Evaluation of Geopolymeric Pastes Through Low Field Nuclear Magnetic Resonance (NMR) Geopolymers Based on Fly Ash

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Keywords: geopolymer, NMR, relaxation time

Abstract: *In this work, mechanical behaviors and microstructural characteristics of geopolymeric cements were studied by varying the addition ratio of fly ash/ metakaolin, kind of sodium silicate and the age by using low field relaxometry NMR. Geopolymeric composites varied fly ash/metakaolin contents in 0, 25; 50; 75 and 100%. The best compressive strength were found for geopolymeric concretes containing the relation fly ash/metakaolin equal to 25%, with 28 days of cure, for both bicomponents and monocomponents composites. The results obtained with mechanical experiments and SEM micrographs were confirmed by measurements of proton spin-lattice relaxation data, obtained from low field NMR spectrometer.*

Resumo: *Neste trabalho buscou-se analisar diferentes composições de cimentos geopoliméricos, na forma de pastas e concretos, em nível microestrutural e de comportamento mecânico. Os compósitos continham zero, 25, 50, 75 e 100% de cinza volante em relação à quantidade de metacaulim em sua composição, com uma porcentagem fixa de CP III, por medidas de relaxação nuclear, via ressonância magnética nuclear de baixo campo.As melhores propriedades foram obtidas para os concretos geopolimericos contendo relação cinza/caulim igual a 25%, após 28 dias de cura, tanto para os compósitos monocomponentes quanto para os compósitos bicomponentes. O comportamento dinâmico observado para as pastas de cimento estudadas foi confirmado pelos dados de relaxação, obtidos por ressonância magnética nuclear de baixo campo.*

Introduction

Since the last decades the world has encountered serious problems related to structural elements in materials deterioration. The employment of Materials Science on the study, improvement and development of new materials has become essential to get and maintain better materials' performance, for these and other applications.

Among these new materials, one may give notability to Geopolymeric cement, patented by Joseph Davidovits[1] in the 80's. Geopolymeric cement is introduced as a recent technological product for structural application. Its great performance (equal or higher than Portland cement ones), allied to the utilization of industrials wastes as source materials and with no emission of CO_2, during its synthesis make it an efficient product, which is able for sustainable development.

Geopolymer term was created by Joseph Davidovids[1,2] in 1978 to designate a family of minerals binders with composition similar to zeolites, but having an amorphous to semi-crystalline microstructure. Geopolymers are also known as polysialates (big molecular chain constituted by siliceous, oxygen and aluminum). Geopolymeric materials are synthesized through geosynthesis –science used to produce artificial rock in a temperature below 100ºC in order to obtain natural characteristics, such as hardness, durability and thermal stability[1].

Polysialates are described as a chain of polymers with Si^{4+} e Al^{3+} in fourfold coordination with oxygen. The aluminosilicates structures are classified according to their polymeric units. The oligomeric building units are depicted in Figure 1.

Geopolymeric materials are synthesized through aluminossilicates' alkali-activation. The negative charge of Al^{3+} in fourfold co-ordination is balanced by the presence of positive ions (Na^+, K^+, Li^+, Ca^{++}, Ba^{++}, NH^{4+}, H_3O^+) (Figure 2).

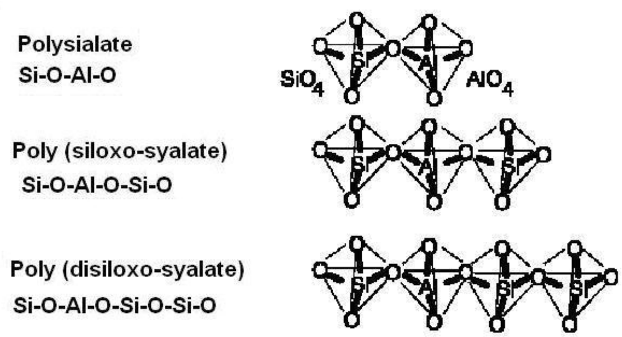

Figure 1. Schematic representation of polysialates[3,4]

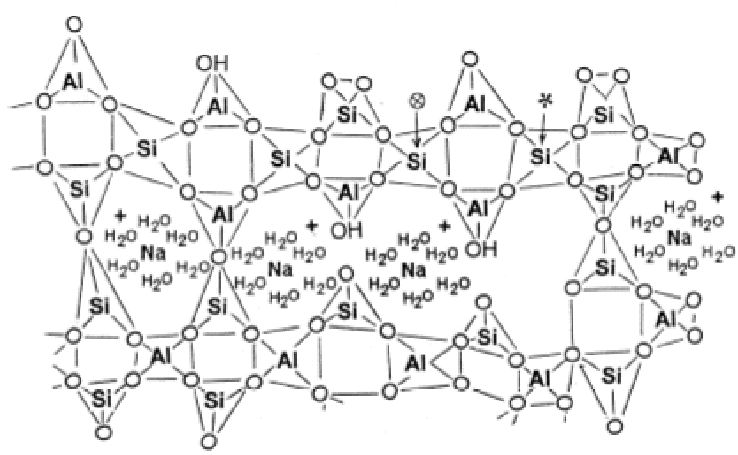

Figure 2. A proposed conceptual view for Na-polysialate[3].

