EFFECT OF PORLAND CEMENT ADDITION ON INITIAL DISSOLUTION OF COAL GANGUE BASED ALKALI-ACTIVATED CEMENT

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Abstract

Release of silicon and alumina from aluminosilicate occurs at early stages of alkaline reaction. Alkalinity and different aluminosilicate could influence dissolution of particles and modify microstructure of alkali-activated systems. However, there is a lack of study regarding the effects of Portland cement (OPC) addition on alkali-activated systems. This paper investigates alkaline dissolution of aluminosilicate by leaching experiments, varying Portland cement content. Chemical stability of AA-hybrid pastes was determined by water immersion and compressive strength at 28 days. Hybrid alkali-activated cement was produced with coal sludge (CS) and coal gangue (CG). Portland cement was added in 10 wt% and 20 wt% of precursor, and the water to binder ratio was of 0.75. Compressive strength increased in hybrid alkali-activated materials after chemical stability test, and leached solutions have a peak of pH and electrical conductivity at seven days. Chemical analysis of leached solutions detected contents of SiO_2, SO_3, K_2O, Fe_2O_3 and CaO. Portland cement addition increased alkaline dissolution of Si and Al from aluminosilicate at initial stages of chemical reaction with a synchronized behaviour. Dissolution efficiency was according to the material reactivity, following CST>CG>CS.

Keywords: alkali-activation, coal gangue, dissolution, chemical stability.

1. INTRODUCTION

Synthesis of alkali-activated cement involves chemical reaction between aluminosilicates and alkaline reagents. Basically, chemical reaction consists of dissolution, condensation and polymerization [1]. Dissolution of aluminosilicate can be influenced by alkalinity [OH]- [2, 3], temperature [4], aluminosilicate characteristic [2, 5] and calcium content [6]. Aluminum is more readily to dissolves than silicon, since Al-O bonds are weaker than Si-O bonds [4]. Sagoe-Crentsil and Weng [7] suggested that the process of condensation occurs in two stages: quick condensation between $[Al(OH)_4]^-$ and $[SiO_2(OH_2)]^{2-}$, and slow condensation of silicate

species. Factors as higher partial charge, larger atomic size and four hydroxyl groups are attributed to higher activity of $[Al(OH)_4]^-$ [3].

Reaction products of alkali-activated cements are amorphous aluminosilicate gel and/or zeolites [1]. Chemical stability of alkali-activated cements (AAM) is related to microstructure formation. Continuous immersion in water can weaken Si-O-Si bonds and increase capillary pore pressure, which implies in the reduction of compressive strength [8].

Fly ash, metakaolin and slags are main aluminosilicate used in AAM [9], however, there are advances in use of mining wastes, such as coal gangue. Cheng et al [10] observed that, the higher alkalinity, the higher the compressive strength of coal gangue alkali-activated cements, reaching a plateau at 12 M. Granulated blast furnace (GBFS) addition in CG-based alkali-activated material can improve the compressive strength; the main reaction products evidenced were C-A-S-H and C-S-H [11].

Low-calcium aluminosilicates based AAM, generally presents difficulty to hardening at room temperature, thus thermal cure is required to accelerate the reaction processes [12]. Synergy between heat released by hydration of Portland cement and presence of alkalis, in hybrids alkaline cements, provide dissolution of aluminosilicate particles [13].

Coal gangue are composed by silicon and aluminum oxides, and lower iron content, whereas the main crystalline phases are quartz and kaolinite [14]. Calcination heat at 500ºC and 700ºC is applied, in order to burn organic material [15] and can induce to kaolinite dehydroxylation [16]. However, this process can release significant levels of CO_2 and SO_2 [15], which may limit large-scale application as a building material.

Effect of Portland cement addition on the alkaline dissolution of calcined and non-calcined coal mining waste were analyzed in this work. Compressive strength and chemical stability test were implemented to observed the influence of OPC in mechanical properties of AAM.

