GEOPOLYMER OBTAINED FROM COAL ASH

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ABSTRACT

Geopolymers are tridimensional aluminosilicates formed rapidly at low temperature by naturally occurring aluminosilicates with a structure similar to zeolites. In this work bottom ash (Tractebel Energy) was used as raw material in eight formulations with three factors (hydroxide type, concentration and temperature) in a two-level complete factorial design. The ashes were dried, ground and hydroxide was added according to the type and concentration. The geopolymers were poured into cylindrical moulds, dried (14 days) and subjected to compression test. The ashes from power plants belong to the Al-Si and thus can easily form geopolymers. The compression tests showed that it is possible to obtain samples with compressive strength superior to conventional Portland cement. As a result, the temperature and molarity are the main factors affecting the compressive strength of the geopolymer obtained.

1. INTRODUCTION

Similar to the geological process of transformation of some volcanic rocks occurring in zeolites at low pressures and temperatures during the formation of sedimentary rocks, the geopolymerization process can be modelled and conducted in cementitious systems (1-5). The direct synthesis of an alkaline aluminosilicate phase in the composition of such cementitious systems can ensure excellent durability of artificial rocks formed side by side with new properties, because the structures and properties of zeolites vary widely. These cementitious systems of alkaline aluminosilicates were first called "solosilicates." Davidovits in 1972 called "geopolymers" tridimensional aluminosilicates formed rapidly at low temperature by naturally occurring aluminosilicates (6-8).

Currently the variety of names that describe these materials, including ceramics linked by alkali-activated cements, hydroceramics and cements activated by alkalis, creates a lot of confusion. However, in all cases the alkali activation is essentially required (9, 10). Probably a more appropriate and wide term that describes these materials would be "inorganic polymers". The sialate network (silicon-oxo-aluminate) consists of SiO_4 and AlO_4 tetrahedra alternatively linked by shared oxygen atoms. Positive ions such as Na^+, K^+ and Ca^{2+} must be present in the spaces of the network to balance the negative charge of Al^{3+}. Poly(sialates) are chain or ring polymers with Si^{4+} and Al^{3+} in tetrahedral coordination with oxygen and its empirical formula is $M_n(\text{-}SiO_2)_z\text{-}AlO_2)_n \cdot wH_2O$, where z is 1, 2 or 3, M is a monovalent cation such as K^+ or Na^+ and n is the degree of polycondensation. The polysialates can be of three types: poly(sialates), poly(sialate-siloxo) and poly(sialate-disiloxo). Thus, the complex structure of the geopolymer consists of networks of chains, sheets and tridimensional units formed by several types of interconnected SiO_4 and AlO_4 tetrahedra Q units (11-14).

The geopolymers are cheap to produce and can be obtained when naturally occurring materials are mixed with NaOH and water (15-17). The geopolymerization is analogous to the synthesis of zeolites, because the chemistry involved is similar, although the resulting products are different in composition and structure. Geopolymer products do not have stoichiometric composition and comprise mixtures of semicrystalline to an amorphous structure with crystalline particles of Al-Si (18). Three sources are necessary for the synthesis of geopolymers: raw materials, an inert load and geopolymer liquor. Raw materials can be natural minerals (aluminosilicates) or industrial waste materials as fly ash, slag and waste glass. The inert load, mainly kaolinite and metakaolinite, is used to provide Al^{3+} ions (19). The geopolymer liquor is an alkaline hydroxide solution required for the dissolution of the raw materials while the solution of sodium silicate (or potassium) acts as a binder, activator and alkaline dispersant or plasticizer (20-21).

During geopolymerization, since the aluminosilicate powder is mixed with the alkaline solution, it forms a paste that quickly turns into a hard geopolymer. Thus there is insufficient time or space for the gel or paste to grow in a well-crystallized form; this is the fundamental difference between the zeolites and geopolymers. After a short period of curing and hardening geopolymers are formed with a very compact polycrystalline structure that exhibit better mechanical properties than the zeolites, which have lower density and exhibit a crystalline structure like cage (22-23). The geopolymerization process involves steps of leaching, diffusion, condensation and hardening, while the synthesis of zeolites is related to the pre-nucleation, nucleation and crystal growth. Moreover, usually the geopolymers cure at temperatures below those required for the manufacture of zeolites. Factors affecting the synthesis of zeolites include temperature, pH and cations, and it is believed that these three factors also affect geopolymerization.

