

ECO-CONCRETE: ONE-PART GEOPOLYMER MIXES

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Abstract: The geopolymerization of alumino-silicate materials is a complex chemical process evolving dissolution of raw materials, transportation or orientation and polycondensation of the reaction products. Publications on the field of geopolymeric binders, state that this new material is likely to have high potential to become an alternative to Portland cement composites. Classical two part geopolymers could be made more eco-efficient with a lower carbon dioxide footprint if the use of sodium silicate is avoided. Besides current geopolymeric mixes can suffer from efflorescence originated by the fact that alkaline and/or soluble silicates that are added during processing cannot be totally consumed during geopolymerisation. Therefore new geopolymer mixes are needed. This paper presents experimental results on a novel kind of mixes termed one-part geopolymers. Compressive strength results and efflorescences observations show that the new mixes already analyzed are promising.

Keywords: eco-concrete, one-part geopolymers, compressive strength, efflorescences

1. Introduction

With an annual production of almost 3 Gt Ordinary Portland cement (OPC) is the dominant binder of the construction industry [1]. The production of one tonne of OPC generates 0.55 tonnes of chemical CO₂ and requires an additional 0.39 tonnes of CO₂ in fuel emissions for baking and grinding, accounting for a total of 0.94 tonnes of CO₂. Other authors [2] reported that the cement industry emitted in 2000, on average, 0.87 kg of CO₂ for every kg of cement produced. As a result the cement industry contributes about 7% of the total worldwide CO₂ emissions [3]. The projections for the global demand of Portland cement show that in the next 40 years it will have a twofold increase reaching 6 Gt/year. The urge to reduce carbon dioxide emissions and the fact that OPC structures which have been build a few decades ago are still facing disintegration problems points out the handicaps of OPC. Portland cement based concrete presents a higher permeability that allows water and other aggressive media to enter leading to carbonation and corrosion problems. The early deterioration of reinforced concrete structures based on ordinary Portland cement (OPC) is a current phenomenon with significant consequences both in terms of the cost for the rehabilitation of these structures, or even in terms of environmental impacts associated with these operations. Research works [4-8] carried out so far in the development of geopolymers showed that much has already been investigated and also that an environmental friendly alternative to Portland cement is rising.

Davidovits [9] was the first author to address the carbon dioxide emissions of these binders stating that they generate just 0.184 tons of CO₂ per ton of binder.

Duxon et al. [10] do not confirm these numbers; they stated that although the CO₂ emissions generated during the production of Na₂O are very high, still the production of geopolymers is associated to a level of carbon dioxide emissions lower than the emissions generated in the production of OPC. According to those authors the reductions can go from 50% to 100%. Duxson & Van Deventer [11] mention an independent study made by Zeobond Pty Ltd in which a low emissions Portland cement (0.67 ton./ton.) and geopolymers were compared, reporting that the latter had 80 % lower CO₂ emissions. Weil et al. [12] mentioned that the sodium hydroxide and the sodium silicate are responsible for the majority of CO₂ emissions in alkali-activated binders. These authors compared Portland cement concrete and geopolymeric concrete with similar durability reporting that latter have 70% lower CO₂ emissions which confirmed the aforementioned reductions. McLellan et al. [13] reported a 44 to 64 % reduction in greenhouse gas emissions of geopolymers when compared to OPC. Habert et al. [14] carry out a detailed environmental evaluation of geopolymers using the Life Cycle Assessment methodology confirming that they have a lower impact on global warming than OPC but on the other side they have a higher environmental impact regarding other impact categories. Lower CO₂ emissions geopolymers are therefore needed.

Besides the durability of geopolymers is still a subject of some controversy [15]. While Duxon et al. [10] state this is the most important issue on determining the success of these new materials and other authors [16] mention that the fact that samples from the former Soviet Union that have been exposed to service conditions for in excess of 30 years showing little degradation means that geopolymers do therefore appear to stand the test of time. But since those materials were of the (Si+Ca) type that conclusion cannot be extended to geopolymers defined as “alkali aluminosilicate gel, with aluminium and silicon linked in a tetrahedral gel framework” [11]. On the other side Juenger et al. [1] argue that “The key unsolved question in the development and application of alkali activation technology is the issue of durability” and more recently Van Deventer et al. [17] recognized that “whether geopolymer concretes are durable remains the major obstacle to recognition in standards for structural concrete”. Efflorescences is an important drawback of two part geopolymers that so far has received very little attention. This phenomenon is influenced by several causes like the reactivity of the alumino-silicate, the mix composition and the curing conditions.

