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Application of Ca-based geopolymer with blast furnace slag, a review

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Abstract

We present the differences that occur in the chemical mechanism of “alkali-activated slag” and slag-based geopolymer. The negative aspects of alkali-activation are essentially due to corrosive mixture conditions, coined “user-hostile” when compared with the mild milieu that governs geopolymerisation, coined “user-friendly”. Ca-based geopolymer with blast furnace slag generates lower CSH and $Al(OH)_3$ content, yielding three-dimensional molecular structures of the anorthite hydrate type embedded in a solid solution comprising poly(sialate) and poly(sialate-disiloxo) structures. One distinguishes 3 types of Ca-based geopolymer, namely: 1) MK-750/slag-based used for toxic and radio-active waste management; 2) Rock/slag-based for cement in building and infrastructure; 3) Fly ash/slag-based for geopolymer concrete.

Introduction

Davidovits coined the term geopolymer in 1978 to represent a broad range of materials characterised by chains or networks of inorganic molecules.¹ Iron blast furnace slag-based geopolymer research started in 1983 at the Central Laboratory of a major American cement company, Lone Star Industries, Inc, Houston, Texas, USA where Davidovits and Sawyer developed a geopolymer cement, later coined *Pyrament* cement.² In the 1930's, alkalis, such as sodium and potassium hydroxide, were originally used to test iron blast furnace ground slag to determine if the slag would set when added to Portland cement. In the course of studying the testing systems for slag, the Belgian scientist Purdon³ discovered in 1940 that the alkali addition produced a new, rapid-hardening binder. Alkali-activated slag cements (called Trief cements) were used in large-scale construction as early as the 1950's. The usual alkalination called for adding 1.5 percent NaCl and 1.5 percent NaOH to 97 percent ground slag mix (U.S. Army Engineer Waterways Experiment Station, 1953). In 1957, the Ukrainian scientist Victor Glukhovsky⁴ developed alkali-activated slag binders for building applications.

Geopolymerisation mechanism with iron blast furnace slag

The mineral composition of the slag glassy phase is mainly composed of melilite, a solid solution of gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$ plus akermanite $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ (Figure 1) and also merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$. Aluminium is only found in gehlenite and magnesium akermanite and merwinite. From a geopolymeric chemistry point of view, gehlenite is the reactive molecule with effective potential as geopolymeric precursor.

Geopolymerisation starts with the alkalination step involving NaOH or KOH. Its mechanism can be followed with MAS-NMR spectroscopy.

In ^{29}Si NMR, the several resonances around -76 ppm for untreated slag (Figure 2a) are characteristic of the resonance reported by Kirkpatrick⁵ for akermanite glass and solid solution of gehlenite glass. They are assigned to Q_1 species in akermanite glass and to $\text{Q}_2(2\text{Al})$ in gehlenite glass. The alkalination with KOH (5 M) performed by Richardson *et al.*⁶ (Figure 2b) produced a shift to -79 ppm for hydrated Q_1 units of akermanite and a strong line at -82 ppm for hydrated $\text{Q}_2(1\text{Al})$ elements in gehlenite. The shoulder around -76 ppm is assigned to unreacted glass and is not taken into account.

In ^{27}Al NMR, the broad resonance at 58.05 ppm (Figure 3a) reflects the presence of Al in highly distorted tetrahedral configuration within the gehlenite glass fraction. On alkalination with KOH (Figure 3b) there is a narrowing and sharpening of this peak and a shift to 63 ppm, a shoulder around 70 ppm and presence of a new narrow resonance at 10 ppm typical for Al in 6-fold coordination. Richardson and Groves⁷ had shown the presence in hardened blast furnace slag of layers with Mg, Al hydroxide phase related to the naturally occurring mineral hydrotalcite $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3)_{0.125}(\text{H}_2\text{O})_{0.5}$. Alkalination with KOH and NaOH liberates $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$, Al in 6-fold coordination which precipitate or react with atmospheric CO_2 .

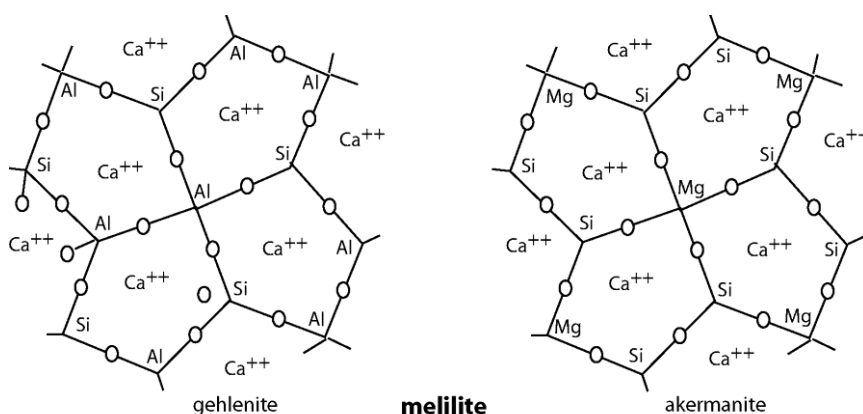


Figure 1: Molecular structure of gehlenite and akermanite in melilite glass

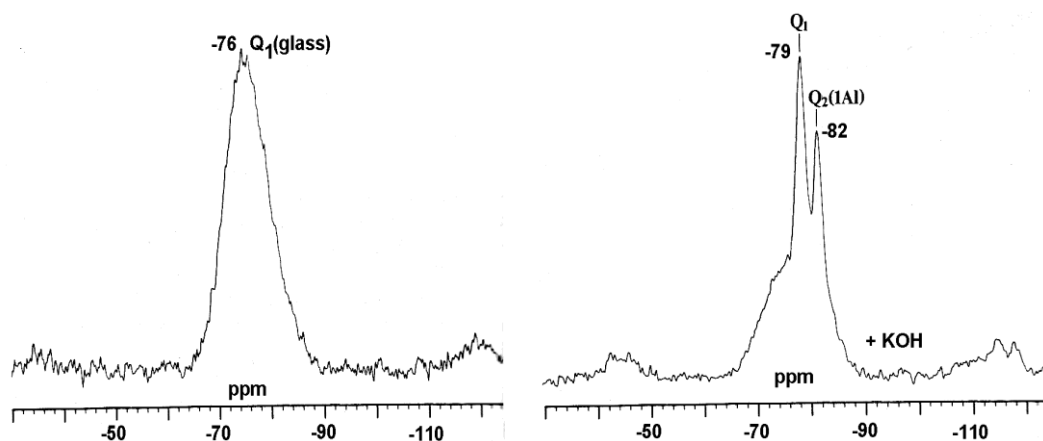


Figure 2: ^{29}Si NMR; a) (left) untreated slag; b) (right) algalinalion with KOH