When industrial sodium silicate was used for the composites activation, they were called "bicomponents" and the ones that used alternatively silicate were called "monocomponents".

In this work the ratio of fly ash/metakaolin, type of sodium silicate and the age, as well as the microstructural characteristics of geopolymeric cements were evaluated to achieve more information about the influence of raw materials on geopolymer microstructure. For this reason they were analyzed by Low Field NMR, through the determination of proton spin-lattice relaxation time. The relaxation measurements could inform through the molecular mobility of hydrogen nucleus; the identification of the different mobility's domains and their main components, as well as the domain that controls the relaxation process.

Experimental

Geopolymer preparation

In this work, the "bicomponents" composites were prepared with industrial sodium silicate and the ones that used alternative silicate were called "monocomponents". Geopolymeric composites ratios fly ash/metakaolin contents varied from 0; 25; 50; 75 to 100%. The composites samples were aged for 6, 12, 24 and 72 hours.

NMR measurements

Low field NMR MARAN ultra 23 spectrometer, operating at 23 MHz (for protons), and equipped with an 18 mm variable temperature probe, was used for the determination of relaxation measurements. Proton spin-lattice relaxation times (T_1H) were determined directly by the traditional inversion recovery pulse sequence (180°- τ - 90°) the 90° pulse of 4.6µs was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.1 to 5000 ms, with 4 scans for each point and 5s of recycle delay[5,6]. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the program WINFIT. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using the software WINDXP.

Results and Discussion

Geopolymeric composites varied fly ash/metakaolin contents in 0, 25; 50; 75 and 100%. The best compressive strength were found for geopolymeric concretes containing the relation fly ash/metakaolin equal to 25%, with 28 days of cure, for both bicomponents and monocomponents composites. Monocomponents concretes had the worst mechanical behavior due to mainly the sodium silicate's bad actuation[4]. As higher the fly ash/ metakaolin contents were, more porous were observed in the matrix-aggregate interfaces, which were showed by SEM micrographics. SEM micrographics also showed that a cure time of 24 hours weren't sufficient for consolidate a good matrix-aggregate interface; even this, geopolymeric concretes contain the relation fly ash/ metakaolin equal to 25%, which could reach 40% of their compressive strength within 28 days in the first 24 hours of cure[3,4].

Through hydrogen's relaxation time from water, containing in geopolymeric composites was possible to follow geopolymeric changes with raw materials content ratio's (fly ash/metakaolin) modification, like changes occurred after some time in these materials. The conservation state – "shelf time" - of geopolymers' activation solution, when stocked before its use, can be investigated through hydrogen relaxation time present in solution water (not evaluated in the present work).

Analyzing the relaxation data for geopolymeric pastes, in the case of monocomponents, an increase in the relaxation time, according to the increase of the fly ash content was detected. This increase, on relaxation time, was associated to the reduction of the ions in the geopolymeric composites' pore solution as the quantity of fly ash content increases, promoting a decrease in the molecular mobility of the hydrogens nuclei in the formed pastes, which causes a diminish in the sites of ^{1}H-^{1}H interaction. Therefore, with the aging process, especially after three days of age (Table 1), a reduction in the nuclear relaxation time value was detected for all percentage of alternative silicate, probably due to a molecular readjust.

In the case of bicomponents pastes, the nuclear relaxation time presented higher values when compared with the values found for the monocomponents pastes, revealing that these materials presented higher molecular rigidity, due to strong intermolecular interactions created during geopolymerization reaction.

Table 1. Hydrogen relaxation time data obtained for Geopolymeric pastes

Composition (fly ash/ metakaolin) Monocomponents (%)	Age (h)	^{1}H Relaxation time (ms)	Composition (fly ash/ metakaolin) Bicomponents (%)	Age (h)	^{1}H Relaxation time (ms)
0	6	2.5	0	6	1997
	12	2.2		12	2310
	24	2.6		24	2150
	72	**2.1**		**72**	**2133**
50	6	1983	50	6	7818
	12	1383		12	6599
	24	1735		24	5605
	72	**1681**		**72**	**4792**
100	6	12141	100	6	12101
	12	3146		12	13180
	24	2592		24	13917
	72	**6581**		**72**	**5197**

Conclusion

According to the results, it may be infer that Low Field NMR, through the determination of spin-lattice relaxation time, showed to be able to evaluate modifications caused on cementations pastes, due to fly ash addition.

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