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The European Research Project GEOASH:
(2004-2007)
The development of room temperature hardening slag / fly ash-based geopolymer cements for Geopolymer Concretes

When compared with the heat-cured conventional method of alkali-activation, room temperature hardened slag / fly ash-based geopolymer cements have better properties: higher strength, safer long-term durability and lower leachates.

Content:

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The European Research Project *GEOASH*:

Geopolymer Cement Based On European Coal Fly Ashes

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The EU sponsored project "*Understanding and mastering coal fired ash geopolymerization process in order to turn potential into profit*", is known under the acronym GEOASH (2004-2007). The Final Technical and Scientific Report was presented mid 2008, and some information were published, by Nugteren et al. (2005) [1], Davidovits (2000) [2], Álvarez-Ayuso et al. (2008) [3], Davidovits et al. (2008) [4], Izquierdo et al. (2009) [5].

ABSTRACT

Seventeen samples of (co-)combustion European fly ashes have been tested on their suitability for geopolymeric cements. The ashes, 60-80% by weight of the mix, were mixed with the various required chemical components used in (Ca,K)-poly(sialate-siloxo) cement and cured at room temperature. There is some variation in behavior of the different fly ashes, ranging from unworkable situations in which the paste hardens during mixing (flash-set) to remarkable and excellent strength of 90 and 95 MPa after 28 days. The properties essentially depend on the combustion technologies: fluidized bed, T° 850°C, PCC coal combustion, T° 1250°C or 1500-1600°C and IGCC, T° 1800°C. When compared with the conventional method of alkali-activation (zeolitic process), fly ash geopolymer matrices have better properties: higher strength, safer long-term durability and lower leachates.

1. INTRODUCTION

In November 2004 the authors started a EU sponsored project "*Understanding and mastering coal fired ash geopolymerization process in order to turn potential into profit*", known under the acronym GEOASH (2004-2007). Normally, curing of fly ash-based alkali-activated matrices is done at temperatures between 60 and 90°C for several hours. In this project, since the idea is to use the geopolymers as a cement, the curing is taking place at ambient temperatures, with a modified (Ca,K)-poly(sialate-siloxo) based geopolymeric system that does not include MK-750 metakaolin [6].

Seventeen samples of (co-)combustion European fly ashes have so far been tested on their suitability for geopolymeric cements. Table 1 lists the fly ash types, fuel combustible, combustion technologies and Code name.

Table 1: Selected fly ashes,

Fuel combustible	Combustion technology	Code
Belgium		
Coal tailings 51%, wood pellets 49%	fluidized-bed (850°C)	ISSEP-1
Wood pellets France	fluidized-bed (734 – 870°C)	ISSEP-2
Sewage sludge Belgium	fluidized-bed (734 – 870°C)	ISSEP-3
Wood pellets 84%, sewage sludge 16%	fluidized-bed (734 – 870°C)	ISSEP-4
Coal tailings Belgium 25%, coal Poland 75%	fluidized-bed (850°C)	ISSEP-5
Coal 65% + 25%, sew sludge 5%, olive 5%	PCC 1 (1250°C)	ISSEP-6
Netherlands		
Co-comb. coal 86%, wood 11%, palmpit 3%	PCC 1 (1250°C)	TUD-1
Co-comb average coal, olive pulp 10%	PCC 1 (1250°C)	TUD-2
Coal alkaline from Silex	PCC 2 (1500°C)	TUD-3
Coal neutral from Silex	PCC 2 (1500°C)	TUD-4
Coal acid from silex	PCC 2 (1500°C)	TUD-5
Spain		
Coal, Narcea	PCC 2 (1500°C)	CSIC-1
Coal, Teruel	PCC 2 (1500°C)	CSIC-2
Co-comb. coal and petr. coke, Compostilla III	PCC 2 (1600 °C)	CSIC-3
Co-comb. coal and petr. coke, Compostilla IV	PCC 2 (1600 °C)	CSIC-4
Co-gasific coal and petr. coke, Elcogas	IGCC (1800°C),	CSIC-5
Coal, Los Barrios	PCC 2 (1500°C)	AICIA-1

Figure 1 displays the microstructures of representative fly ash types. The low temperature firing yields coarse and irregular aggregates. On the opposite, high temperature firing creates typical vitrified spheres and cenospheres. There exists a relationship between the nature of the minerals present in coals and the phases formed after combustion. In Table 2, the mineral calcite is transformed into lime CaO at 850°C (and also up to 1200°C), yet participates in the formation of glass at 1500-1600°C and 1800°C. The presence of lime CaO is not recommended in any geopolymeric sytems because it generates flash setting (fast hardening).