Among the various existing patents is the development of an aluminosilicate mineral polymer that is formed at temperatures around 120°C as a solid solution, a method for obtaining a geopolymer binder and the production of fully hydrated aluminosilicate geopolymer. A new theory for the structure of geopolymer materials based on the understanding of the chemistry of zeolites is in development at the University of Melbourne. It is postulated that the geopolymer binder phase consists of a cluster of zeolitic nanocrystallites joined by an aluminosilicate gel. This concept is plausible on the chemical, thermodynamic and mechanical points of view, and allows the interpretation of various features of existing experimental data that have so far resisted a more comprehensive analysis (24-25).

Although geopolymers have been used in a variety of applications their wider use is limited due to lack of scientific understanding and detailed studies of long-term durability. The current lack of commercialization and application of the geopolymer technology is partially due to the confusion and incongruity of the design of its chemical nature. The variation of mechanical and thermal properties is also a source of concern in relation to industrial and commercial maturity of geopolymer materials. Experimental variations can be induced by an inadequate sample preparation or a poor quantification of system parameters (26-27). The main barrier that geopolymerization must overcome to become acceptable by the industry is mainly due to the entrenched position of the regulators. Another issue to consider is that the industry is very conservative in adopting new technologies and products to replace existing ones. To overcome these barriers more intensive and continuous efforts are needed by the scientific community (28).

Therefore, the objective of this study was to recycle the bottom ash generated by the burning of mineral coal in the southern region of the Santa Catarina State for the development of geopolymers by the alkaline synthesis.

2. EXPERIMENTAL PROCEDURE

Coal ash obtained from Tractebel Energy was used as a source of aluminosilicates. From a standard lot the ash was dried and milled in laboratory ball mill (grinding jar and elements of high-alumina) for 12 hours. The ground ash was characterized by X-ray fluorescence (XRF) to determine its chemical composition and laser diffraction to determine its particle size distribution (PSD) after grinding.

For the synthesis alkaline NaOH and KOH of analytical grade and sodium silicate (SiO_2: Na_2O molar ratio =3:1) were used. According to the literature (20-25) the stoichiometry ratio more appropriate for geopolymerization are: SiO_2/Al_2O_3 = 3.0~4.5; M_xO/SiO_2 = 0.2~0.5, and H_2O/M_xO = 10~25. Therefore, only ash was used as raw material, with the addition of NaOH, KOH and sodium silicate for geopolymerization, with temperature varying between 50°C and 80°C during the synthesis.

From the chemical analysis of the ash, mixtures were prepared with the following stoichiometry: SiO_2:Al_2O_3 = 2.5, Na Al = 0.85, K Al = 0.85 and H_2O:SiO_2 = 2.0 (24-25). The synthesis of geopolymers was made by mixing the ash with alkaline solution of NaOH and KOH 10 M and 20 M, using sodium silicate 1%, and mixing the gel for 5 min in a mechanical mixer. After mixing the gel was poured into cylindrical shapes (φ = 40 mm, h = 40 mm) and cured in an oven between 50°C and 80°C for 24 h.

Finally, the specimens were subjected to compression tests (universal testing machine, 10 mm/min and average of 3 specimens) after drying for 14 days. A 2^k factorial design was used for analysis of the synthesis variables, Table 1. The levels used were the type of alkaline (NaOH or KOH), the amount of alkaline during synthesis (10% and 20%), and the synthesis temperature (50°C and 80°C) being the room temperature used for comparison.

Run	Alkaline (type)	Alkaline (%)	Temp. (°C)	$\sigma_{comp.}$ (MPa)
1	NaOH	10	50	6.7
2	KOH	10	50	8.0
3	NaOH	20	50	2.9
4	KOH	20	50	4.9
5	NaOH	10	80	3.7
6	KOH	10	80	2.3
7	NaOH	20	80	2.6
8	KOH	20	80	2.1

Table 1. 2^k factorial design for geopolymer synthesis

3. RESULTS AND DISCUSSION

The chemical analysis of the coal ash (Table 2) shows that it is formed mainly by silica and alumina and small amount of alkali and alkaline earth metals oxides, being contaminated mainly with iron and titanium oxides. The loss on ignition of the ash shows that the combustion was not complete. As the stoichiometric ratio between silica and alumina is close to that given in the literature (SiO_2/Al_2O_3 = 2.5) the ash was used as the sole source of aluminosilicate.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	MgO	Na_2O	L.O.I.
(mass %)	57.9	22.8	4.1	2.1	1.4	1.1	0.4	0.3	9.6

Table 2. Chemical analysis of the mineral coal ash

After milling the ash presents very fine particles, Figure 1, suitable for the synthesis of geopolymer, with an average diameter of 7,6 µm, D_{50} = 3,7 µm, and D_{90} = 21 µm.