The algalinalion and dissolution of gehlenite glassy slag produces low molecular Q_1 and $Q_2(1\text{Al})$, Q_2 species, monomers, dimers, and several hydroxides. Yet, according to Astutiningsih and Liu⁸ the major drawback in utilising blast furnace slag for geopolymers is the high content of CaO, composing 41% of the precursor's total weight. These authors believe that CaO, which is integrated in the gehlenite, akermanite and merwinite phases, does not interfere with the geopolymerisation of the alumina-silica constituents. During mixing, Ca^{++} would react with OH^- in the alkaline aqueous system to form $\text{Ca}(\text{OH})_2$, which then reacts with CO_2 in the atmosphere, forming calcite, CaCO_3 . According to them, these reactions would be in essence the hardening mechanism of mortar. At the same time, dissolution of alumina-silica precursor proceeds.

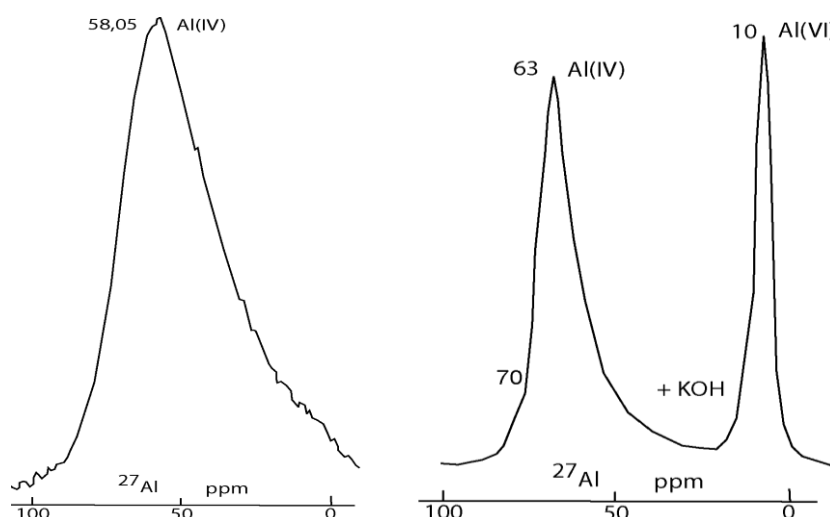


Figure 3: ^{27}Al NMR; a) (left) untreated slag; b) (right) algalinalion with KOH.

However, our laboratory experience shows that carbonation into CaCO_3 or MgCO_3 does not occur in the reaction mixture, but later, after the geopolymer has set and comes in contact with the atmosphere, during the first drying process. Hardening is therefore only governed by geopolymerisation. Alkalinisation induces the splitting of the Al-O-Al sequence in Ca-poly(alumino-sialate) glass, gehlenite. One Al atom participates in geopolymerisation, the second goes into the solution as the Mg. The chemical mechanism of the alkalinisation of melilite glass may be interpreted in this way.

Step 1

The melilite constituents undergo a severe alkaline cleavage yielding:

- for gehlenite: ortho-sialate hydrate molecules and liberation of aluminum hydroxide $\text{Al}(\text{OH})_3$,
- for akermanite: Ca-di-siloxonate (CSH) molecules with Q_1 Si units, *i.e.* a dimer, and liberation of magnesium hydroxide $\text{Mg}(\text{OH})_2$. The third component of the glassy phase of slag, namely merwinite, undergoes the same cleavage as akermanite with additional production of $\text{Ca}(\text{OH})_2$.

Step 2

One ortho-sialate hydrate molecule condenses with one Ca-di-siloxonate hydrate and forms the quadratic ortho-(sialate-di-siloxo) molecule $[\text{Si}-\text{O}-\text{Al}-\text{Si}-\text{O}-\text{Si}-\text{O}]$ with its typical $Q_2(1\text{Al})$ unit. The Ca-di-siloxonate hydrate molecules produced in excess during the cleavage of akermanite and merwinite remain isolated, do not condense into higher polymers, in order to comply with their Q_1 structural unit set forth by NMR spectroscopy. Free hydroxides, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ precipitate and react with atmospheric CO_2 yielding various simple carbonates (CaCO_3 , MgCO_3) and hydrotalcite.

In pore solution chemistry studies carried out by cement scientists, (K,Ca)-cyclo-ortho-(sialate-disiloxo) molecule is called C_3AS_3 for grossular ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) and Ca-di-siloxonate is CSH, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$.⁹⁻¹¹

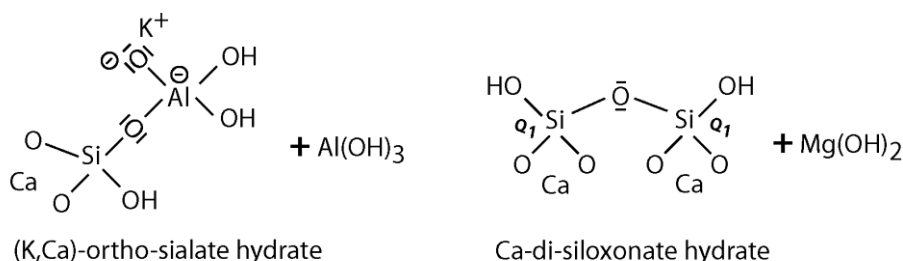


Figure 4: Step 1 in the chemical mechanism of the alkalinisation of melilite glass

