

Hybrid cements from metakaolin, slag and clinker mixtures. Influence of activators

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ABSTRACT

Hybrid cements containing a mixture of aluminates gels-substituted CSH (CASH) and NASH phases and other phases are investigated. The mechanical strength and structures of hybrid cement with geopolymeric matrix of aluminosilicates and clinker are examined. These geopolymeric matrixes are based on polycondensation of the powder precursors by alkaline activation. The activators can be solids (alkalis of sulfates and carbonates,) or liquid (alkaline solutions of silicates). The type of alkaline cation (Na, K) influences the activation.

The phase's transformations are characterised by the following parameters: the effect of cures (2, 7, 28 days) and their impact on the hardening, the texture and the mechanical strength. These properties are correlated by complementary techniques of DRX, FTIR, SEM / EDX. Alkaline potassium K more than the sodium Na allows the obtaining of products of denser reactions what increases the strength of cohesion of the matrix and show higher mechanical resistances.

Keywords: hybrid cements; Geopolymers; Mechanical strength; FTIR; SEM

I. Introduction

The search for low-CO₂ cements as partial replacements or complete alternatives to Portland cement has prompted innovative thinking in the development of new binders, [1] as alkali-activated aluminosilicates [2-3]. The search for low-CO₂ cements as partial replacements or complete alternatives to Portland cement has prompted innovative thinking in the development of new binders, as alkali-activated aluminosilicates. [2-3]. Alkali-activated aluminosilicates are differentiated from hydrated Portland cements by their higher initial alkalinity and the absence of lime.

The gel of hydrated sodium aluminosilicate (NASH), is the main reaction product of alkali-activated aluminosilicates. It differs from the gels of hydrated calcium aluminosilicate (CASH) from Portland Cement. The introduction of (Supplement Cementitious Materials) such as processed natural materials (metakaolin), industrial wastes (blast furnace slag) to reduce the amount of binders Portland Cement have become a common measure. The activation of alkaline systems containing amounts SCM represents a possible solution environmentally sustainable manner. [3-4]. Activating admixtures have been used to promote aluminosilicate reactivity (sodium or potassium hydroxide) and consolidation of microstructure through enhanced gel formation (sodium or potassium silicate solutions) in these studies.

The variability in materials used, activator concentrations and mix proportioning means that interpreting the 'geopolymerisation' contribution to product performance from one system to another is particularly challenging.

The reaction mechanisms leading to phase formation in alkali-activated systems was discussed and summarised more schematically in the review by Duxson *et al.* [2]. The hydrolysis of silicates (and aluminosilicates) defines the initial reactivity of the substrate. The fundamental chemistry of aqueous silica and silicate systems were initially reviewed but even within the cement chemistry theme, there has been much interest, *e.g.* in the context of the alkali-silica reaction. [5-6]. The alkaline activation of aluminosilicates leads to geopolymers having higher mechanical performances and fast hardening) with regard to the cement Portland. The formation of these binders crosses by a reaction of polycondensation [7]. Their amorphous three-dimensional network through the XRD is constituted with units of silicate of alkaline captions balancing the charge [7-9] of the initial aluminates. The various parameters of the compositions, the processing time and the temperature have a direct influence on the final properties of the formed inorganic polymer.

The aim of this work is to study a MK/GBFS/Clinker-based composite geopolymers synthesis and esteemed physical and mechanical strength. The cohesion, the mechanical resistance of these composites base on the formation of the matrix mixed geopolymeric. Several formulations using a various minerals as alkaline precursor to the

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geopolymeric binder, are prepared from raw component cement, slag, metakaolin, eau), and solid activators like alkaline carbonates and sulphates, or liquid activator as alkali silicate solutions. The formulation optimisation of the MK/GBFS/Clinker-based composite geopolymer appear as an alternative competitive to the traditional cementitious materials.

Alkali activation of Slag is a (Si + Ca) system, and that of geopolymer is a (Si + Al) system with metakaolin as main material. The study consists in estimating the interactions of the various constituents of the system and in finding a compromise enter a series of generally contradictory requirements.