2. MATERIALS AND METHODS

2.1 Materials

Two different coal mining wastes were used as aluminosilicates, (i) coal sludge (CS) and (ii) granular coal gangue (CG); they were oven dried at 105°C for 24 hours and ball milled for 30 minutes. Part of CS was calcined at 700°C for 1 hour, then designated by CST. Portland cement replaced wastes in 10 wt% and 20 wt%. Chemical and mineralogical wastes characteristic were explained in a previous work [17] and are summarized in Table 1. Alkaline solution (AS) was prepared by dissolving NaOH (97% Na_2O – solid) in sodium silicate (12.7% Na_2O, 30.4% SiO_2 and 56.9% H_2O - solution), to obtain silica modulus (SiO_2/Na_2O) of 1.5.

2.2 Methods

Alkali-activated paste was prepared by pre-mixing OPC and wastes (dry-mix), adding AS with AS/solid of 1: 1 by weight, and 0.75 (wt) water to binder ratio. Cylindrical samples, 2 x 4 cm (diameter x height), were cast and hermetically sealed. Three series of AAM were studied, using different aluminosilicate, (i) CS, (ii) CG and (iii) CST. OPC replaced aluminosilicate in contents of zero wt% (control groups), 10 wt% and 20 wt%. Hybrid-AA were cured at room temperature (25°C). Control groups (CST-0, CS-0 and CG-0) were heat-cured in 50ºC for 24 hours, due to its non-hardening, until seven days at room temperature. CST series were demolded after 24 hours, but hybrid-CS and hybrid-CG after 48 hours.

Samples were sealed with PVC film, until test ages. Compressive strength test was implemented at 7 and 28 days in Instron press with 50 kN static load cell and 7000 N/min loading speed.

Chemical stability test was performed by immersed samples (at 7 days) in distilled water, 1: 4 (by weight) over 21 days. Samples were weighed and the contact solution was subjected to electrical conductivity, pH and chemical analysis, at intervals of one hour, 7 days, 14 days and 21 days. Compressive strength test was performed after 21 days of immersion. Chemical analyzes were implemented in X-Ray fluorescence Shimadzu 7000.

Alkaline dissolution test consists of: weigh one gram of powder (waste and OPC), add 25 g of NaOH (10.3M) and mix it on a magnetic stirrer for 10 and 60 minutes. The solution is vacuum filtered with a quantitative filter (8 μm), diluted with 50 ml distilled water and acidified (HNO_3 - pH <2). The concentration (mg/l) of dissolved aluminum and silicon was analyzed by atomic absorption (AA).

Table 1: Main Chemical and mineralogical characterization

Characterization	CST	CS	CG	OPC
SiO_2	60.0	28.8	47.1	17.2
Al_2O_3	30.4	10.2	21.03	-
Fe_2O_3	2.5	8.0	4.2	0.1
CaO	0.7	1.9	0.22	68.7
L.O.I	1.9	24.8	19.35	0.9
Others	26.3	4.5	8.1	9.2
Main crystalline phases	Quartz Muscovite	Quartz Kaolinite Muscovite	Quartz Kaolinite Pyrite	-

3. RESULTS AND DISCUSSION

3.1 Alkaline dissolution

Alkaline dissolution test was performed, at 10 and 60 minutes, to analyze OPC influence in Al and Si dissolution from coal mining wastes. Since the initial formation of AAM involves dissolution of aluminosilicate, which yields aluminates and silicates species, and they will hydrolyze to form monomers, those process can occur simultaneously [7].

Table 2 shows that Si and Al dissolution from coal wastes increase over the time. CST series show higher ions dissolution than the others series (CS and CG). OPC addition increases the dissolution of Si at 60 minutes for all samples, but does not affect the Al dissolution in CS and CG series. Dissolution of Si and Al seem to have a synchronized behavior in CST series, the Si/Al molar ratio have range from 1.0 to 1.8 at 60 minutes, the CST are composed mainly by quartz and metakaolin. Although the CS series and CG, due to their mineral composition, can have different degree of dissolution, thus, varying the

dissolution of aluminosilicates, the CS and CG series have range of Si/Al molar ratio from 1.3 to 3.6, at 60 minutes.

Transformation of kaolin during calcination leads to a metastable phase, metakaolin, and can be related to higher leaching of Si and Al, from CST series. Silicon and aluminum amorphous have lower bond energy and higher degree of ion dissolution [18]. Sagoe-Crentsil and Weng [7] by means of partial charge model evidenced aluminates species are consumed by condensation with silicates species, alongside with continuous dissolution and hydrolysis, which can result in hardening and setting of AAM.