Table 2: The principal phases found in coals and the phases formed after combustion.

Common coal minerals	Phases formed after combustion at		
	850°C	1500°C	1800°C
Quartz	quartz	cristobalite	glass
Kaolinite	metakaolin	glass + mullite	glass
Illite	illite	glass + mullite	glass
Pyrite FeS_2	iron sulphide FeS/FeO	Fe_2O_3 haematite + glass Fe_3O_4 magnetite + glass	glass
Calcite	lime CaO	glass	glass

Although the 17 studied fly ash samples were obtained from different fuel blends and combustion technologies, the ranges of concentrations of major oxides obtained were very similar to those determined previously for 23 EU PCC fly ash [7]. Considering the main major elements, and according to the American Society for Testing and Materials [8], one can consider that almost all the samples belong to the class F.

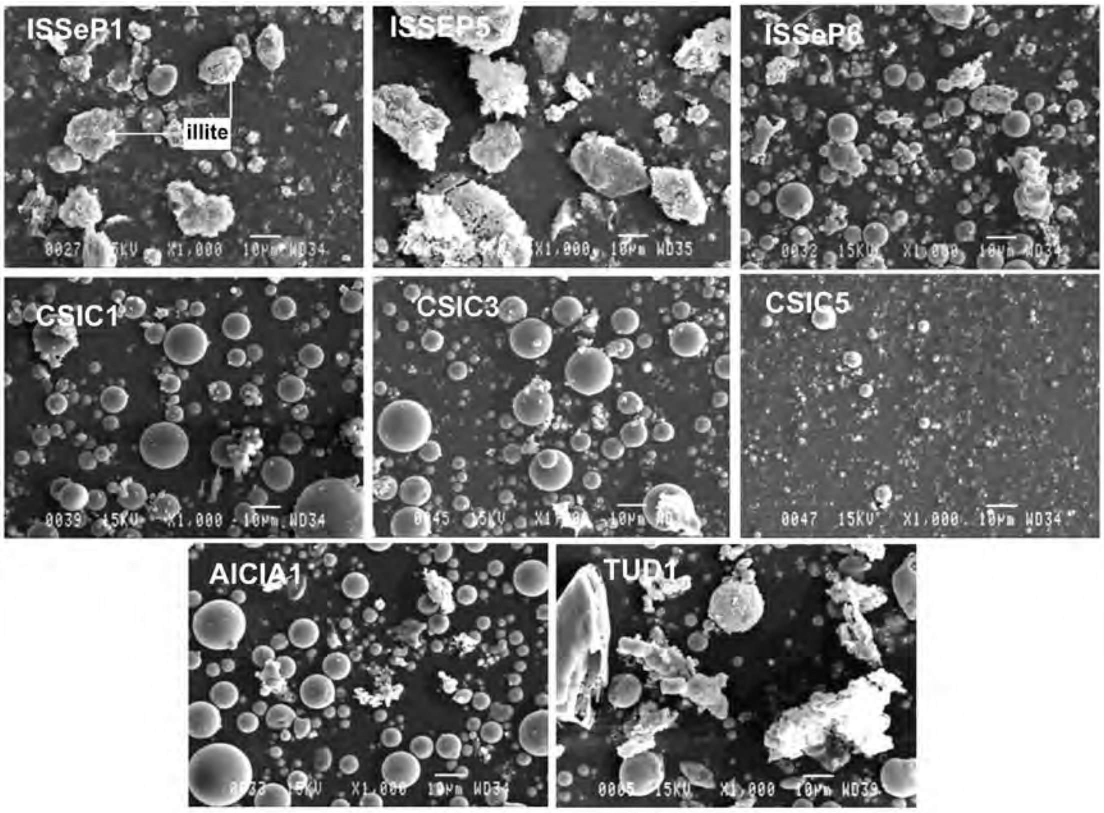

Figure 1: Microstructures of selected fly ashes

Table 3: Mineralogical composition of fly ash in % wt as deduced from XRD analysis

