlands | EPZ |
| Nijmegen | The Netherlands | Centrale Gelderland |
| Neutral | The Netherlands | EPZ |
| CCB | The Netherlands | Centrale Borssele |
| Acid | The Netherlands | EPZ |
| Amer-8 | The Netherlands | Amer Centrale |
| Amer-9 | The Netherlands | Amer Centrale |
| Hemweg-8 | The Netherlands | Centrale Amsterdam |
| Lignite | N Greece | AMYNTAION and LKPA |
| Fusina | Italy | ENEL S.p.A. |
| Monfalcone | Italy | ENEL S.p.A. |
| Sardegna | Italy | ENEL S.p.A. |

3 MAIN OBJECTIVE

The main objective of the SILEX project was to indicate whether the fly ashes would serve as sources of silicium to be used for the production of **pure (fly ash based) zeolites** and if it is so then to indicate whether this or the extraction would be carried out under realistic process conditions and at a competitive price.

The experiments were to be carried out mainly at a laboratory scale level as the SILEX project belongs to the "Brite Euram basic research project" type and as the silica extraction from fly ashes and its conversion into pure zeolites have been indicated as a major innovation and a breakthrough in the field of fly ash utilisation for this purpose.

4 TECHNICAL ACHIEVEMENTS

The technical achievements presented in this report will mainly concern the background of the results obtained on the silicon extraction under realistic conditions for a representative group of fly ashes, as this was the main objective of the SILEX project. For the more detailed information on the other (accompanying) subjects is the reader kindly referred to the Final Technical Report on the SILEX project (report no. 98560236-KPS/MEC 02-6132).

4.1 Maximisation of silica extraction

From all results obtained from the silica extraction experiments, the following optimal conditions for the selected fly ashes, using the conventional single extraction step were obtained: **120 °C, 3M NaOH, 3 l/kg and from 2 to 10h**, depending on the fly ash (7h for Alkaline, 2h for Meirama, 5h for Monfalcone, 10h for Neutral and 9h for Puertollano). The silica extraction yields reached: 87, 179, 186, 166 and 405 g /kg fly ash (equivalent to 262, 538, 558, 500 and 1216 g A zeolite/kg of fly ash) for Alkaline, Meirama, Monfalcone, Neutral and Puertollano fly ashes, respectively. The fastest silica extraction is obtained from the Meirama fly ash (180 g SiO₂/kg, equivalent to 540 g of 4A zeolite/kg, are reached in only 2 hours using a Parr autoclave reactor) due to the presence of soluble opaline phases. This fast extraction allows the precipitation of zeolites from the initial stages of the process (first hour), but the extraction rate does not increase with time further, due to the low solubility of the other silica bearing phases. The other fly ashes showed a delayed zeolite crystallisation parallel with a progressive silica extraction rate.

Applying these extraction conditions to Alkaline and Meirama ashes yielded extracts with a Na₂O/SiO₂ ratio > 1,3. Consequently, this high Na/Si ratio does not allow its utilisation as starting solution for the synthesis of high cation exchange capacity (CEC) zeolites such as 4A, NaP1 or X zeolites. Low CEC zeolites (such as sodalite) may be synthesised with this high Na/Si ratios.

Furthermore, those optimal extraction conditions also favour the crystallisation of neomorphic zeolites in the solid residue. This is a key result since a high Si extract and a zeolitised residue are obtained in relatively short times using a single step process.

Based on the combination of the results on the optimal silica extraction yields and on Na/Si ratio of the extracts, optimal extraction conditions were determined for the selected fly ashes as presented in table 2.