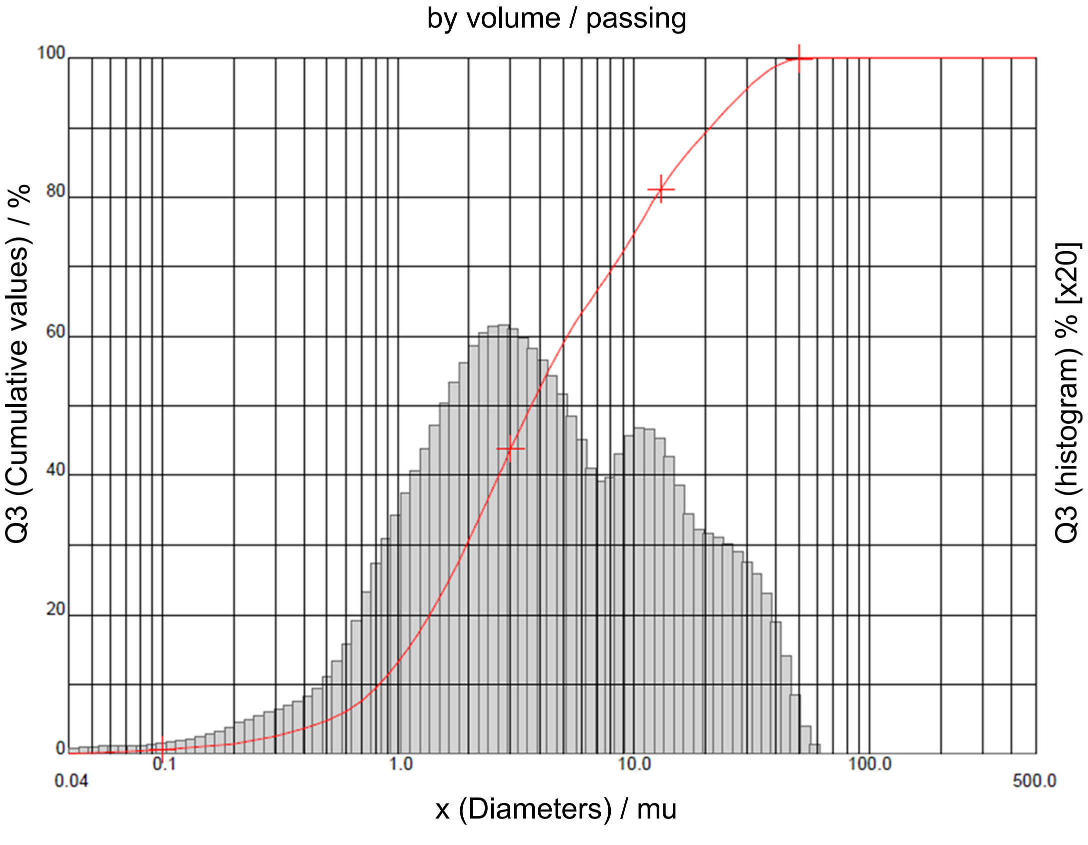

Figure 1. Particle size distribution of the coal ash after milling

The analysis of the results (ANOVA) for the compressive strength of samples in function of type and content of alkaline hydroxide and temperature of synthesis (Table 3) shows that the most important factors for the compressive strength are primarily temperature and then the percentage of hydroxide used with great reliability of the results (α = 0.01 and 0.02, respectively, meaning a reliability of 99% and 98% for temperature and hydroxide percentage). The type of hydroxide used had a lower significance.

Factor	**SQ**	**dF**	**MQ**	**F**	**p**
Hydroxide (type)	0.245	1	0.245	49	0.090
Hydroxide (%)	8.405	1	8.405	1681	0.016
Temp. (°C)	17.405	1	17.405	3481	0,011
Type×%	0.320	1	0.320	64	0.079
Type×°C	3.380	1	3.380	676	0.024
%×°C	3.920	1	3.920	784	0.023
Error	0.005	1	0.005		
Total	33.680	7			

Where: SQ = sum of squares; dF = degree of freedom; MQ = mean squares; F = Fischer test; p = reliability.

Table 3. Analysis of variance (ANOVA) for the compressive strength

The contour curve analysis for the interaction between the hydroxide type and temperature of synthesis, Figure 2, shows the strong effect of temperature, as the highest values of compressive strength are obtained for the lowest temperature, and for the use of KOH as hydroxide in the synthesis.