The presence of more silicon species, provided by OPC addition, may justify the hardening of hybrid cements at room temperature, since the condensation occurs between silicates and aluminates species, and silicates species only [7]. Therefore, the results show Portland cement content, wastes chemical composition and crystalline phases influence dissolution of Al and Si, which will imply in AAM hardening.

Table 2: Si and Al concentration (ppm) after alkaline dissolution

Description	Si		Al	
	10 min.	60 min.	10 min.	60 min.
CST-0	128.4	210.2	-	205.0
CST-10	218.9	230.5	65.7	177.6
CST-20	186.2	362.8	73.5	192.8
CG-0	57.1	136.5	54.2	70.0
CG-10	78.8	161.4	53.7	70.3
CG-20	232.7	294.3	55.0	78.9
CS-0	53.2	117.4	53.2	87.4
CS-10	95.7	148.1	62.0	80.4
CS-20	145.9	214.3	70.6	88.1

3.2 Mechanical Properties

Fig. 1 shows compressive strength at 7 and 28 days, and after the chemical stability test (water). CST samples present higher mechanical strength than the other materials. Portland cement addition induce hardening at room temperature and increased mechanical strength. CS-0 and CG-0 systems did not harden at either oven cure, or room temperature, so demold was not possible.

Hybrid cements show increase in compressive strength after chemical stability test. Compressive strength may be affected by continued hydration of anhydrous OPC particles immersed in water. CS-20 and CG-20 present an increase of about 67% after chemical stability test in compressive strength, which is more significant than CST-series. However, CS-10 and CG-10 show, after the chemical stability test, a decrease in compressive strength and volumetric expansion, this behavior can be related to the oxidation of sulfates such as pyrite.
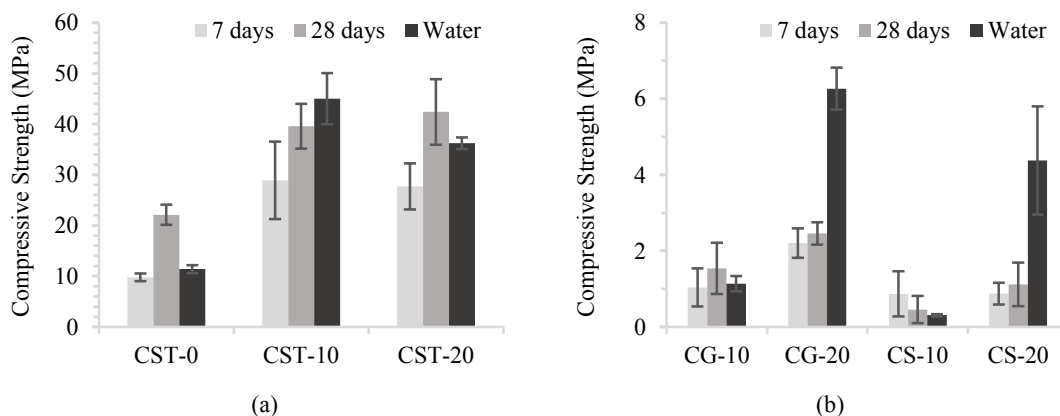
(a)

(b)

Figure 1: Compressive Strength (a) burnt waste; (b) unburnt wastes.

Fig. 2 shows the correlation between ions alkaline dissolution at 60 minutes and compressive strength. The data was linearly normalized, as Eq. 1, wherein the L is normalized values (MPa/MPa or ppm/ppm), X_i is value (MPa or ppm) to be normalized, X_{min} is minimum values of each series (MPa or ppm) and X_{max} is maximum values of each series (MPa or ppm). Alkaline dissolution of Al and Si can be an indicator of mechanical development, the higher initial ions dissolution, the greater compressive strength. The r-square are higher than 0.90, evidencing a higher linear correlation.