	Glass	Quartz	Mullite	Hematite	Magnetite	Anhydrite	Illite	Calcite	Albite Anortite
ISSEP-1	73	16	<0.1	0.9	<0.1	1.3	7.8	0.7	<0.1
ISSEP-2	82	8.8	4.0	0.7	0.3	1.3	1.4	0.7	0.4
ISSEP-3	63	17	4.1	11	<0.1	1.4	<0.1	0.3	2.6
ISSEP-4	57	26	7.0	3.4	1.4	0.3	0.6	0.2	1.1
ISSEP-5	72	16	3.6	1.2	<0.1	1.5	3.7	0.1	1.9
ISSEP-6	77	3.5	17	0.4	<0.1	<0.1	0.1	<0.1	2.0
AICIA-1	85	4.6	10	0.5	<0.1	0.2	<0.1	<0.1	<0.1
CSIC-1	94	0.8	4.4	<0.1	<0.1	0.4	<0.1	<0.1	<0.1
CSIC-2	80	2.5	9.3	3.4	3.4	0.7	<0.1	<0.1	<0.1
CSIC-3	97	1.3	<0.1	0.5	0.4	0.7	<0.1	<0.1	<0.1
CSIC-4	93	1.6	4.6	<0.1	<0.1	0.7	<0.1	0.1	<0.1
CSIC-5	99	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TUD-1	80	3.2	16	<0.1	0.1	0.2	<0.1	<0.1	<0.1
TUD-2	87	5.0	5.9	0.3	0.2	0.9	<0.1	0.2	<0.1
TUD-3	86	2.2	11	0.1	0.1	0.9	<0.1	<0.1	<0.1
TUD-4	80	2.8	16	0.1	<0.1	0.6	<0.1	<0.1	<0.1
TUD-5	84	2.7	12	0.3	<0.1	0.3	<0.1	<0.1	<0.1

In Table 3, the major inorganic phases present in the fly ashes studied are aluminosilicate glass, quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3) and/or magnetite (Fe_3O_4), anhydrite ($CaSO_4$), calcite ($CaCO_3$), lime (CaO), microcline ($KAlSi_3O_8$), anorthite-albite $(Ca,Na)(Al,Si)_4O_8$, gehlenite ($Ca_2Al_2SiO_7$) and illite ($(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$). The aforementioned species are present in different concentrations depending on the fly ash.

2. METHODS

Two methods are used and compared with. One, called the classical or conventional method, relies on alkali-activation. The second is based on geopolymerization with (Ca,K) geopolymeric systems.

2.1 Conventional method: alkali-activation, dissolution and zeolite formation: User-hostile

The synthesis of zeolite from coal fly ash was introduced by Höller and Wirshing [9]. They highlighted the compositional similarity of fly ash to volcanic material, the precursor of natural zeolites. Since this study, a number of hydrothermal processes have been proposed to synthesize different zeolites. NaOH or KOH solutions, at atmospheric and water vapor pressures, from 80°C to 200°C and for 3 to 48 hours have been combined to synthesize up to 15 different zeolites from the same fly ash [10, 11]. They involved with NaOH Phillipsite, Hydrosodalite, Hydrocancrinite, Zeolite A, Analcime, Hershelite, Chabazite, Na-P1-zeolite, and with KOH, Kalsilite, Zeolite K and Zeolite F [12-16].

The best compressive strength values for the conventional alkali-activated zeolitic method were obtained by applying the following conditions:

- 0.3-0.4 L/kg, NaOH 12M, mixture 5-10 min,
- ultrasonic vibration,
- 24h room temperature,
- curing at 80^{o}C for 48h.

These are very caustic and corrosive conditions (*User-hostile* system). KOH is not optimal for the zeolitization 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.

2.2 Geopolymeric method: room temperature hardening, polycondensation, User-friendly.

The geopolymeric method was developed for the implementation of all kind of geological materials and successfully experimented in a previous European Research project, coined GEOCISTEM (BRITE-EURAM BE-7355-93). It is based on the system fly ash / slag / Ksil / H_2O reacting at room temperature. The ashes, 60-80% by weight of the mix, were mixed with the geopolymeric slurry containing K-silicate solution (molar $SiO_2:K_2O > 1.40$), 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 for the geopolymeric method were obtained by applying the following conditions:

- 10 g K-silicate solution,
- 15 g slag,
- 5 g water,
- 50g to 85 g fly ash.