Table 2 Optimum Si-extraction conditions for the 5 selected fly ashes

| fly ash | conditions | extraction yield | | fixed as zeolite g SiO ₂ /kg |
|-------------|---------------------------------|------------------------|-------|--|
| | | g SiO ₂ /kg | Na/Si | |
| Alkaline | 150 °C, 2M NaOH, 2 l/kg and 5h | 70 | 1,0 | 168 |
| Meirama | 150 °C, 2M NaOH, 2 l/kg and 4h | 127 | 0,7 | 199 |
| Monfalcone | 120 °C, 3M NaOH, 3 l/kg and 5h | 186 | 1,2 | 135 |
| Neutral | 120 °C, 3M NaOH, 3 l/kg and 10h | 166 | 1,2 | 245 |
| Puertollano | 120 °C, 3M NaOH, 3 l/kg and 9h | 405 | 0,6 | 111 |

The results from the two-step silica extraction in closed reactors at 90 °C, 6h, 2M NaOH and a solution/fly ash ratio of 3 l/kg, showed that the CCB, Hemweg, Meirama, Monfalcone, Neutral and Puertollano fly ashes reached from 110 to 207 g SiO₂/kg fly ash (equal to 335-630 g A zeolite/kg fly ash). Moreover, the solid residue arising from these extraction experiments contains around 60-75% of NaP1 zeolite, mixed with unconverted fly ash phases such as residual glass, mullite, quartz and magnetite. From these fly ashes, the Puertollano, Monfalcone, and Hemweg have an important disadvantage for zeolite synthesis and silica extraction with respect the CCB, Meirama and Neutral fly ashes, due to the very high contents of Pb, Zn, Ba, Sr, V and other heavy metals.

Using the optimal conditions for direct zeolite conversion conditions for silica extraction, very low extraction yields (<25 g SiO₂/Kg) were obtained for most synthesis conditions, with the exception of the experimental setting at 150 °C, 1 M, 24 h and 18 ml/g due to the incorporation of the silica into zeolite in the solid residue.

Using microwaves, very high extraction yields have been reached for the experimental optimisation of the process. Extraction amount of 138 to 358 g SiO₂/kg fly ash was obtained in very short time (3 to 8 minutes). However, the limitations of the process are:

- high water consumption (from 4 to 9 l/kg)
- the high NaOH and Na₂CO₃ concentrations needed results in a high Na/Si ratio in the extracts, and
- the costs of scaling-up to industrial silica extraction.

The milestone fixed for silica extraction in the original proposal of the SILEX project has been achieved, since this was fixed at 166 g SiO₂/kg fly ash (equivalent to 500 g of pure A4 zeolite/kg of fly ash). The results allowed reaching the following yields:

- 405 g SiO₂/kg in the single extraction (equivalent to 1216 g of pure A4 zeolite/kg)
- 210 g SiO₂/ kg in the two step extraction (equivalent to 630 g of pure A4 zeolite/kg)
- 250 g SiO₂/kg in the single extraction with previous thermal treatment (equivalent to 750 g of pure A4 zeolite/kg)
- 368 g SiO₂/kg in the single extraction with microwaves assisted activation (equivalent to 1104 g of pure A4 zeolite/kg).

4.2 **Parameters determining the suitability of a fly ash for silica extraction**

The comparison of the results obtained on the characterisation of fly ashes and silica extraction allowed us to identify the following decisive factors favouring the silica extraction process:

- high bulk silica content and low contents of Fe- and Ca- impurities
- a high silica and a low alumina content of the glass matrix. This will account for the extraction of silica with minor zeolite precipitation. When Al-bearing phases are dissolved the precipitation of zeolites immediately occurs with the subsequent capture of silica in solution
- the presence of opaline silica in the original fly ash, also product of a high silica/alumina ratio in glass.

The first parameter to be considered in the Si extraction concerns the bulk Si content in the starting fly ash. Using the optimal conditions for 5 selected fly ashes (table 3), it is demonstrated that for a higher bulk SiO₂ content in fly ash, a higher Si extraction yield can be reached (figure 1a), according to the following relationship:

$$\begin{aligned} \text{extraction yield (g/kg)} &= 17,1 \times \text{bulk SiO}_2 (\%) - 650 \text{ (microwaves, } R^2=0,84) \\ &24,4 \times \text{bulk SiO}_2 (\%) - 1055 \text{ (conventional } 120 \text{ }^\circ\text{C, } R^2=0,85) \\ &6,0 \times \text{bulk SiO}_2 (\%) - 212 \text{ (conventional } 90 \text{ }^\circ\text{C, } R^2=0,71). \end{aligned}$$