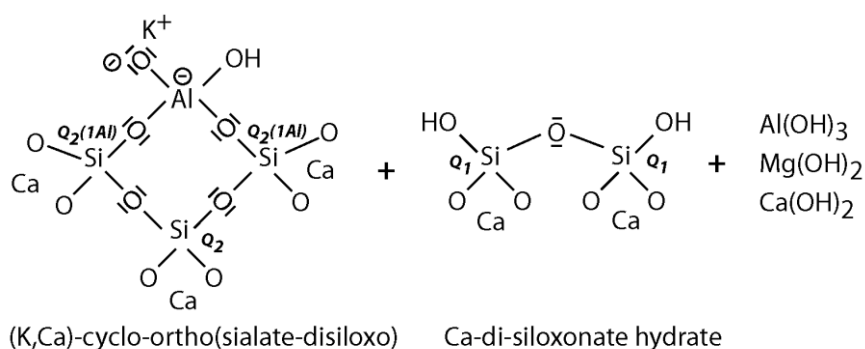


Figure 5: Step 2 in the chemical mechanism of the alkalination of melilite glass

Alternative step

According to cement scientists, the alkalination of glassy gehlenite slag is similar to the hydration of Portland cement paste into calcium silicate hydrate, written CSH.^{7,12,13} Instead of the simple dimer, Ca-di-siloxonate hydrate, typical for CSH, Richardson *et al.*⁶ suggest the incorporation of a bridging function for the aluminium atom, between two dimer molecules. They describe a tobermorite linear chain structure with Al substitution. However, alumino-silicate molecules, geopolymer precursors, oligomers, form cyclic structures, quadratic, pentahedral or hexahedral arrangements, not linear molecules. The chemical mechanism set forth in Step 1 and Step 2 is, therefore, more representative of the alkalination of gehlenite glassy slag than the linear alternative step.

Negative aspect of alkalination

For Astutiningsih and Liu⁸ the major drawback in utilising blast furnace slag is the high content of CaO. The truth is that the main negative aspect is the alkalination itself. In the ortho-sialate-di-siloxo molecule generated in Step 2 (as well as in the tobermorite of the Alternative step), the alkalis K^+ or Na^+ are located at a non-bridging oxygen site $Al-O^- K^+$. The cation is not attached chemically or trapped physically by the structure. It may move and build free alkalinity KOH or NaOH. Several studies¹⁴⁻¹⁶ demonstrate that, in alkali-activated slag, Na and K are not structurally incorporated but are physically adsorbed onto the surface structure. Despite this negative aspect, alkalination has been promoted for cementitious systems and coined “alkali-activated slag” by Glukhovskiy and others.¹⁷⁻²⁵ They built a storehouse in 1974 made of alkali-activated slag. Deja²⁶ studied the evolution of the free alkalinity remaining in the pore solutions of this concrete. The amount of free alkali did not change from 28 days (35.6%) to 27 years (38%). However, the industrial implementation of iron blast furnace slag in geopolymeric systems requires the absence of free alkali in the geopolymer matrix. This implies the development of “User-friendly” systems.

Development of user-friendly geopolymeric systems

Material Safety Data Sheets provide a classification of alkaline chemicals ordered in two categories: corrosive products and irritant products. The two classes are recognizable through their respective logos displayed in Figure 6.

Table 1: Corrosive and irritant chemicals

Corrosive: User-hostile	Irritant: User-friendly
CaO (quick lime)	Ca(OH) ₂
NaOH	Portland cement
KOH	Iron slag
Sodium metasilicate	Slurry soluble silicate/kaolin
SiO ₂ :Na ₂ O = 1	MR 1.25<SiO ₂ :M ₂ O<1.45
Any soluble silicate	Any soluble silicate
MR SiO ₂ :M ₂ O <1.45	MR SiO ₂ :M ₂ O >1.45

Table 1 lists some alkaline chemicals and their corresponding safety label. The corrosive products must be handled with gloves, glasses and masks. They are user-hostile and cannot be implemented in mass applications without the appropriate safety procedures. In the second category one finds Portland cement or hydrated lime, typical mass products. Those geopolymeric ingredients belonging to this class may also be termed user-friendly. When we started the research on geopolymers we decided to select alkaline conditions that could be classified as merely “irritant”, *i.e.* user-friendly.

The alkaline conditions were reached with a MR ratio SiO₂:M₂O > 1.45, and as it turned out, SiO₂:M₂O = 1.85. Unfortunately, our recommendation was not followed by other engineers and scientists involved in the development of geopolymeric systems, or “alkali-activation”. Table 2 provides details on recently published patents dedicated to “geopolymer” cements, based or not on iron blast furnace slag.

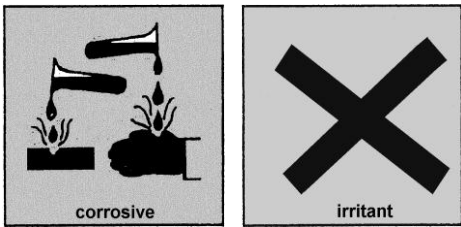


Figure 6: Logos for corrosive (left) and irritant (right) chemicals

Table 2: Comparison between state of the art patents

	WO 03/ 099738	WO 05/ 019130	US 508 4102	US 464 2137	CZ 289 735	WO 03/ 078349	US 560 1643
MK-750	XX	XX	--	XX	XX	--	--
slag	XX	XX	XX	XX	XX	--	--
Fly ash	--	XX (C,F))	XX (F)	XX (C,F)	XX	XX (C)	XX (F)
SiO ₂ :M ₂ O	1.25-2.0	0.31	0.8-1.20	3.0	0.4-1.0	0.6-1.0	0.2-1.0
temperature	20°C	90°C	20°C	20°C	60-70°C	20-95°C	60-90°C
time	-	12-18h	-	-	8-12h	8-12h	15-60h
activator	--	Borax	clinker	KOH + clinker	clinker	Ca++	--
USER- FRIENDLY	YES	NO	NO	NO	NO	NO	NO