The alumina dissolution at early stages of reaction plays a role in development of initial mechanical strength, due to cross-linked gel. However, the silicon contribution in mechanical strength occurs in later stages of microstructural development [19]. Hardening of alkali-activated cement can be influenced by the presence of more reactive Al and the heat released from hydration of OPC particle. CST raw material is more reactive in an alkaline medium than CS and CG, thus, the results shows that the mechanical properties and initial microstructure formation seem to be influenced by reactivity of raw materials and OPC content.
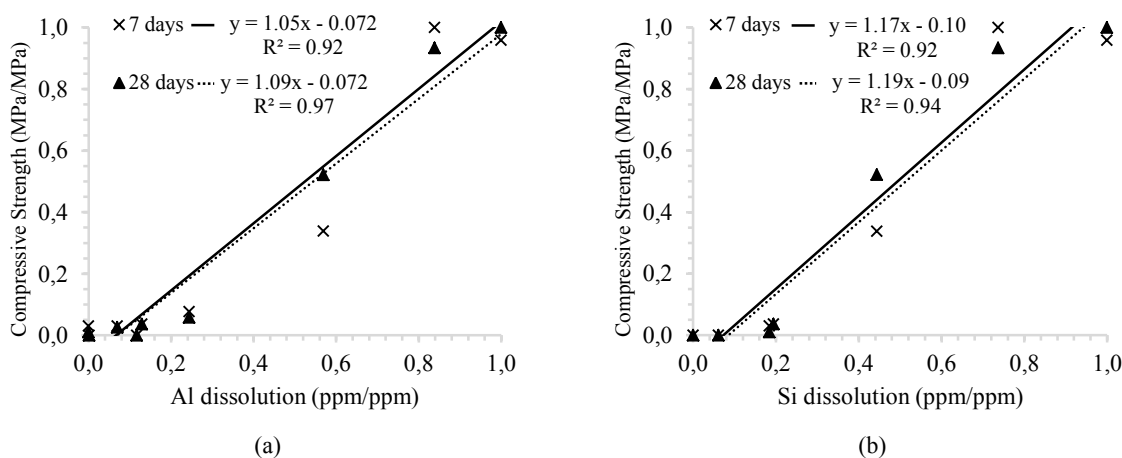

(a)

(b)

Figure 2: Normalized compressive Strength by (a) normalized Al dissolution; (b) normalized Si dissolution CST-systems.

$$L = (X_i - X_{min})/(X_{max} - X_{min}) \tag{1}$$

3.3 Chemical Stability

Salt solubility in aqueous medium can be analyzed by electrical conductivity (EC), the higher ion concentration, the higher the EC. EC and pH were measured in aqueous solution after chemical stability test, at intervals of 60 minutes, 7, 21 and 28 days. Fig. 3 presents pH and EC variation over time.

CS and CG systems present higher EC and pH values at seven days, which indicates that alkalis and metal ions did not participate of the alkaline reaction, and are free to leach. CST systems have lower EC and pH values, thus, the development of more stable microstructure. Hybrids CST-systems present higher values of EC at seven days than the CST-0, probably due to the OPC addition which leads to an increase in leached calcium ion.
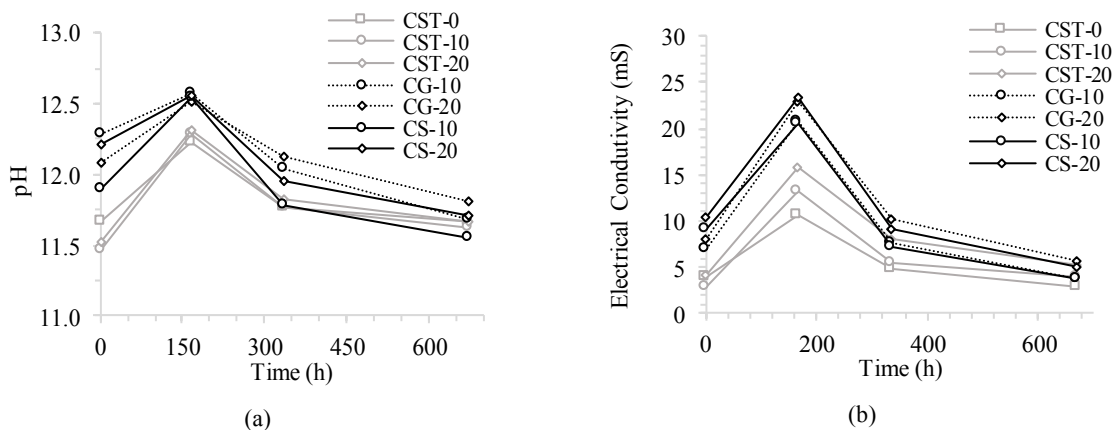

(a) (b)

Figure 3: Chemical stability test (a) pH; (b) electric conductibility.