If the 23 fly ashes are considered and extraction is carried out at 90 °C, 2M, 3 l/kg and 6 h, with 3 consecutive extraction steps with the residue (figure 2):

$$\text{extraction yield (g/kg)} = 6,9 \times \text{bulk SiO}_2 (\%) - 245 \text{ (} R^2=0,61).$$

If only 21 fly ashes are considered (with the exclusion of Meirama and Narcea fly ashes, indicated by arrows in figure 2), the correlation considerably improves:

$$\text{extraction yield (g/kg)} = 7,6 \times \text{bulk SiO}_2 (\%) - 284 \text{ (} R^2=0,80).$$

From the above equations it may be concluded that for obtaining at least an extraction yield of 100 g SiO₂/kg, the bulk SiO₂ content in the starting fly ash has to be at least:

- >52% SiO₂ using conventional extraction, optimised conditions at 90 °C
- >47% SiO₂ using conventional extraction, optimised conditions at 120 °C
- >44% SiO₂ using optimised microwave extraction (140-185 °C).

Therefore, the starting bulk SiO₂ content needed to reach the 100 g SiO₂/kg decreases as a function of the efficiency of the extraction process.

Figure 1b shows that in addition to the bulk SiO₂ content, there is another parameter that better reflects the SiO₂ extraction potential. Since the more soluble Si species present in fly ash are silica in the easily degradable glass matrix and the opaline silica, there is a very good correlation between the extractable SiO₂ using optimised conditions for each fly ash (table 3) and the content of SiO₂ of the glass matrix and the opaline silica content in fly ash. The equations and correlation coefficients are:

$$\begin{aligned} \text{extraction yield (g/kg)} &= 12,5 \times \text{SiO}_2 \text{ in glass+opal} (\%) - 461 \text{ (microwaves, } R^2=0,98) \\ &18,0 \times \text{SiO}_2 \text{ in glass+opal} (\%) - 791 \text{ (conventional, } 120 \text{ }^\circ\text{C, } R^2=0,97) \\ &4,7 \times \text{SiO}_2 \text{ in glass+opal} (\%) - 162 \text{ (conventional, } 90 \text{ }^\circ\text{C, } R^2=0,91). \end{aligned}$$

Table 3 Optimised SiO₂ extraction parameters for the selected fly ashes using the microwave assisted method (top) and conventional extraction procedures (bottom). (T refers to temperature, t refers to time and L/S refers to Liquid to Solid ratio)

| microwave | T °C | t min | L/S l/kg | NaOH M | Na₂CO₃ M | SiO₂ extr. g/kg |
|------------------|-----------------|------------------|---------------------|-------------------|---|---------------------------------------|
| Puertollano | 174 | 8 | 5,8 | 5,0 | 1,5 | 358 |
| Meirama | 148 | 5 | 8,6 | 3,5 | 1,0 | 239 |
| Monfalcone | 159 | 5 | 6,7 | 5,0 | 2,0 | 226 |
| Compostilla | 185 | 5 | 6,5 | 7,0 | 2,0 | 183 |
| Alkaline | 143 | 3 | 4,4 | 7,0 | 2,0 | 138 |

| conventional | T °C | t h | L/S l/kg | NaOH M | SiO₂ extr. g/kg |
|---------------------|-----------------|----------------|---------------------|-------------------|---------------------------------------|
| Puertollano | 90 | 9 | 3 | 2 | 140 |
| Meirama | 90 | 4 | 3 | 2 | 111 |
| Monfalcone | 90 | 4 | 3 | 2 | 99 |
| Neutral | 90 | 9 | 3 | 2 | 99 |
| Alkaline | 90 | 5 | 3 | 2 | 51 |
| Puertollano | 120 | 9 | 3 | 3 | 405 |
| Meirama | 120 | 2 | 3 | 3 | 179 |
| Monfalcone | 120 | 5 | 3 | 3 | 186 |
| Neutral | 120 | 9 | 3 | 3 | 166 |
| Alkaline | 120 | 7 | 3 | 3 | 87 |

Where SiO₂ in glass+opal is the percentage of glass made up by SiO₂ (as determined from the mass balance using chemical and mineralogical analysis) added to the bulk percentage of SiO₂ present as opal. To obtain this value, the determination of the bulk SiO₂ contents and quantitative XRD analyses (using the internal reference standard methodology, by Klug and Alexander, 1974) have to be carried out. The tridimite content represents the opaline silica. Furthermore, once the glass content is determined (removing the contribution from the known crystal phases from the overall fly ash composition), the proportion of glass made by SiO₂ can be determined from the mass balance difference between the bulk SiO₂ content of the fly ash, the theoretical SiO₂ content of each crystalline phase present in the fly ash (quartz, mullite, tridimite, feldspar) and the respective content of each of these phases in the fly ash.