These are not corrosive conditions but rather *User-friendly* handling methods.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

In the geopolymeric method there is some variation in behavior of the different fly ashes, ranging from unworkable situations in which the paste hardens during mixing (flash-set) to remarkable and excellent strength of 90 and 95 MPa after 28 days. In general, fly ashes from biomass only are unfavorable for geopolymerization, because they cause high gas release during the reactions, thus leading to non cohesive geopolymer bodies. In addition, they contain free lime CaO that generates flash set. The high quantities of unburned carbon ($\geq$10%) inhibit also the geopolymerization reactions.

The investigations on the main characteristics of fly ashes suitable for the classic conventional method (alkali-activation of zeolitic method) [17] have been taken as a reference to foresee the properties of the fly ashes to be tested for geopolymer applications. The published recent State of the Art [18] claimed that, for fly ash, the pure NaOH based zeolitic system should be considered as the reference in the determination of the chemical parameters leading to a material with optimal binding properties. These characteristics are the following:

- SiO_2/Al_2O_3 ratio by mass of the fly ash should preferably be in the range of 2.0 to 3.5, i.e. Si:Al ratio > 2,0.
- Percentage of unburned material lower than 5%.
- Fe_2O_3 content not higher than 10%.
- Low content of CaO.
- Content of reactive silica, such as glass, higher than 40%..
- Percentage of particles with size lower than 45 µm between 80 and 90%.
- High content of vitreous phase. The higher the amount of glassy constituent in the fly ash, the faster is the alkalination process and the higher the degree of reaction.
- Conversely, if high content of mullite or quartz are present, the reactivity of the Al-Si bearing fraction decreases drastically. The mullite content should be below 5%.

Six fly ashes of the PCC and IGCC types were selected and submitted to the criteria cited above. Fluidized-bed fly ashes do not work in both systems (alkali-activated or geopolymer methods). Table 4 gives their major chemical parameters and the suitability for geopolymeric reaction according to the standard criteria listed above and the results obtained with the (Ca,K)-based geopolymer method.

According to the standard criteria set forth above, any fly ash with a mullite content higher than 5% is not suitable and may not be used. These fly ashes are given the criteria “no”, in Table 4. On the opposite, the results extrapolated from Figure 2 determine a positive suitability, “yes”, for all fly ashes tested with the geopolymeric method, except those that underwent flash set (fluidized-bed).

Table 4: Major parameters of some GEOASH fly ashes

Fly ash	SiO_2 total %	Al_2O_3 total %	SiO_2: Al_2O_3 total	Mullite %	Suitability	
					Standard criteria	(Ca,K) -based method
TUD-1	49	28	1,8	16	no	yes
TUD-3	46	25	1,9	11	no	yes
AICIA-1	58	23	2,6	10	no	yes
ISSEP-6	50	20	1,7	17	no	yes
CSIC-4	51	25	2	4,6	yes	yes
CSIC-5	53	25	2,1	0,1	yes	yes

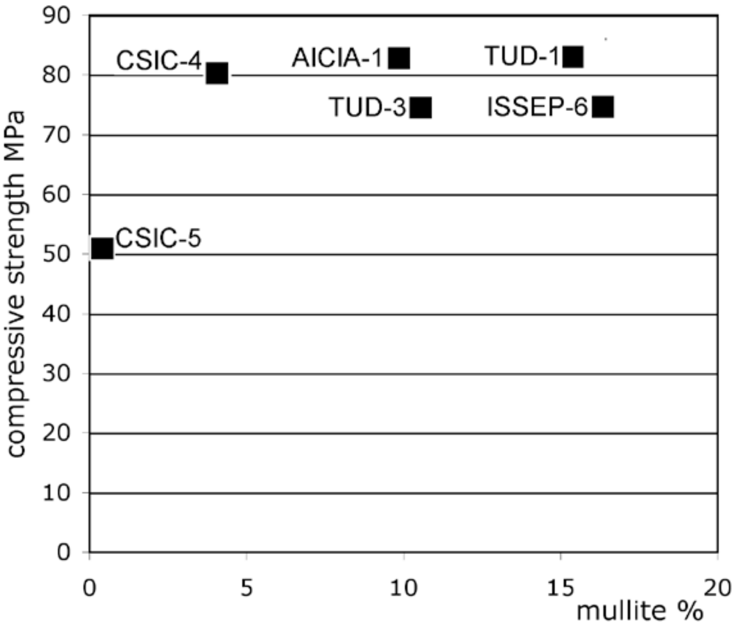

Figure 2: (Ca,K)-based geopolymer method; compressive strength at 28 days in relation with mullite content, room temperature curing.