TABLE1.
CHEMICAL COMPOSITION OF RAW MATERIALS (% BY MASS - XRF)

Material	Abbreviation	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O
Métakaolin	MK	0.04	55.03	37.69	2.89	0.44	3.20	0.02
Slag ^a	BFS	38.09	36.63	7.25	0.46	8.51	0.62	0.53
Ciment	CEM	60.07	22.40	7.56	3.92	3.26	1.18	0.89

^a Ground granulated blast furnace slag.

II. Experimental procedures

II.1. Materials

Commercial clinker CEM, Algerian Slag BFS (blast furnace, and metakaolin MK, are used. An analysis by fluorescence X, indicates the chemical composition of these materials sources, which are summarized on the table1.

Powders are crushed up to a size grading lower than 45 µm. The study grading distribution of the powder raw materials: BFS, CEM, and MK, are characterized by a granulomètre. The alkaline precursors are: Na₂SO₄, K₂SO₄, NaOH, KOH, (Merck in 99 % of purity), of the silica-gel): K-silicate (8,2 K₂O 27,8 % H₂O), and Na-silicate (8,2 Na₂O 27,8 % H₂O).

II.2. Preparation

A powders mixture formed by 2/5 of métakaolin MK, 2/5 of slag BFS and 1/5 of clinker is the base of the binder subjected to the alkaline activation. The activators are: either solids as Na₂SO₄ (5-8%) and K₂SO₄(5-8%), either liquid and prepared with 15 % M-silicate in MOH 4M solution (M: Na / K).

The paste of the various composites are prepared with a liquid proportion/solid W/B = 0.4. The sample dimensions are 6×1×1 cm. They are cured out in time of 2, 7 and 28 days in temperature of 25°C.

II.3. Methods and characterisation

After the cure, samples are reduced on powder, to be analyzed by using the data of diffraction of X-rays from a Bruker D8 Advance powder diffractometer according to the following parameters; 40KV, 30 my, radiation CuK_α, variable length : 6 mm, time / Step: 0.5, step size: 0.0197436, 2theta: 5-60, Scan time: 23 ' 46 "

FTIR spectral are obtained by analysis on a spectrometer NICOLET 6700. The pastilles sample

are prepared by grinding of 1 mg of sample with 3 000 mg of KBr. The spectrum analysis is realized in transmission in a range from 450 to 4000 cm⁻¹.

A scanning electron microscope with JEOL JSM 5400 equipped with an analyzer (EDX) LINKISIS; in dispersive energy was used for the characterization of the microstructure and chemical composition of samples geopolymeric.

The prepared samples are stored under vacuum during a week, covered with 12 mm of gold of thickness and examined. Tests of compression are executed according to the standard ASTM C39-96. Six samples of every formulation are estimated and the average data are raised by using a universal machine of test IBETEST 200-10-W.

In these measures, the geopolymeric samples are placed between two pistons. A compressive strength increasing is applied up to fracture. The maximal strength applied by crossed sector, is registered and taken as measure of the mechanical strength of the material.

III. Results

III.1. Mechanical strength

The table2 show the values of compression and flexion resistances of every formulation after two days of cure. The obtained mechanical properties for the various samples are in accordance with the results of previous works [9]. The table2 presents the values of mechanical resistances, flexion and compression of geopolymeric composites after two days of cure.

TABLE 2
MECHANICAL STRENGTH AFTER 02 DAYS OF CURE.

Formulations	F5NS	F8NS	F5KS	F8KS	F15KSi	F15NSi
Compression	16,11	15,78	13,02	14,58	19,30	14,03
Flexion	3,53	3,65	2,47	1,97	3,33	3,83

III.2. Analyse des phases par diffraction de X rays

Results obtained for after two days of cure are illustrated by the figure1. The amorphous phase characteristic of geopolymers is observed all samples formulation. Les following minerals phases are observed in the formulations using the activators reactors' sulphates sodics and/or potassics: CaCO₃ JCPDS :01-072-1937, SiO₂ (JCPDS : 01-083-0539), alite C₃S (JCPDS: 01-086-0402). Ettringite Ca₆Al₂(SO₄)₃(OH)₁₂.26 H₂O. (JCPDS : 00-013-0350).

The illite is also observed. The potassium sulfates activators show in addition, an d'Orthoclase K(AlSi₃O₈) (JCPDS : 01-086-0439) phase.