According to Skvara et al. [18,19] the bond between the sodium ions (Na⁺) and the aluminosilicate structure is weak and that explains the leaching behaviour. Kani et al. [20] showed that efflorescences can be reduced either by the addition of alumina-rich admixtures or by hydrothermal curing at temperatures of 65 °C or higher. These authors found that the use of 8% of calcium aluminate cement greatly reduces the mobility of alkalis leading to minimum efflorescences (this cement has 28% of CaO). These results are very important because they constitute a step back in the development of geopolymers. For one the use of hydrothermal curing has serious limitations for on-site concrete placement operations. On the other hand the use of calcium based mixtures reduces the acid resistance and raises the chances for the occurrence of ASR. This means that this subject merits further investigations. One-part geopolymers represent a key event on geopolymer technology having been described by the first time in 2008. In this work, experimental results on a novel kind of mixes termed one-part geopolymers are presented.

2. Experimental work

2.1. Materials

The composition of dry mix in this study was: kaolin, fly ash, ordinary Portland cement (OPC), sodium hydroxide, calcium hydroxide, water and superplasticizer. The OPC is of class I 42,5 R type with a clinker content between 95-100% and with a specific weight of 3.15 g/cm³ and a Blaine fineness of 3842 cm²/g (Table 1). The superplasticizer (SP) used was SIKA 3002 HE. The SP was used to maintain a uniform consistency between the different mixes. The chemical composition of the fly ash complies with the minimum requirements indicated in EN-450-1 [21] for being used as a partial replacement of cement in concrete. Based on this standard the fly ash was categorized in class B and group N for the loss of ignition and fineness, respectively. It has a specific weight of 2.42 g/cm³ and the chemical composition is shown in Table 2. Some characteristics of fly ash are shown in Table 3.

Table 1. Chemical composition of the Portland cement

Loss on ignition %	Cl- %	SO ₃ %	CaO Free %	CaO Reactive %	SiO ₂ %	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ %	MgO %	Al ₂ O ₃ %	Total alkalis %
1.7	0.01	2.83	1.53	63.1	20.9	92.29	2.71	5.03	-

Table 2. Chemical composition of the fly ash

Cl- %	SO ₃ %	CaO Free %	CaO Reactive %	SiO ₂ %	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ %	MgO %	P ₂ O ₅ %	Total alkalis %
0	0.12	0.1	2.7	40.8	89.9	1.9	1.92	0.25

Table 3. Characterization of the fly ash

Retained on No. 325 sieve %	I.A.28D %	I.A.90D %
15	79	99

2.2. Mix proportioning and testing

A mixture of kaolin and sodium hydroxide was calcined in a furnace at 650 °C during 140 minutes. The cooled mixture was grinded into powder. Phases A (Tables 4 and 5) and B (Tables 6 and 7) were made to evaluate the influence of aggregate and calcium hydroxide. Tests were performed on 50x50x50 mm³ concrete specimens according to NP EN 206-1[22]. The specimens were located in the chamber room during the curing time with relative humidity of 58 °C. Compressive strength for each mixture was obtained from an average of 3 cubic specimens. The specimens were tested with the pace of 0.36-0.72 N/s.mm². The selection of the speed rate depends on test duration. If test would be able to be done with the speed rate of 0.36 N/s.mm² in 30-90 seconds,

the pace is acceptable. But, if with this pace exceed this duration, the pace has to be increased up to 0.72 N/s.mm². Efflorescences were evaluated by means of visual observation. The specimens are immersed in water during 24 hours and then placed at room temperature. After 48 hours visualizations are recorded.

Table 4. Mix proportions used in phase A

Mix	Calcined kaolin+ potassium hydroxide	Fly ash	OPC	Ca(OH) ₂	W/b	Sand(gr)	SP
1-A	5 %	32.0%	40 %	23.0%	34%	2114	3%
2-A					34%	2045	2%
3-A					29%	1937	2%
4-A					30%	1898	3%

Table 5. Phase A-Volumetric ratios

Vs/Vp	Vw/Vp	Vsp/Vp
1	0.77	0.023
0.95	0.77	0.023
0.9	0.77	0.023
0.85	0.77	0.023

Table 6. Mix proportions used in phase B

Mix	Calcined kaolin+ potassium hydroxide	Fly ash	OPC	Ca(OH) ₂	W/b	Sand(gr)	SP
1-B	5%	32.0 %	40 %	21.0%	29%	2199	2%
2-B				24.0 %			1%
3-B				27.0 %			1%
4-B				19.0%			4%

Table 7. Phase B -Weigth ratios

WCa(OH) ₂ /Wc	WCa/Wc	WFA/Wc	WSP/Wc
0.45	0.12	0.79	0.01
0.5	0.12	0.79	0.01
0.65	0.12	0.79	0.01
0.7	0.12	0.79	0.01

3. RESULTS AND DISCUSSION

Figure 1 shows the compressive strength of the mixtures test in Phase A. Vs relates to the volume of sand and Vp for the volume of powder (OPC, FA, Kaolin, potassium hydroxide and Ca (OH)₂). Increasing the sand content leads to lower compressive strength because the w/b ratio has also increased.