Figure 2 displays the results of the (Ca,K)-based geopolymeric method. It shows the 28 day compressive strength obtained in relation with the mullite content. All values are higher than 50 MPa, the majority reaching strengths higher than 70 MPa. It is therefore important to notice that practically all class F fly ash types, i.e. those with low free CaO, can be used with this user-friendly system [19].

For a given fly ash, the conventional alkali-activation (zeolitic method) provides lower compressive strength than the (Ca,K)-based geopolymeric procedure (Figure 3). It can be deduced that the geopolymeric method yields higher strengths as well as lower costs (no thermal activation needed) as well as safer and easier handling treatment.

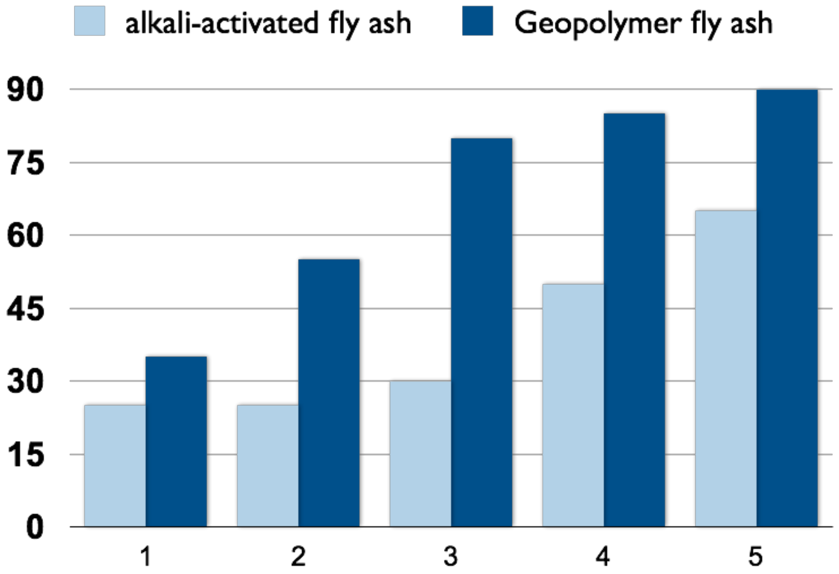

Figure 3: 28 day compressive strength MPa; comparison between alkali-activated (conventional) and geopolymeric processes.

3.2 X-ray diffraction

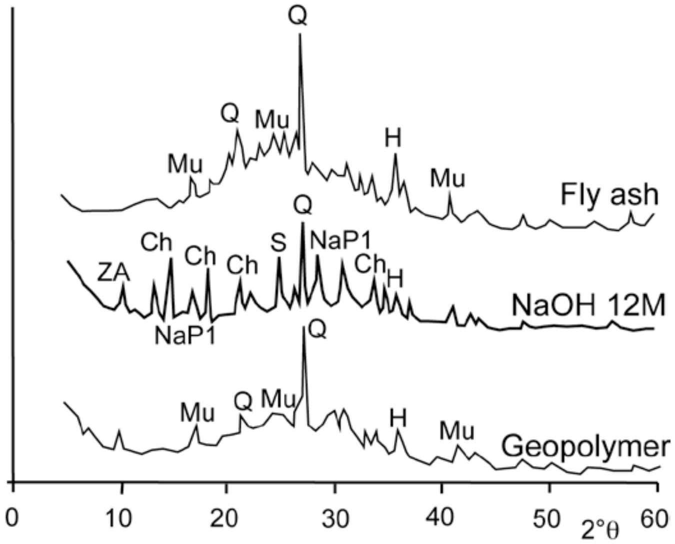

Figure 4: X-ray diffraction of fly ash and resulting matrices with NaOH 12M (zeolitic conventional method) and (Ca,K)-based geopolymeric process (Geopolymer).