From these equations it may be concluded that for obtaining at least an extraction yield of 100 gSiO₂/kg, in addition to the requirements on bulk SiO₂ contents in the starting fly ash, the following limiting values have to be considered:

>56%SiO₂ in glass+opal using conventional extraction, optimal conditions at 90 °C

>50%SiO₂ in glass+opal using conventional extraction, optimal conditions at 120 °C

>45% SiO₂ in glass+opal using optimised microwave extraction (140-185 °C).

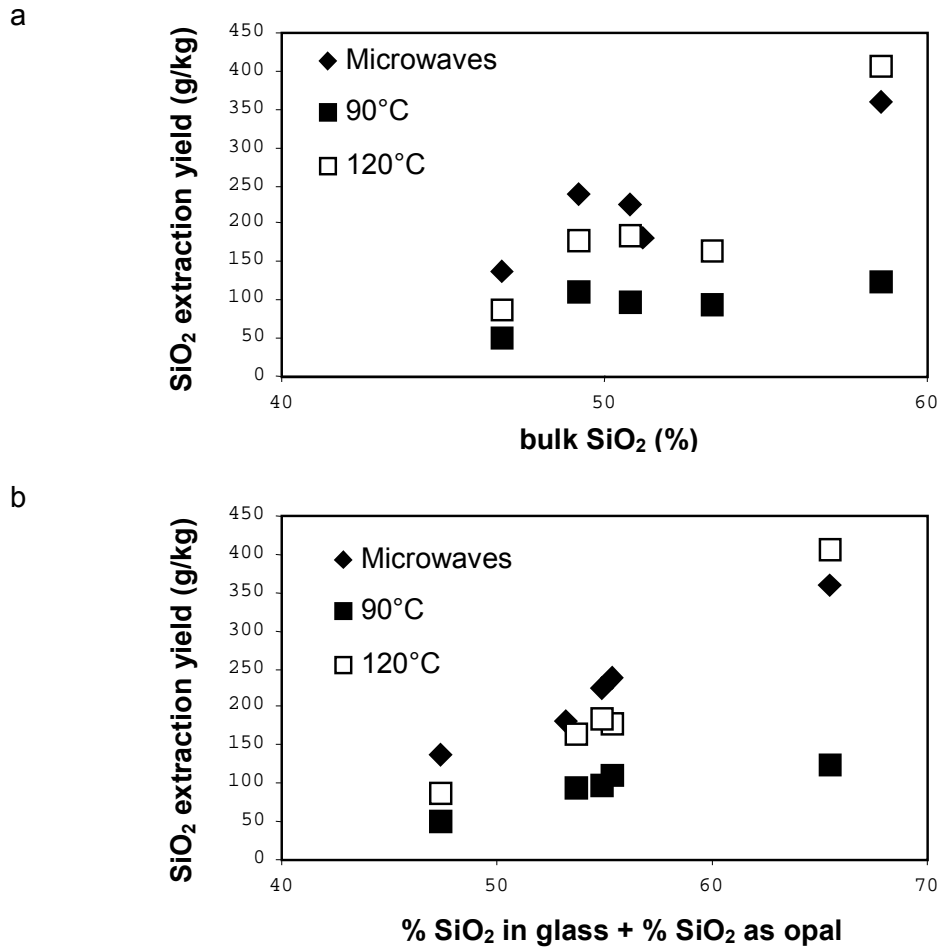


Figure 1 Correlation between the silica extraction yields obtained at optimised conditions for the selected fly ashes and the bulk SiO₂ content in fly ash (a) and the SiO₂ content of glass+opaline SiO₂ (b)

As in the case of the bulk SiO₂ content, also the highly soluble SiO₂ in glass+opal needed to reach the 100 g SiO₂/kg extraction decreases as a function of the efficiency of the extraction process. Furthermore, the presence of high tridimite contents in the fly ash (as in Meirama) favours the silica extraction in such a way that higher yields can be reached than expected.