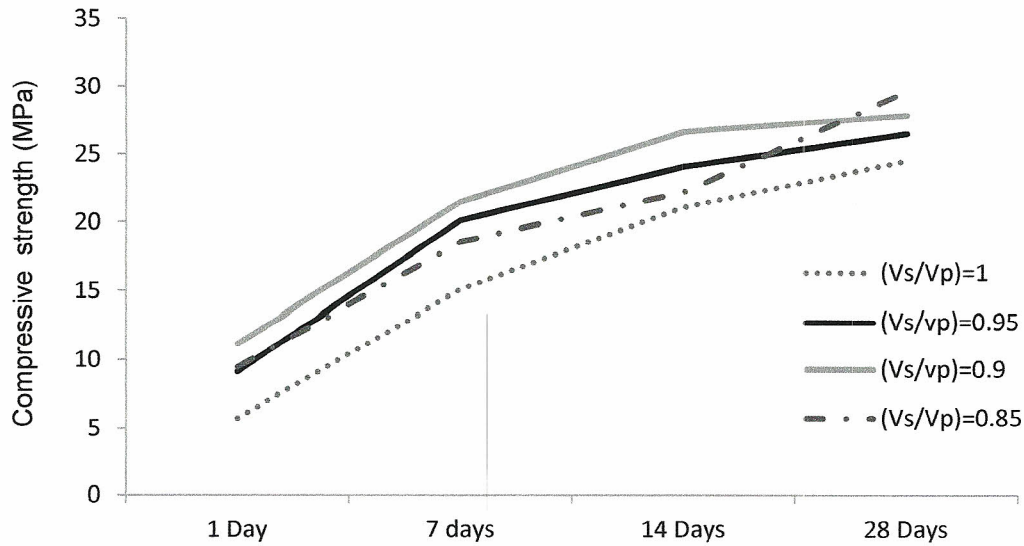


Figure 1. Compressive strength: Phase A

Figure 2 shows the compressive strength of the mixtures tested in Phase B. The calcium hydroxide is presented as a function of the Portland cement quantity.

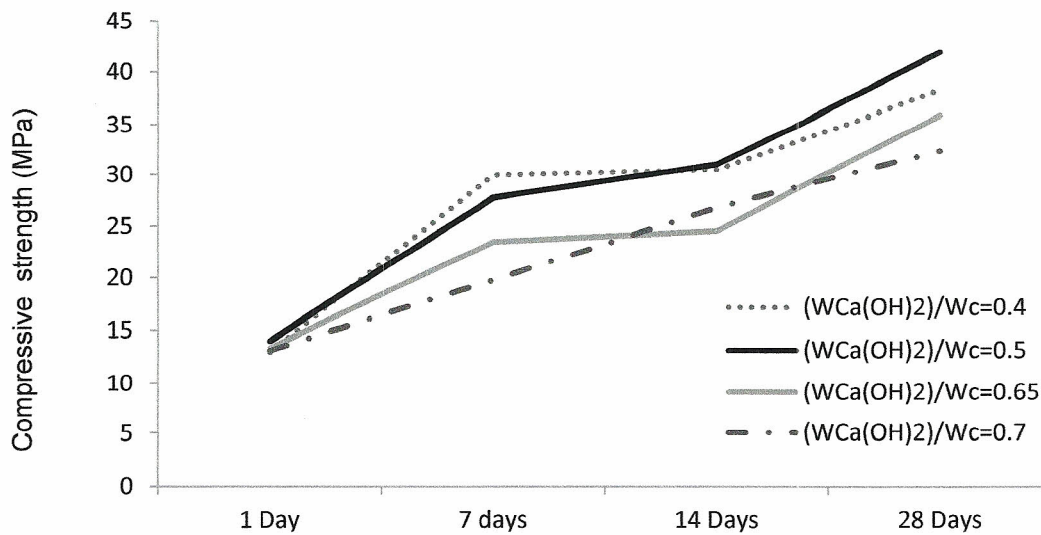


Figure 2. Compressive strength: Phase B

The results show that there is not a direct linear relationship between the calcium hydroxide content and the compressive strength. The use of calcium hydroxide as much as 50% of Portland cement leads to the highest compressive strength. Increasing the Ca(OH)₂ percentage beyond that percentage can lead to a decrease in the compressive strength. Concerning the efflorescences no relevant presence was observed. This is a promising result of the new one-part geopolymers.

4. CONCLUSION

- Several one-part geopolymers were developed some having a high compressive strength suitable for construction purposes.
- A general trend was observed linking compressive strength evolution with

curing age which is typical of OPC chemistry but not for two-part geopolymer

- The results show that there is not a direct linear relationship between the calcium hydroxide content and the compressive strength.
- All the mixtures show no signs of efflorescences
- Further investigations on mixture composition are still needed in order to select mixtures with a high compressive strength and a high eco-efficient performance

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