XX indicates the presence of the ingredient in the recipe

This is not an exhaustive list but it shows that the mainstream of researchers, scientists and engineers, do not consider the end user’s safety at all. Only one patent, WO 03/099738, out of eight presents a user-friendly SiO₂:M₂O ratio in the range of 1.25-2.0. In all cited patents, except one, the safety label states “user-hostile”. Another problem is also that practically all papers dealing with “alkali-activated” cements describe recipes that are user-hostile. For example, Glukhovsky,⁴ Krivenko,²⁴ Palomo *et al.*²⁷ suggest the use of sodium metasilicate MR = 1. Van Jaarsveld and van Deventer²⁸ get the best results for MR ranging between 0.69 and 1.11. Others present even stronger alkaline conditions, like Astutiningsih and Liu⁸ who keep the MR in the range of 0.60. All these alkaline conditions are corrosive to strongly corrosive. Although, during the Geopolymer 2005 Conference in Saint-Quentin, end users representatives complained about this situation, several scientists do not take this situation into account and continue to promote user-hostile systems. See for example the recent review by Duxson *et al.*²⁹

Chemistry mechanism of MK-750/slag-based geopolymer matrix

In order to better understand the chemistry of Ca-based geopolymer matrix we make the following geopolymeric mixture, called Cement Base in various documents:³⁰⁻³²

- Calcined kaolinitic clay MK-750
aluminosilicate oxide (Si₂O₅, Al₂O₂), 0, 20 and 30 parts
- K silicate solution,
(by weight) K₂O: 26%, SiO₂: 21%, H₂O: 53% 25 parts

- Blast furnace slag (calcium melilite)
average grain size 8 microns 27 parts
- Water 31 parts

Subsequently, we pour the mixture into a container covered with a plastic film or a lid and allow to harden at room temperature. The interaction of MK-750 neutralises any risks of free alkalinity. Its action may be followed with MAS-NMR spectroscopy. Figure 7 plots the 8-day compressive strength for different MK-750 contents added to slag. It shows that the strength diminishes with the increase of MK-750.

The knowledge on the chemical structural make-up of this hardened Ca-based geopolymer matrix is essential for the understanding towards long-term behaviour.

MAS-NMR Spectroscopy

The NMR spectra in Figure 6 show the transformation from the simple alkali activated slag (no MK-750 addition) into a three-dimensional alumino-silicate network typical for equilibrated geopolymer. In the ^{29}Si NMR spectrum, the major resonance at -82/-83 ppm in alkali-activated slag (no MK-750 added) is similar to the one of Figure 2b discussed previously for KOH alkalination. They can be assigned to $\text{Q}_2(1\text{Al})$ and Q_2 species. The addition of 20 parts MK-750 shifts the resonances to -86 ppm assigned to Q_3 branched units. The resonance is broader, with values at -88 and around -90 ppm, suggesting the formation of Q_4 networking elements. With the addition of 30 parts MK-750 the shifts reaches -88, -90, -92 and higher, suggesting three-dimensional networking of the types $\text{Q}_4(3\text{Si}.1\text{Al})$, $\text{Q}_4(2\text{Si}.2\text{Al})$, $\text{Q}_4(1\text{Si}.3\text{Al})$ and $\text{Q}_4(4\text{Al})$.

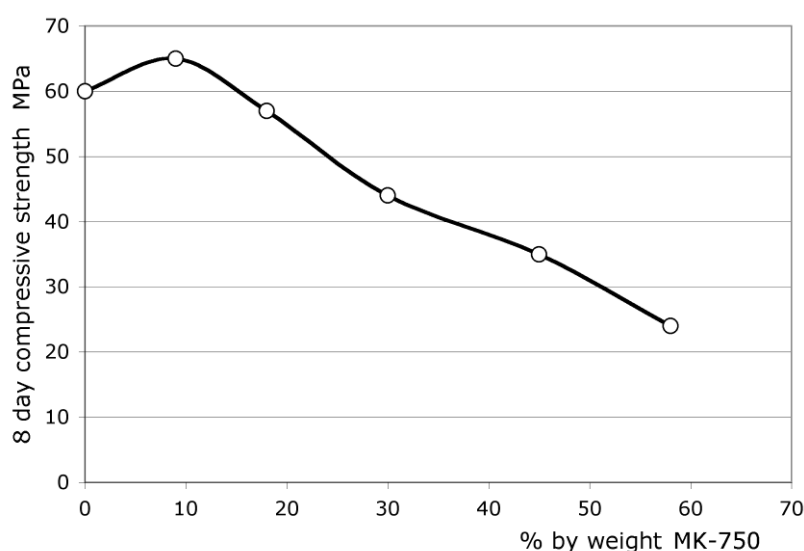


Figure 7: 8-day compressive strength for different MK-750 contents, after Geocistem²⁹

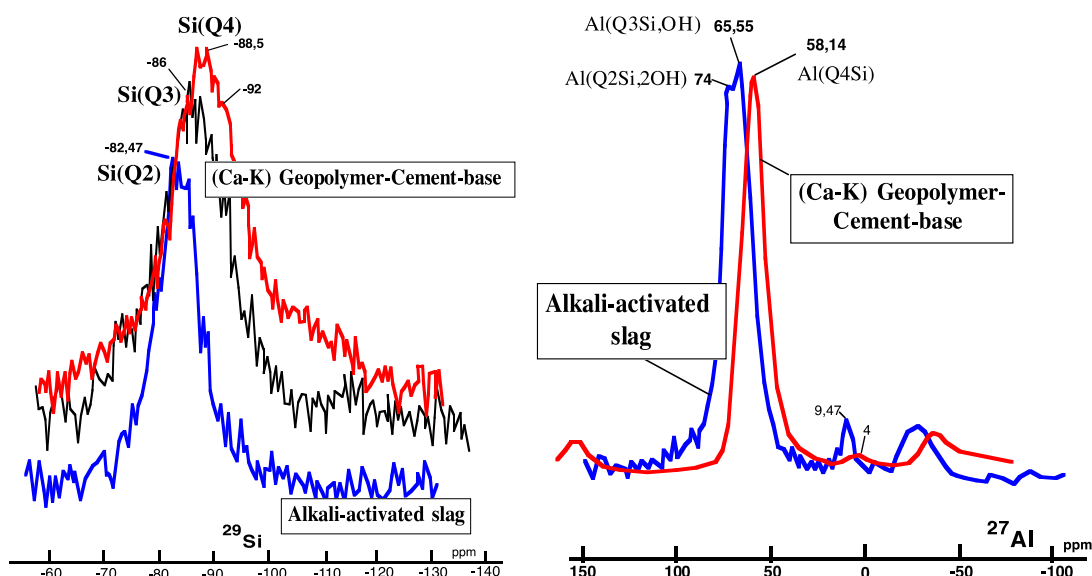


Figure 8: ^{29}Si NMR (left) and ^{27}Al NMR (right) of hardened geopolymeric Cement Base, evolution from alkali-activated slag towards geopolymer cement: no MK-750 added; middle curve, with 20 parts MK-750; top curve, with 30 parts MK-750