As previously stated, a low SiO₂/Al₂O₃ ratio in the extract may cause the fast precipitation of silica in zeolites during the extraction and consequently this may inhibit high Si extraction yields in the solution. Therefore, the SiO₂/Al₂O₃ ratio of the fly ash is the third parameter influencing the SiO₂ extraction process. Figure 3 shows that if 4 from the 23 fly ashes are excluded (Narcea, Monfalcone, Lignite and Robla indicated by arrows), the SiO₂ extraction yields may be deduced by the SiO₂/Al₂O₃ ratios in bulk fly ash based on the following equation:

$$\text{extraction yield (g/kg)} = 69,0 \times (\text{SiO}_2 / \text{Al}_2\text{O}_3) - 40,0 \text{ (conventional, } 90 \text{ }^\circ\text{C, } R^2=0,66).$$

From this correlation it may be concluded that a SiO₂/Al₂O₃ (%wt) ratio in the bulk fly ash of >2,0 results in the fly ashes yielding extraction values of >100 g SiO₂/kg, in at least 19 of the 23 fly ashes studied.

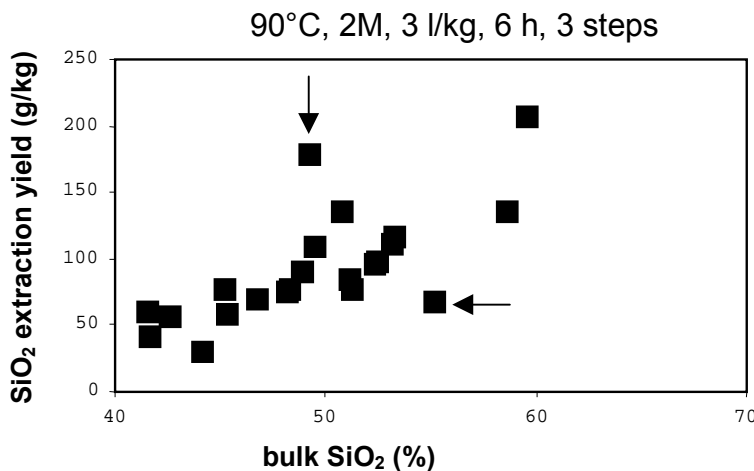


Figure 2 Correlation between the silica extraction yields and the bulk SiO₂ content in fly ash for the 23 fly ashes obtained at 90 °C, 2M, 3 l/kg and 6 h, with 3 consecutive extraction steps with the residue. Outliers Meirama and Narcea are indicated by arrows

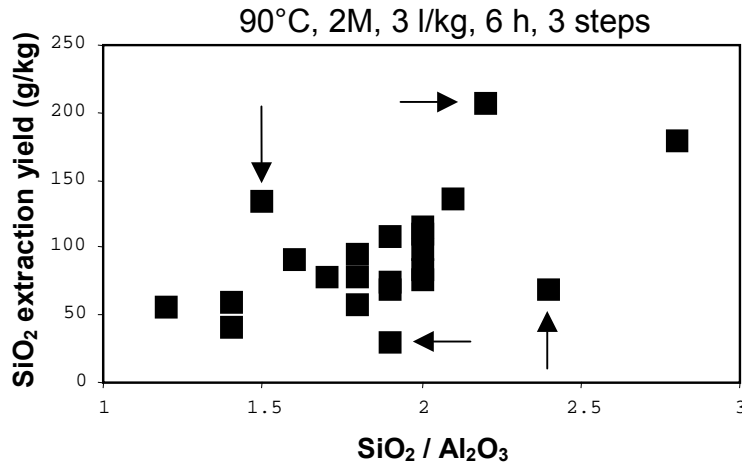


Figure 3 Correlation between SiO₂/Al₂O₃ ratios in bulk fly ashes and SiO₂ extraction yields obtained at 90 °C, 2M, 3 l/kg and 6 h, with 3 consecutive extraction steps with the 23 fly ashes. Outliers Narcea, Monfalcone, Lignite and Robla are indicated by arrows