When activators are sodium or potassium silicates, the observed phases are quartz SiO₂ (JCPDS : 01-083-0539), alite C₃S (JCPDS: 01-086-0402), illite and Brownmillerite C₄AF (JCPDS: 01-071-0667). It

is necessary to note that the phases of quartz and illite are secondary phases of the métakaolin. Theses phases did not react under the alkaline activation and play the role of load. [10].

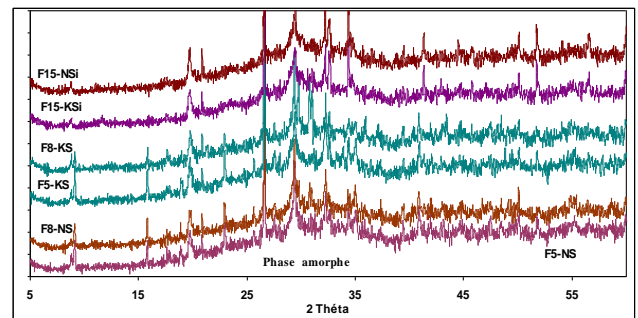


Fig.1. X-ray diffraction patterns of composites based geopolymeric matrix for different activators

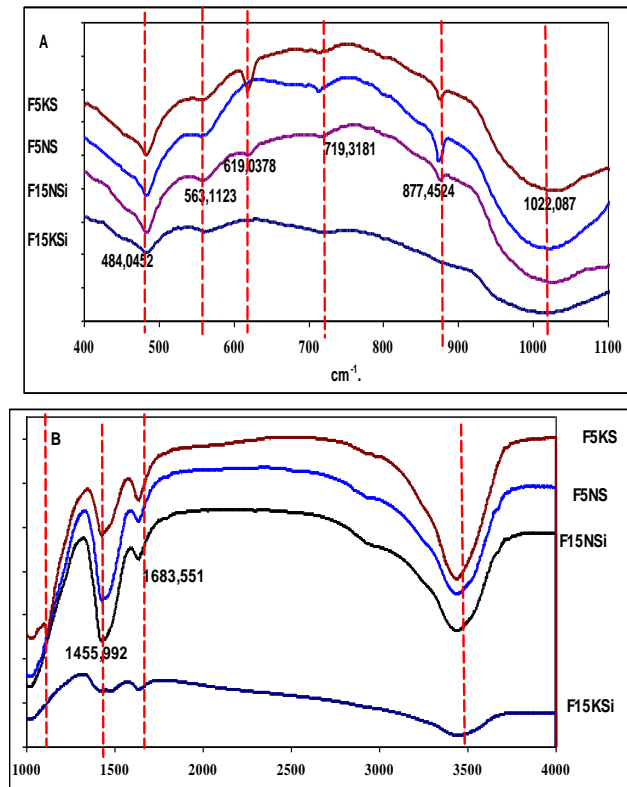


Fig.2: FTIR spectral of formulations activated after two days. (A: 400-110 cm⁻¹. and B: 1000-4000 cm⁻¹)

III.4. SEM/EDX

Figure3 presents scanning electronic microscopic micrographics of three composites based geopolymeric matrix, with elementary analysis of a same region by EDX. These EDX analysis indicate dense region in the right side of the micrograph, characteristic of high content of silicon and aluminium et a low quantity of calcium, suggesting that this region is the one of geopolymer.

They show a microstructure with connected pores, structured precipitates, and what would seem to be sheets of metakaolin having partially reacted. As the geopolymerisation is a process ground sol-gel implying alkaline on the precursors aluminosilicates, and an intermediate dissolution of water, followed by the precipitation of the dissolved species via a nucleation and the growth, the observed microstructure is formed by clusters of nanoparticles as phase of binder of the composite.