In the ^{27}Al NMR spectrum, the major resonances at 74/65 ppm in alkali-activated slag (no MK-750 added) are similar to those of Figure 3b discussed previously for KOH alkalination. They can be assigned to $\text{Al}(\text{Q}2\text{Si},2\text{OH})$ and $\text{Al}(\text{Q}3\text{Si},\text{OH})$ species. With the addition of 30 parts MK-750 the resonance is narrower at 58 ppm suggesting three-dimensional networking of the type $\text{Al}(\text{Q}4\text{Si})$. In alkali-activated slag, the peak at 9 ppm is assigned to 6-fold coordinated Al. Its intensity is much smaller than its equivalent in Figure 3b for KOH alkalination. With geopolymerisation, some potassium silicate molecules (dimer, trimer and higher) have reacted with the free $\text{Al}(\text{OH})_3$ to generate a geopolymer phase. With the addition of 30 parts MK-750, the initial amount of 6-fold Al, 8%, drops below 3% and 4-fold Al reaches 97%. The very small amount of $\text{Al}(6)$ may be also explained by some unreacted MK-750, not by the presence of $\text{Al}(\text{OH})_3$.

Both spectra demonstrate that, in opposition to alkali-activated slag, the Al in (Ca,K) geopolymers is entirely chemically connected, *i.e.* the cations Na^+ and K^+ are trapped within the structure, providing long-term stability and corrosion resistance. End-users may have a choice between high strength and low stability (alkali-activation) or lower strength and optimal long-term and corrosion resistance (geopolymerisation).

Electron microscopy

Figure 9 shows the electron micrograph of this Ca-based geopolymer that consists of an amorphous matrix (shown in black) in which small white grains are embedded.

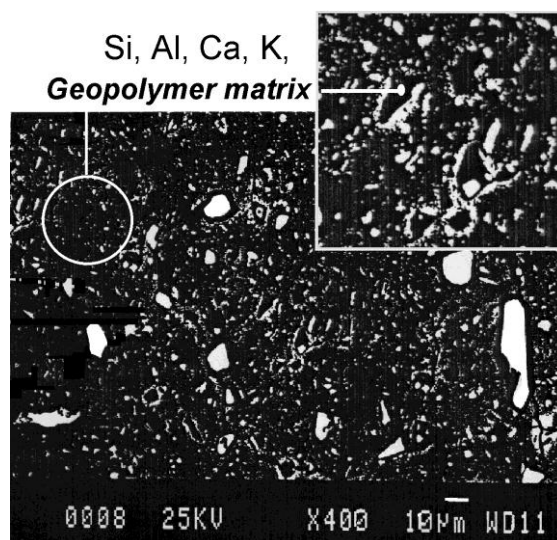


Figure 9: Electron micrograph of the Ca-based geopolymer (Scale bar = 10 microns). The picture on the top right is an enlargement of the central part of the picture with the imprints of digested slag particles.³²

These are remains of the slag. One notices that the majority of the slag grains have disappeared. One only sees an imprint of their initial shape, in the form of a skin, probably made up of ingredients which did not react. We may conclude that slag crystals are digested by the K-silicate slurry, and then react with MK-750, leaving the imprint of the grain surrounded with materials non-participating into the reaction (Mg, Ca, Si).

The chemical composition of the amorphous matrix (circle and grain interior) comprises Si, Al, Ca and K atoms, with practically no Mg, the latter being found in the white powders and grains. This process is very regular and can be complete within 30 minutes, at ambient temperature. The overall chemical composition for the Ca-based geopolymer is given as oxides in Table 3. The values for water were omitted voluntarily.

Table 3: Overall composition of the Ca-based geopolymer mix (water omitted)

	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %	K ₂ O %
MK-750	16.33	12.76	0.15	0.096	0.012	0.042	0.439
Ca melilite	9.58	3.24	0.054	2.43	11.34	0.054	0.135
K-silicate.	5.23	0	0	0	0	0	6.495
Total oxides by weight	31.15	16.00	0.210	2.52	11.35	0.096	7.069
Total in mole	0.519	0.157		0.063	0.20	0.0015	0.0752

The oxide mole values provide the following atomic ratios:

Si:Al	1.65	Si:K	3.43
K:Al	0.48	Si:Ca	2.57
Ca:Al	0.64	Si:Mg	8.22

After hardening, the Electron Micro Beam Analysis gives the oxide chemical composition for the geopolymer matrix in which the calcium melilite grains have practically all disappeared. Only some coarse grains and small fragments remain with a size greater than 20 microns. 14 micro beam measurements were made of the geopolymer matrix. The average value of these measurements provides the following atomic ratios (between brackets, the lowest and the highest values):

Si:Al	1.655 (1.317 to 1.832)	Si:K	2.46
K:Al	0.670 (0.30 to 0.97)	Si:Ca	3.75,
Ca:Al	0.44 (0.16 to 0.610)	Si:Mg	21.26 (3.73 to 49.33)

Chemistry mechanism, solid solution in MK-750/slag-based geopolymer matrix

It is striking to notice that in the overall composition and in the electron beam analysis the Si:Al ratio equals 1.65. Each aluminium atom is involved in the geopolymer matrix, none is found in the slag debris. We know that the negative charge of every Al atom must be balanced with a corresponding positive charge, *i.e.* one K^+ or half Ca^{++} . In the matrix, the ratio K:Al equals 0.67, implying that 0.33 positive charge must be found with a Ca double cation, *i.e.* 0.165 Ca. The negative charge of one Al is therefore balanced with 0.67 K^+ and 0.165 Ca^{++} . The Si:Al ratio = 1.65 is equal to the ratio of 5 Si to 3 Al that could be achieved by mixing several types of geopolymer molecules:

- poly(sialate), Si:Al = 1:1
- poly(sialate-disiloxo) Si:Al = 3:1
- ortho(di-siloxonate) Si:Al = 1:0

A satisfactory composition would be achieved by having a solid solution of:

- 2.5 molecules (K,Ca)-poly(sialate), hydrate
- 0.5 (K,Ca)-poly(sialate-di-siloxo), hydrate
- 0.5 Ca-di-siloxonate, hydrate (CSH)

The simultaneous presence of Ca-di-siloxonate/CSH in a geopolymer matrix remained a puzzle for researchers working on geopolymers, until Yip and van

Deventer³³ mentioned that the CSH element formed in the geopolymer matrix had a significantly lower Ca/Si ratio than the CSH commonly formed from the hydration of OPC. Actually, we do not have in (K,Ca)-poly(sialate) an alternation between K^+ and Ca^{++} along the macromolecular chain. Indeed, geological analogues derived from the melt suggest rather a solid solution between K-poly(sialate), kalsilite, and Ca-poly(di-sialate), anorthite $CaSi_2Al_2O_8$, as well as K-poly(sialate-disiloxo), orthoclase-sanidine, and anorthite. Ca and K would be more probably involved in two parallel chemical mechanisms yielding the joint formation of a solid solution containing:

- 1.67[K-poly(sialate)], kalsilite, hydrate + 0.41[Ca-poly(di-sialate)], anorthite hydrate;
- 0.33[K-poly(sialate-disiloxo)], orthoclase hydrate, + 0.08[Ca-poly(di-sialate)], anorthite hydrate;
- 0.5[Ca-di-siloxonate] (CSH).

Industrial Applications of Ca-based geopolymer

One distinguishes 3 types of Ca-based geopolymer, namely:

1. MK-750/slag-based (calcined kaolinitic clay-based binder);
2. Rock/slag-based (silica-rich rock-based cement);
3. Fly ash/slag-based (class C fly ash-based cement).

Below, we give one example of a successful application for each type.

MK-750/slag-based geopolymer binder for toxic and radio-active waste management

Any safe heavy metals or radioactive containment requires the implementation of a technology involving MK-750-based geopolymers, exclusively. The disposal of radioactive and toxic sludge must meet at least two conditions:

1. Safe chemical encapsulation of the contaminants, *i.e.*, prevention of their release into ground and seepage water in order to minimise the health risks via the water path. Contaminant release is controlled by the leaching properties of the immobilisation matrix.
2. Structural stability with respect to adverse environmental conditions such as rapid changes of temperature and humidity, microbial and chemical aggression and mechanical stress, in order to guarantee safe handling during operation time and minimise the risk of uncontrolled spread of contaminated matter over the next several hundred years.

In November/December 1998, a pilot-scale experiment was carried out in WISMUT's Uranium Mine Water Treatment Facility at Aue, Saxen, Germany. This facility was built to remove Uranium, Radium, Arsenic and other toxic metals from the flooding water of the Schlema-Alberoda Uranium mine. The technological principle is a consecutive selective precipitation/flocculation. At a flow rate of about 450 m³/h, approximately 3.5 to 4 tons of dewatered hydroxide sludges were to be solidified and disposed of every day. The pilot-scale experimentation involved 20 tons of material. The user-friendly geopolymer system was safely handled.

Immediately after mixing the pre-product with the MK-750 based (Ca,K)-Poly(sialate-siloxo) geopolymer cement, the mortar flowed easily into moulds or big bags. After 2 days, 90% of the final compressive strength was reached, and the final compressive strength of about 20 MPa within 28 days.

Table 4: Leachate concentrations for U, Ra-226 and As

Element	Leachate concentration
U _{nat}	1...6 µg/l
Ra-226	< 10 mBq/l
As	< 100 µg/l, typ. 10 µg/l

Several leach tests were carried out in order to cover a large range of environmental stress conditions that may possibly occur over the next centuries. Standard leach tests according to DIN 38 414-S4 (24 hours, intact 7 cm cubes) were performed to get information about the overall containment, while sequential leach tests according to ANS 16.1 (slightly adapted to locally relevant conditions) provide an estimate of the diffusive transport in the geopolymer matrix. Table 4 gives the results for the leachate concentrations according to DIN 38 414-S4 while the diffusion constant of uranium is given in Table 5. Because solid-state processes within the geopolymer matrix exclusively determine diffusion, the diffusion constants are expected to be independent of the leachate pH.

Table 5: Diffusion constant D for uranium at pH 3 and pH 5

	pH 3	pH 5
D (Uranium)	3.8 x 10 ⁻¹⁶ cm ² /s	1 x 10 ⁻¹⁶ cm ² /s

Rock/slag-based geopolymer cement for building and infrastructure

One takes a rock of the strongly weathered granitic type in which kaolinisation is very advanced, for example coal mining waste.³⁵ Throughout the world, coal veins are very often imprisoned between geological layers of kaolinitic granite. Kaolinitic coal-mining rock waste can be advantageously calcined, because it generally contains

residual coal that provides additional free energy during calcination at 750°-800°C. It contains approximately 25% plagioclase (feldspar), 30% quartz, 10% amphibole, 27% kaolinite, 3% coal and 6% of other elements. It is calcined at 750°C for 3 hours and ground to an average grain size of 15-25 microns. Then, the following reactive mixture is prepared:

- | | |
|---|----------|
| • coal-mining waste, | 90 parts |
| • blast furnace slag ground to 15-25 microns | 30 parts |
| • K silicate solution,
(by weight) K ₂ O:26%, SiO ₂ :21%, H ₂ O:53% | 30 parts |
| • water | 20 parts |

Ambient temperature hardening yields a compressive strength of 40 MPa at 7 days, and 105 MPa at 28 days.

Sometimes, with naturally ignited coal, the heat was sufficient to transform kaolinite into MK-750. Such natural layers exist in several countries for example in Australia and Czech Republic and deserve to be exploited. In this particular case, there is no need for calcination so that the saving in energy and the reduction of CO₂ emissions are the highest, in the same order as for fly ash-based geopolymer cements.