In the zeolitic procedure, Na-aluminium-silicates (mainly zeolitic products) are formed as a result of the alkaline and thermal activation. The method implies the dissolution of the fly ash particles in such a way that the original mineralogy is significantly modified. Fly ash aluminosilicate glassy spheres are dissolved. Figure 4 shows the clear decrease in the background hump of the diffraction patterns between fly ash and NaOH 12M (alkali-activation). This results in new species, mainly chabazite-Na ($NaAlSi_2O_6 \cdot 3H_2O$) and sodalite ($Na_4Al_3Si_3O_{12}(OH)$. Quartz, mullite and magnetite are low reactive phases only partially involved in the zeolitization and remain as relict mineralogy of fly ash. KOH is not an optimal activator in this conventional method since the degree of reactivity is lower than with NaOH.

The (Ca,K)-based geopolymeric method is performed at room temperature and entails a low degree of dissolution since only the surface of the starting materials is taking part in the reaction. For the Geopolymer pattern in Figure 4, the original mineralogy of fly ash is not significantly modified. The (Ca,K)-poly(sialate-siloxo) amorphous matrix results from the inter-geopolymerization of the fly ash aluminosilicate glassy spheres (slight decrease in the background hump), with the alkaline solution and the slag.

3.3 Leaching properties

Conventional zeolitic procedure leads to products in which the mobility of oxyanionic species is 5 to 50 times higher than the geopolymerization method (Figure 5). For example Vanadium values are: 10 mg/kg in geopolymer and 500 mg/kg in alkali-activated. In the geopolymeric matrices, the cations are fixed or trapped inside the synthesized poly(sialate) frameworks. Taking into account other relevant properties (higher compressive strengths and lower conversion costs), it can be concluded that the geopolymerization method is more attractive and safer than the conventional process.

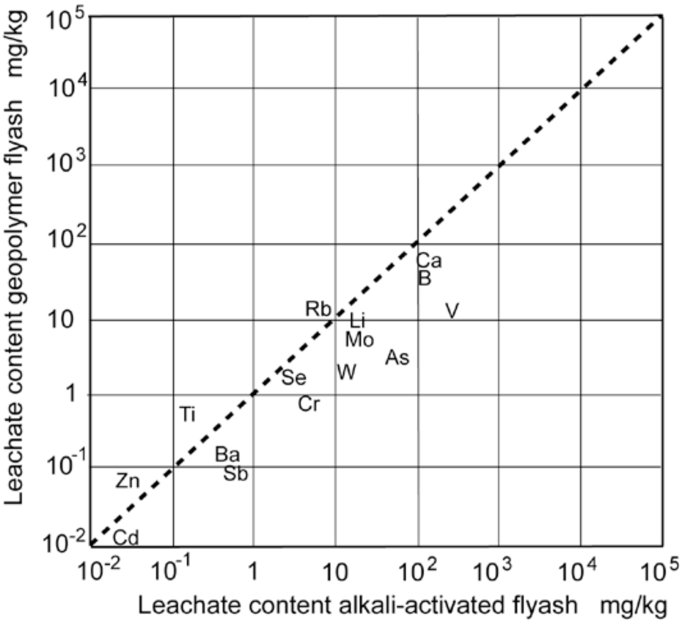

Figure 5. Leachable contents (EN12457-2 leaching test) of matrices obtained from geopolymeric process and conventional alkali-activated (zeolitic) procedure.

3.4 (Ca,K)-based geopolymer matrix: composition and structure

In microprobe analyses (Figure 6) of the geopolymer matrix, SiO_2 is the most abundant constituent of the geopolymer matrix (39-56%, typically around 50%), followed by Al_2O_3 (17-37%, most values in the 20-25% range) and CaO (mainly 12-15%). The proportion among these main constituents does not vary widely, especially the silica proportion (Figure 6, ternary diagram). Minor constituents also present are K_2O (1-10%, most common values ranging from 3 to 8%), Fe_2O_3 (mostly about 4%), MgO (1-4%), SO_3 (around 1.5%) and Na_2O (about 0.6%). Based on the above composition the bulk geopolymer composition is:

$$4SiO_2 \cdot Al_2O_3 \cdot CaO \cdot 0.3K_2O$$

i.e. poly(sialate-siloxo), (Ca,K)-(Si-O-Al-O-Si-O-), with Si:Al = 2

Results show that the main contributors to the geopolymer matrix (responsible of the compressive strength) are the glassy fly ash particles (supplying Si and Al), the high Ca slag (supplying Ca) and the alkaline solution (K-silicate). The analyses also suggest that the composition of the geopolymer matrix is homogeneous and the vicinity of other constituents does not exert a significant impact on the overall chemistry.