5 CONCLUSIONS

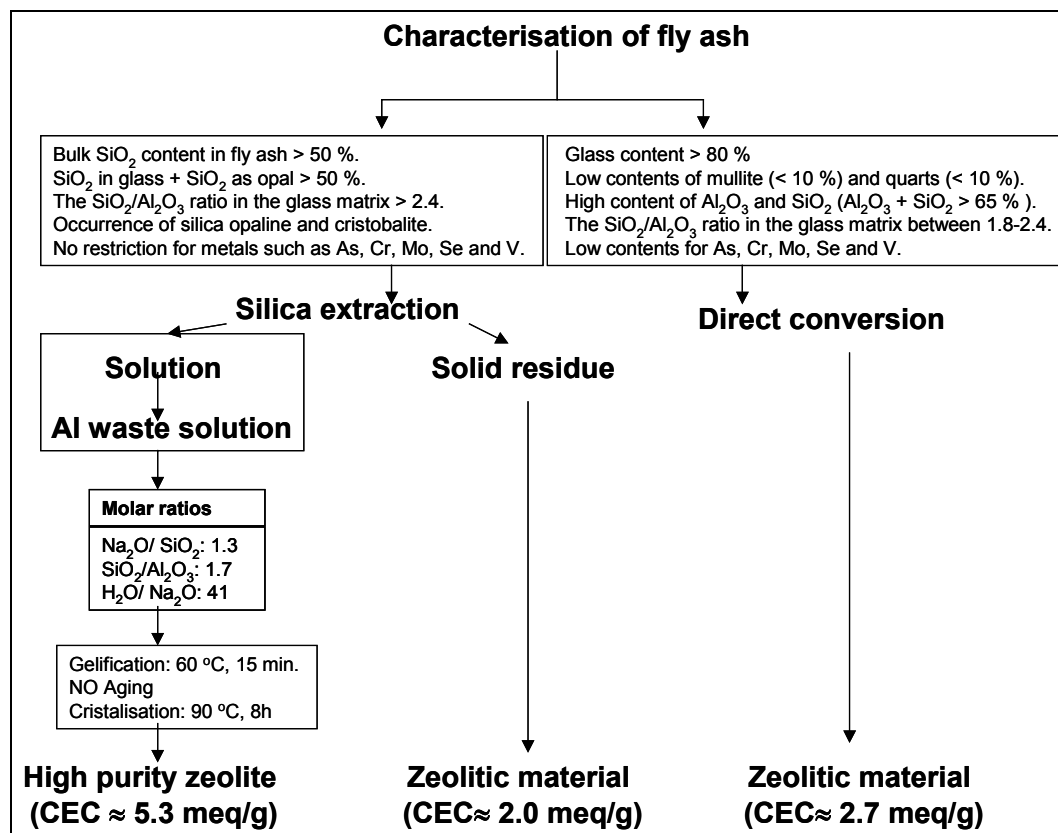
The amount of silicon extracted (as “Si” free in the reaction solution, thus available for converting into pure zeolites) depends on many factors. The following ones are the most important of them:

- the total amount of Si in a fly ash
- the amount of Si available in the glass phase + opaline silica
- the ratio SiO₂/Al₂O₃ should be 2,4 or higher (in order to prevent the synthesis of zeolites during the extraction process)
- extraction conditions in general.

As it is known (and as indicated in this study for 23 fly ashes) the fly ashes can differ considerably in their chemical composition and physical parameters. Their varying “technical” and “environmental quality” has as consequence that not all fly ashes are suitable for the conversion into zeolites. With other words the parameters cited here above have consequences for the marketability of fly ashes as raw materials in particular at assessing their suitability for the market segment of fly ash based zeolites (in the future).

Therefore the “Checklist on Suitability of Fly Ashes for the Conversion into Zeolites” as produced in the SILEX project (scheme 1) is of great value for the selection of the suitable ones. This is a remarkable step forward in strengthening the position of fly ashes in the market place for secondary raw materials.