The X-rays diffraction of the various composites after 28 days of cure shows a composition of phases which explains their mechanical behaviour. Several parameters influence in the synthesis of products and make complicated the interpretation for behaviour of

the obtained products. Several parameters enter sets: the role of the alkaline, sodic / potassium cation, the influence of the type(chap) of solid activators (sulphates) / liquid (solution silicate alkaline) besides the correlations between the various formed species, the amorphous phase, the silicates of calcium, hydrates of silicates CSH obtained from the diverse cures and the mechanical behaviour. Although the characteristic amorphous phase of geopolymers is present in samples, the others phases are existed (observations realized by EDX), The formation of Ca(OH)₂ often takes place during the hydration of hydrates of calcium. Nevertheless, in that case, there is rather appearance of gypsum CaSO₄ which competes with the formation of Ca(OH)₂. The mechanical properties are connected to the microstructure and to the composition. Figure 4, shows the evolution of samples cured out for 28 days, in natural conditions ±20°C 2°C, with a relative humidity of 99 %, to increase the structural connection.

IV. Discussion

Materials with liquid silicates activators of Na / K, see their mechanicals strength passing of the simple to the double according to the time of cure, although the potassium shows a stronger resistance. The weak mechanical performances of composites obtained with the activators in anions treat with sulphate anions, suggest a competition where the formation of an essential component which supplies the strength in the hydrated OPC, the minerals of hydrated calcium silicate C-S-H, is slowed down. The C-S-H gels formation can be delayed by the presence of the geopolymer. It is also possible that the geopolymeric phase formation can collide with the formation of the C-S-H gels by competition for the silicon in the system.

V. Conclusion

The number of parameters occurring during the processes of geopolymerisation and polycondensation of these hybrid cements is connected to the complexity of three components of the powder mixture precursor. The slag and the metakaolin are pouzzolanics, reagent materials subjects to produce of the geopolymerisation. The hydration products of BFS and MK subjected to the activation of alkaline are different and it recognized that the hydrate of silicate of calcium (CSH) is result of the activation of the BFS. The interpretation of the behaviour of the obtained products is influenced by the type of the alkaline activation, sodic/potassium cations, the type of solid activators (sulphates)/(alkaline silicate solution).

Besides the correlations between the various formed species), the amorphous phase, the hydrates calcium,

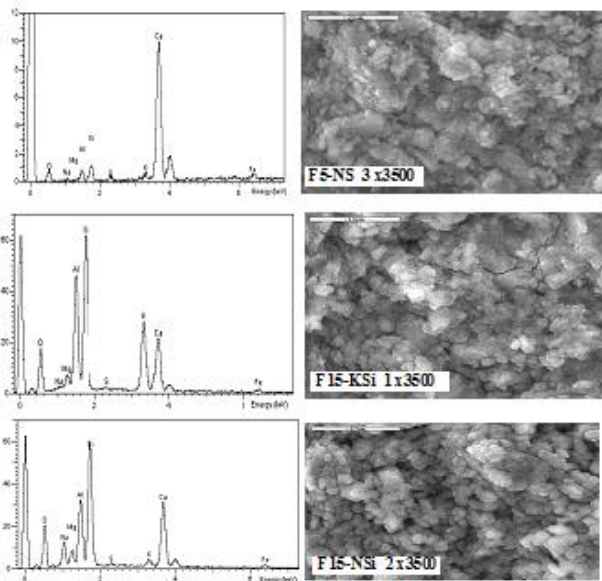


Figure3: SEM of fracture surfaces of samples obtained after alkaline activations sulphates and silicates

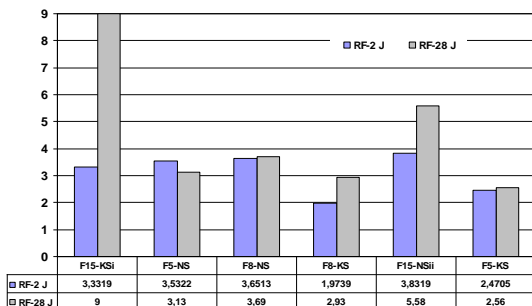


Fig.4. compression strength at 2 and 28 days of curing time

silicates (CSH) were obtained from the diverse cures and the mechanical behaviour. Composites activated by silicates of Na / K, see their mechanical strength passing of the simple to the double according to the time of cure, although the potassium shows a stronger resistance.

A competition between the formation of an essential component the hydrates of calcium silicate C-S-H and the amorphous geopolymeric phase distorts the mechanical performances because there is no continuity of phase in the matrix of composites.

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