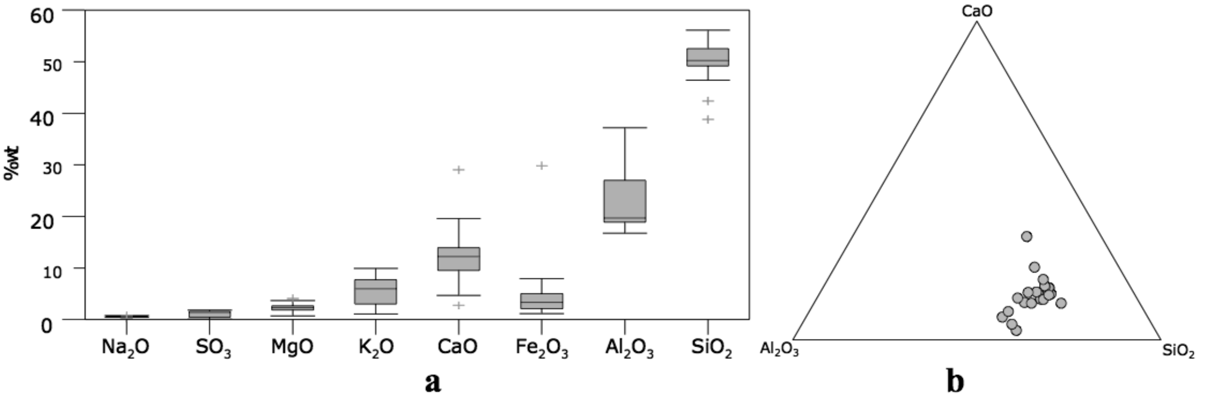

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Figure 6: fly ash-based geopolymer matrix composition

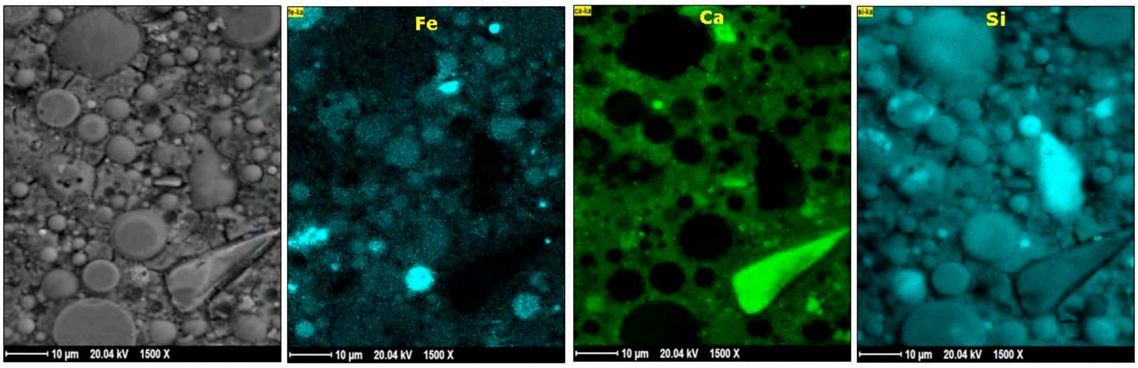

Figure 7: Distribution of Fe, Ca and Si in CSIC1 geopolymer (microprobe mapping)

Si is the most abundant element in geopolymer system (Figure 7). Since both fly ash and the alkaline/slag reactant mixture are the main sources of this element, Si mapping does not allow distinguishing the possible fly ash contribution. Ca distribution allows the identification of the 3 main constituents of geopolymer. Bright angular grains are slag particles, evidencing that slag is the source of Ca. Dark spherical zones depleted in Ca are quartz and low-Ca aluminosilicate glassy particles, a relict from fly ash. Ca mapping yields a map of the occurrence of the geopolymer matrix surrounding the aforementioned particles. This area is dark green, which indicates that the geopolymer contains a certain amount of Ca. Geopolymer matrix seems to be relatively homogeneous regarding Ca proportion. Fe is essentially concentrated in magnetite particles. Particle boundaries are well delimited, suggesting that these particles are not involved in geopolymerization reactions.

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