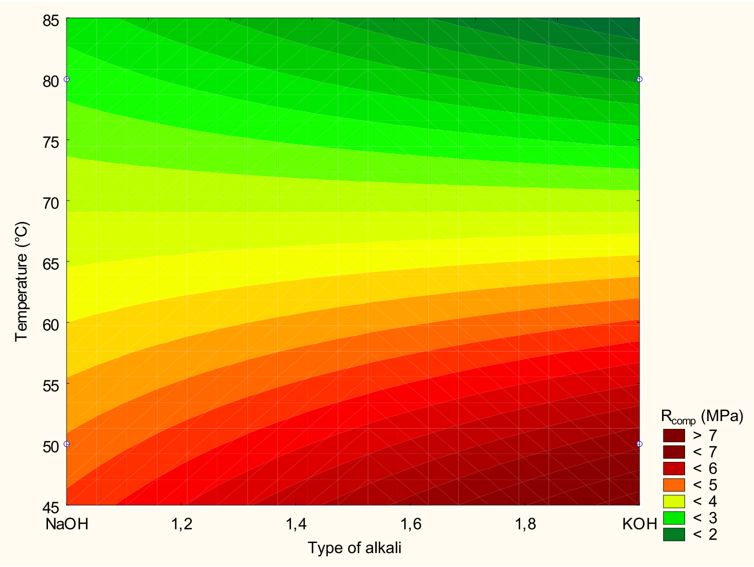

Figure 2. Contour curve for the interaction between the hydroxide type and temperature of synthesis

Analysing the interaction between the percentage of hydroxide and temperature of synthesis, Figure 3, again it is clear that the highest values for the mechanical strength of the samples occur for the combination of lower synthesis temperature and lower content of hydroxide. The analysis of results shows that the type of base used, KOH or NaOH, does not affect the compressive strength. Although the literature (20-25) indicates temperatures of 120°C for the synthesis of geopolymers, the results of this study suggested the opposite: the higher the synthesis temperature (80°C), the lower the compressive strength of the geopolymers obtained. Another important result was the contents of the alkaline solution used: the higher the molarity used, the lower the resistance obtained. These effects are directly related to the formation of the structure in the geopolymer samples, the alkaline synthesis promoting the linking of the silica and alumina tetrahedra through the ions dissolved in the geopolymer gel, in this case Na^+ and K^+. Another possibility of the decreased need of the alkaline solution would be the very chemical composition of the ash used, which contain small amounts of Na_2O and K_2O in its composition (see Table 2).

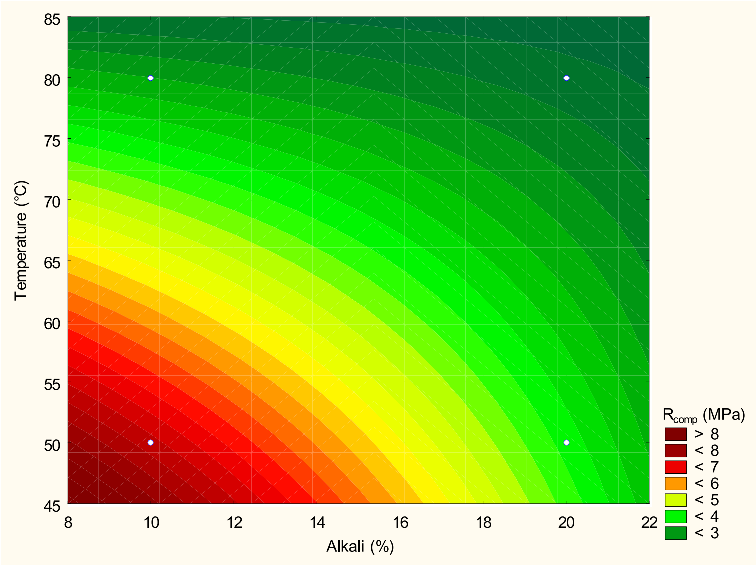

Figure 3. Contour curve for the interaction between the hydroxide percentage and temperature of synthesis

4. CONCLUSION

Geopolymers can be obtained from bottom ash from burning coal. The only treatment needed in the waste is to reduce the size of the particles. From the results it was possible to conclude that the type of alkaline solution does not alter the compressive strength of the system, but both the molarity of the solution but rather the temperature of synthesis strongly alter this property. The compressive strength results obtained are superior to the mortar paste made with Portland cement type II, which show resistance to compression close to 2 MPa without the addition of aggregates. Microstructural analysis (FTIR and SEM) is being carried out on samples to determine the effect of synthesis conditions on the structure of geopolymers. Synthesis at room temperature is being carried out in function of the results.

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