Table 3 shows that during the chemical stability test, SiO_2 leached more from materials than the other oxides. OPC addition decrease the SiO_2 released, and the CST samples have the lowest values. Therefore, factors such as waste reactivity and calcium content can induce formation of stable microstructure, which results in less leached silica oxide. The higher SiO_2 leachate the lower compressive strength after water immersion, as evidenced in CST systems.

Table 3: Total leaching oxides (mol/kg) from chemical stability test;

Description	SiO_2	Fe_2O_3	K_2O	CaO	SO_3
CST-0	3.74	0.08	0.37	-	1.17
CST-10	2.91	0.13	0.65	0.10	1.11
CST-20	2.39	0.09	0.58	0.56	1.42
CG-10	4.82	0.02	0.11	0.11	0.16
CG-20	4.52	0.02	0.13	0.09	0.33
CS-10	5.86	0.02	0.02	-	0.20
CS-20	5.04	0.04	0.17	0.12	0.30

Highest leached SiO_2 was for CST-0, which did not show increase in compressive strength after chemical stability test. Water immersion may have inhibited the continuous alkaline reaction in CST-0, so there was no increase in mechanical strength compared to seven days. Water weakens Si-O-Si bonds and capillary action induces pore wall pressures, affecting microstructure and mechanical properties [8].

Correlation between compressive strength, EC and pH are present in Fig. 3, exponential correlation is evidenced, EC and pH values are from 60 minutes after water immersion. Electric conductivity and pH values can be indicators of mechanical development, when performed at early ages.
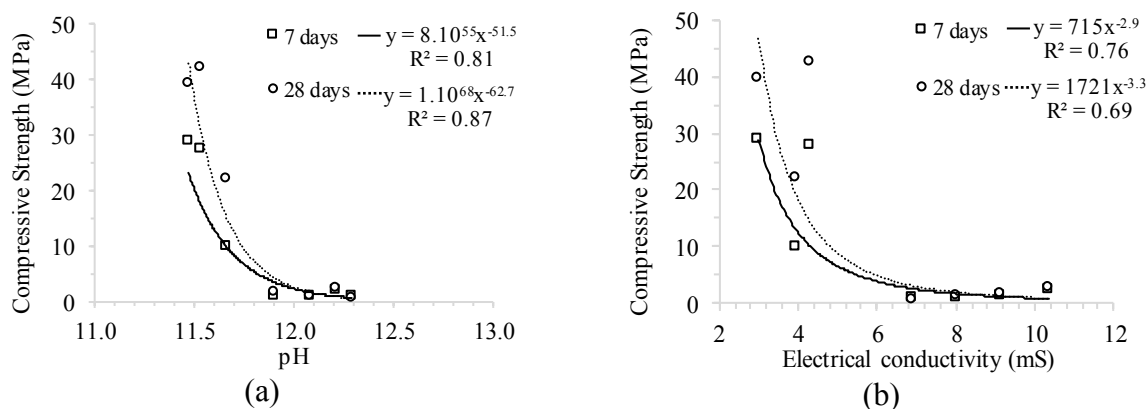

Figure 4: Chemical stability test exponential fit of (a) pH, (b) electrical conductivity.

4. CONCLUSIONS

The main conclusions obtained from the experimental results are listed below:

- Portland cement addition influenced alkaline dissolution of Si and Al ions, for all samples analyzed. The higher OPC addition, the greater dissolution of Al and Si ions. Concentration of aluminum dissolution at 60 minutes can be an indicator of mechanical development;
- Hybrids cement presents an increase in compressive strength after chemical stability test excepting CST-0. Hydration of anhydrous OPC particles may have positively affected hybrids cement. Whilst, CST-0 was negatively affected by internal pore pressure and weakened bonds of Si-O-Si;
- Electrical conductivity and pH were lower for CST-systems which may be related to formation of more stable microstructure. EC and pH values of chemical stability after 60 minutes of immersion, may be an indicator of mechanical strength as evidenced by exponential correlation.

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