Fly ash/slag-based geopolymer cement for geopolymer concrete

The EU sponsored project “Understanding and mastering coal fired ash geopolymerisation process in order to turn potential into profit”, is known under the acronym GEOASH (2004-2007).^{36,37} Normally, curing of alkali-activated fly ash is done at temperatures between 60 and 90°C. In this technology, since the idea is to use the geopolymer as a cement, the curing is taking place at ambient temperature, due to the (Ca,K) geopolymer/slag-based system. Seventeen European fly ashes were tested. Two methods were used and compared with. One, called the classical or conventional method, relies on alkali-activation. The second is based on geopolymerisation with (Ca,K) geopolymeric systems.

Conventional method: alkali-activation, dissolution and zeolite formation. The best compressive strength values for the conventional alkali-activated method were obtained by applying the following conditions: 0.3-0.4 L/kg, NaOH 12 M, mixture 5-10 min, ultrasonic vibration, 24 h room temperature, curing at 80°C for 48h. These are very caustic user-hostile conditions. KOH is not optimal for the geopolymerisation following the conventional method, since high concentrations are required to obtain compressive strengths that are far lower (mostly 90% lower) than those obtained when NaOH with similar concentration is used.

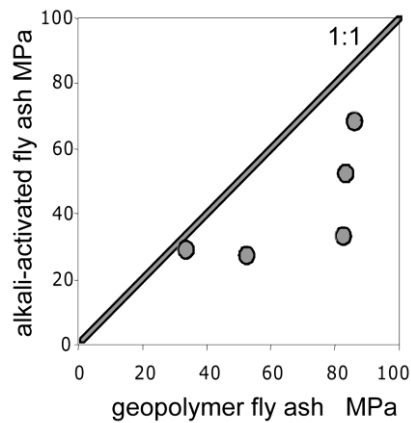


Figure 10: 28 day compressive strength; comparison between alkali-activated (conventional) and geopolymeric processes (GEOASH)^{36,37}

Geopolymeric method: room temperature hardening, polycondensation. The (K,Ca)-poly(sialate-siloxo) process is based on the system fly ash/slag/Ksil/H₂O reacting at room temperature. The ashes, 60-80% by weight of the mix, were mixed with the geopolymeric slurry containing K-silicate solution (molar SiO₂:K₂O > 1.40), blast furnace slag and water, the various required chemical components used in (K,Ca)-poly(sialate-siloxo) cement and cured at room temperature. The best compressive strength values, in the 70-100 MPa range, for the geopolymeric method were obtained by applying the following conditions: 10 g K-silicate solution, 15 g slag, 5 g water, 50 g to 85 g fly ash. These are user-friendly handling methods.

For a given fly ash, the conventional alkali-activation (zeolitic method) provides lower compressive strength than the (Ca,K)-based geopolymeric procedure (Figure 10). It can be deduced that the geopolymeric method yields higher strengths as well as lower costs (no thermal activation needed) and safer and easier handling treatment, *i.e.* user-friendly.

Conclusion

Slag-based geopolymer binders and cements are a real alternative to conventional Portland cement for use in toxic waste management as well as transportation infrastructure and construction. They rely on minimally processed natural materials and industrial by-products to significantly reduce the carbon footprint of cement applications, while also being very resistant to many of the durability issues that can plague conventional concrete. User-friendly slag-based geopolymer cements that can be used under conditions similar to those suitable for Portland cement are the current focus of extensive worldwide research efforts. These cements are capable of being mixed with a relatively low-alkali activating solution and must cure in a reasonable time under ambient conditions. The production of versatile, cost-

effective slag-based geopolymer cements that can be mixed and hardened essentially like Portland cement would represent a “*game changing*” advancement, revolutionising the construction of transportation infrastructure and the building industry..

References

1. J. Davidovits, *Geopolymer Chemistry and Applications*, Institut Géopolymère, Saint-Quentin, France, (2008).
2. J. Davidovits and J. Sawyer, “Early high-strength mineral polymer”, *US Patent 4509.985*, 1985, filed February 22, (1984).
3. A.O. Purdon, “L'action des alcalis sur le laitier de haut-fourneau”, *Journal de la Société des Industries Chimiques*, Bruxelles, Belgium, **59** 191-202 (1940).
4. V. D. Glukhovskiy, *Soil silicates, Their Properties, Technology and Manufacturing and Fields of Application*, Doct Tech Sc. Degree thesis. Civil Engineering Institute. Kiev (1965).
5. R.J. Kirkpatrick, “MAS NMR Spectroscopy of Minerals and Glasses”, *Reviews in Mineralogy*, **18** 99-175 (1998).
6. I.G. Richardson, A.R. Brough, R. Brydson, G.W. Groves and C.M. Dobson, “Location of Aluminum in Substituted Calcium Silicate Hydrate (CSH) Gels as Determined by ²⁹Si and ²⁷Al NMR and EELS”, *J. Am. Ceram. Soc.*, **76** (9) 2285-2288 (1993).
7. I.G. Richardson, G.W. Groves, “The Microstructure and Microanalysis of Hardened Cement Paste Involving Ground Granulated Blast-Furnace Slag”, *J. Mater. Sci.*, **27** 6204-6212 (1992).
8. S. Astutiningsih and Y. Liu, “Geopolymerization of Australian Slag with Effective Dissolution by the alkali”, in *Geopolymer 2005 Proceedings*, 69-73 (2005).
9. W. Jiang, M.R. Silsbee and D.M. Roy, “Alkali activation reaction mechanism and its influence on microstructure of slag cement”, in *10th International Congress on the Chemistry of Cement*, Gothenburg, Sweden, 3, 9 pp. (1997).
10. F. Puertas, A. Fernandez-Jimenez and M.T. Blanco-Varela, “Pore Solution in Alkali-activated slag cement pastes, relation to the composition and structure of calcium silicate hydrate,” *Cement and Concrete Research*, **34** (1) 139-148 (2004).
11. C. Shi, P.V. Krivenko and D.M. Roy, *Alkali-Activated Cements and Concretes*, Chapter 4, Hydration and microstructure of alkali-activated slag cements, Taylor & Francis ed., London, (2006).
12. S. Komarneni, R. Roy, D.M. Roy, C.A. Fyfe, G.J. Kennedy, A.A. Bothner, J. Dadok and A.S. Chesnick, “²⁷Al and ²⁹Si Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy of Al-substituted Tobermorites”, *J. Mater. Sci.*, **20** 4209-4214 (1985).
13. H.F. Taylor, “Proposed Structure do Calcium Silicate Hydrate Gel”, *J. Am. Ceram. Soc.*, **69** 464-467 (1986).
14. I.V. Belitsky, A. Sakata and S. Goto, “Kinetics of the hydration of slag in the slag-alkaline cements”, in *3rd Beijing International Symposium on Cement and Concrete, Beijing*, **2** 1028-1031 (1993).
15. J. Malolepszy, “Some Aspects of Alkali Activated Cementitious Materials Setting and Hardening”, in *3rd Beijing International Symposium on Cement and Concrete, Beijing*, **2** 1043-1046 (1993).
16. S.D. Wang, “The role of sodium during the hydration of alkali-activated slag”, *Advances in Cement Research*, **12** (2) 65-69 (2000).
17. V.D. Glukhovskiy, *Slag Alkaline Fine Aggregate Concretes*, Kiev, USSR, 1981.
18. F. Skvara, “Alkali-activated slag cements”, *J. Stavivo*, Prague, **63** (1) 16-20 (1985).
19. J. Malolepszy and M. Petri, “High-strength slag-alkaline binders”, in *8th Intern. Congress on the Chemistry of Cement*, Rio de Janeiro, Brazil, **4** 108-111 (1986).