Scheme 1 Checklist on Suitability of Fly Ashes for the Conversion into Zeolites



6 DISSEMINATION OF RESULTS

6.1 Thematic Networks

The partners of the SILEX project personally or their organisation have on the one side been disseminating information on the SILEX project and on the other side gathering supporting information for the SILEX project in the following Networks.

- PROGRES: EC Thematic Network on Novel Products from Glassy combustion Residues (1998-2002), BRRT-CT98-5055.
- EUROKIN: Kinetic Research on Heterogeneously Catalyzed Processes (1998-2003).
- Educating the European public for Biotechnology (2002-2004), HPRP-CT-1999-00007.
- ILE: IMS Thematic Network on Industrial Liquid Effluents (2002-2006).
- Use of Recycled Materials as Aggregates in the Construction Industry (1998-2002), BRRT985064.
- NESMI: Network on European Sustainable Minerals Industry (2003-2005), G1RT-CT-2002-05078.
- ETNRecy: EC Thematic Network on the Use of Recycled Materials as Aggregates in the Construction Industry (BRRT CT98-5064).

6.2 Conferences

- **International Workshop on novel products from combustion residues, Morella, Spain, June 2001**

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7 COLLABORATION SOUGHT

7.1 Existing collaboration

Indirect contacts with the PROGRES Network partners and associates dealing with zeolitisation and Al-silicate chemistry in fly ashes contributed to the accumulation of knowledge in the SILEX project. To mention are AICIA (ES), the University of Messina (I), the Hebrew University of Jerusalem (IL), the Technical University of Wien (A), the Institute of Geopolymers (FR) and ISSeP (BE).

An excellent example of interest in the research on fly ash based zeolites is that one of Junta de Andalucía (the Autonomous Council of Andalucía). This organisation allowed the Spanish partners of the project to use the selected fields for studying the immobilisation of heavy metals in highly polluted soils by the zeolites made of fly ash under practical conditions. Clariant has been actively helping with providing the facilities for the production of zeolites at the pilot scale level. Elcogas requested CSIC for carrying experiments on suitability of their gasification coal ashes for the production of zeolites. IQE a producer of synthetic zeolites offered the opportunity for the comparison of SILEX zeolites with their zeolites.

During the SILEX project there has also been continuous contact and collaboration with the Al anodising company ALUMET in Etten-Leur, the Netherlands. This company is producing an Al-rich waste solution in NaOH, from which they provided us samples to work with for the adjustment of Si/Al ratios in the fly ash extracts in order to synthesise zeolites from it.

7.2 Collaboration expected

The final results of the SILEX project demonstrate that the SILEX zeolites (pure and zeolitic product) are comparable to the commercially available products. It has also been indicated that a technology for the production of these zeolites (at a competitive price) is available. However, it should be stated that these zeolites are unknown on the (worldwide) market for zeolites at the moment. Therefore further work is needed in order to indicate that these up to now unknown products would be one of the important players in the field of environmental technology in the future.

In the first place the **Application fields** and the **Market volume** (on annual bases) should be indicated and the technical and environmental quality of the product should clearly (according to the market requirements) be described.

Since positive results were obtained from the testing of soil remediation in the toxic mining spill in Southern Spain, this encourages testing also other similar applications. One of the possibilities is to test the ability of reducing the metal mobility in soil (mainly Zn, Cd and Pb) around a large Zn metallurgical plant in the South of the Netherlands. Currently, some activities are running on soil remediation using other methods. Therefore it is advisable to offer collaboration and to join such activities in order to make the property of these zeolites known and comparable to those methods tested previously. In the same area a large polluted jarosite landfill threatens the environment and might be immobilised and/or isolated by applying such zeolites as well.

For further understanding the dissolution reactions and phase relations in fly ash particles in an alkaline environment, collaboration between the SILEX partners with the earlier mentioned external partners should be continued. The Delft University of Technology has already tied the contacts with the Institute of Geopolymers, AICIA, CSIC and ISSeP through a joint project proposal on the geopolymerisation of fly ash (ECSC) for which the principles of Al-silicate dissolution and phase equilibria in alkaline environment are also of prime importance.