20. P. Parameswaran and A.K. Chatterjee, "Alkaline activation of Indian blast furnace slag", in *8th Intern. Congress on the Chemistry of Cement*, Rio de Janeiro, Brazil, **4** 86-91 (1986).
21. C. Shi, "Alkali-aggregate Reaction of alkali-slag cements", *Concrete and Cement Products* **4**, 28-32, (1988) (in Chinese).
22. B. Talling and J. Brandstetr, "Present and future of alkali-activated slag concrete", in *3rd International Conference on the Use of Fly Ash, Silica Fume, Slag & Natural Pozzolans in Concrete*, ACI SP-114, Trondheim, Norway, 1519-1546 (1989).
23. E. Douglas and J. Brandstetr, "A preliminary study on the alkali activation of granulated blast furnace slag", *Cement and Concrete Research*, **20** (5) 509-516 (1990).
24. P.V. Krivenko, *Special Slag Alkaline Cements*, Budivel'nik Publisher, Kiev, 19-54, (1992).
25. T. Bakharev, J.G. Sanyavan and Y.B. Cheng, "Alkaline activation of Australian slag cements", *Cement and Concrete Research*, **29** (1) 113-120 (1999).
26. J. Deja, "Carbonation Aspects of Alkali Activated Slag Mortars and Concretes", *Silicates Industriels*, **67** (3-4) 37-42 (2002).
27. A. Palomo, M.W. Grutzeck and M.T. Blanco, "Alkali-activated fly ashes: a cement for the future", *Cement Concrete Res.* **29** 1323-1329 (1999).
28. J.G.S. Van Jaarsveld and J.S.J van Deventer, "Effect of the Alkali Metal Activator on the Properties of Fly Ash-Based Geopolymers", *Ind. Eng. Chem. Res.*, **38** 3932-3941 (1999).
29. P. Duxson, A. Fernandez-Jimenez, J.L. Provis, G.C. Lukey, A. Palomo and J.S.J van Deventer, "Geopolymer technology: the current state of the art", *J. Mater. Sci.*, **42**, 2917-2933 (2007).
30. Geocistem, *Cost Effective Geopolymeric Cements For Innocuous Stabilisation of Toxic Elements, Final Technical Report*, April 30, 1997, Brussels, European Commission, Brite-Euram BE--7355-93, Jan. 1, 1994 to Feb. 28, 1997.
31. J. Davidovits, Method for obtaining a geopolymeric binder allowing to stabilize, solidify and consolidate toxic or waste materials, *US Patent 5.539.140* (1996).
32. J. Davidovits, L. Buzzi, P. Rocher, D. Gimeno, C. Marini and S. Tocco, Geopolymeric Cement based on low cost geological materials. Results from the European Research Project Geocistem, in *Geopolymer '99 Proceedings*, 83-96 (1999).
33. C.K. Yip and J.S.J van Deventer, "Microanalysis of calcium silicate hydrate gel formed within a geopolymeric binder", *J. Mater. Sci.*, **38** 3851-3860 (2003).
34. E. Hermann, C. Kunze, R. Gatzweiler, G. Kiessig and J. Davidovits, "Solidification of various radioactive residues by Geopolymere with special emphasis on long-term stability", in *Geopolymer '99 Proceedings*, 211-228 (1999).
35. J. Davidovits and R. Davidovits, "Poly(sialate-disiloxo)-based geopolymeric cement and production method thereof", *PCT Patent publication WO03/099738, US Patent US 7,229,491*. (2003).
36. GEOASH (2004--2007), The GEOASH project is carried out with a financial grant from the Research Fund for Coal and Steel of the European Community. The GEOASH project is known under the contract number RFC-CR-04005. It involves: Antenucci D., ISSeP, Liège, Belgium; Nugteren H. and Butselaar-Orthlieb V., Delft University of Technology, Delft, The Netherlands; Davidovits J., Cordi-Géopolymère Sarl, Saint-Quentin, France; Fernández-Pereira C. and Luna Y., University of Seville, School of Industrial Engineering, Sevilla, Spain; Izquierdo and M., Querol X., CSIC, Institute of Earth Sciences "Jaume Almera", Barcelona, Spain.
37. M. Izquierdo, X. Querol, J. Davidovits, D. Antenucci, H. Nugteren and C. Fernández-Pereira, "Coal fly ash-based geopolymers: microstructure and metal leaching", *Journal of Hazardous Materials*, **166** (1) 561-566 (2009).