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# Effect of Activators on Strength of Hybrid Alkaline Cement

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**Abstract.** Hybrid alkaline cement is a class of alkaline cement resulted from alkali activation of the medium calcium content of aluminosilicate materials. This paper presents an experimental analysis of alkali activators effect on strength of hybrid alkaline cement produced from 80% fly ash and 20% ordinary Portland cement. Two alkali activators were observed i.e. 5% sodium sulfate and a combination of 5% of sodium sulfate-1.1 M SiO<sub>2</sub> of sodium silicate solution. Compressive strength tests were performed on 20mmx 40mm cylinder paste specimens while setting time tests were conducted by Vicat needle. Scanning electron microscopy analysis and measurement of fly ash reaction degree were performed to explain the compressive strength of paste. It is concluded that addition of soluble silicate on the dry mix of hybrid cement-sodium sulfate activator reduce compressive strength and shorten the setting time. Both of activators give relative low fly ash reaction degree.

## 1. Introduction

Portland cement shows high performance as a binder in the concrete mixture. Nevertheless, its manufacture is energy-intensive for clinker processing at temperatures of 1450–1550°C [1]. In addition, production of one tonne of Portland cement release 0,55 tonnes of CO<sub>2</sub> from lime stone calcination and 0.40 tonnes of carbon-dioxide from fuel combustion [2]. Alkaline cement, which is a group of binders, have great potential as Portland cement alternatives to overcome those problems [3-6].

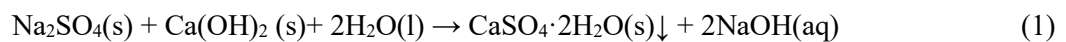
The system of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> alkaline cement are divided into three main categories namely moderately calcium rich cement, low calcium cement, and hybrid alkaline cement. Moderately calcium rich cement (for example blast furnace slag) activated by relatively moderate alkaline conditions and gives C-S-H (calcium silicate hydrate) gel as the main reaction product. Low CaO contents such as metakaolin or class F fly ash requires highly alkaline media at curing temperatures of 60–200°C. The main reaction product, in this case, is an N-A-S-H (natrium aluminum silicate hydrate) or geopolymer gel. Hybrid alkaline cement or hybrid cement is the result of the alkaline activation of materials with more than 20% of CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents. The cement is subclassified into two sub groups i.e. with and without cement clinker. The reaction products are mixtures of C-A-S-H (containing sodium) and (N,C)-A-S-H (high calcium content N-A-S-H) gels [7].



Hybrid cement with low clinker cement content is an interesting area of study by many researchers [8-13]. Moreover, Shi et al. [3] revealed that hybrid alkaline cement system had higher possibility to encounter the aforementioned environmental issue than the other type of alkaline cement without Portland cement. One of the root cause is the quality of a prime material of alkaline cement has not been standardized yet.

Two essential factors influence the strength of alkaline cement are raw materials and alkali activators. Different anions or cations result in a distinctive effect on activation process. Common types of anion are hydroxyl (OH<sup>-</sup>), silicate, carbonate, and sulfate, while usual cations are Na<sup>+</sup> and K<sup>+</sup> [14]. Mechanical strength developed by the same raw material may significantly different depending on activators being used.

Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) activator could increase the strength of hybrid cement significantly [15]. Addition of Na<sub>2</sub>SO<sub>4</sub> promotes NaOH formation through reaction with Ca(OH)<sub>2</sub>, expressed in equation (1) [16]:



In this case (Ca(OH)<sub>2</sub>) is produced by Portland cement hydration. Sodium hydroxide increases the pH of the solution, accelerates the dissolution of fly ash and promotes the pozzolanic reaction.

Palomo et al. [12] studied hybrid alkaline cement activated by NaOH solution, sodium silicate + NaOH solution and pure water as a control specimen. System hydrated with sodium silicate + NaOH solution reached the highest strength. Surprisingly, NaOH activation showed the lowest strength, which was even lower than water hydration. The authors concluded that Portland cement hydration strongly influenced by OH<sup>-</sup> concentration and the presence of soluble silicate in the medium. The finding was also supported by another research team [17]. A combination of soluble silicate and sodium hydroxide showed positive role in strength development of hybrid alkaline cement.

Silicate species in the sodium silicate solution exist in the form of the monomer, dimer, membered rings, and polymer. Minimum silicate monomer concentration for geopolymer gel formation is approximately 0.6 M SiO<sub>2</sub> which corresponds to 0.8M SiO<sub>2</sub> for Na/Al about 0.5 and 0.4 SiO<sub>2</sub> for Na/Al =0.75 [18].

Since NaOH demonstrates corrosive and hygroscopic behavior, it can not be mixed with prime materials in the solid state. In contrast, sodium sulfate is readily dry mixed with Portland cement-fly and gives processing advantage similar to ordinary cement. However, the combination of this activator with sodium silicate solution has not been focused by researchers yet. This study investigates comparison of compressive strength between hybrid alkaline cement activated by solid sodium sulfate versus combination of solid sodium sulfate- sodium silicate solution activator.

## 2. Materials and method

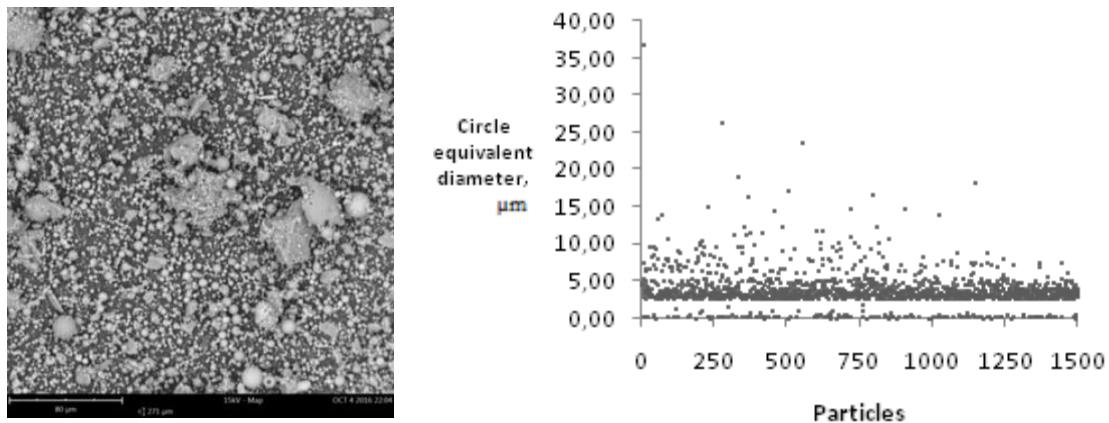
### 2.1 Materials

This study was conducted at hybrid alkaline cement system made of 80% class F fly ash and 20% ordinary Portland cement (OPC) mixture. SEM image of fly ash particles prepared with Nebula™ particles dispersion and particles size counted by Phenom illustrated in Figure 1. The chemical composition of these materials listed in Table 1 was determined by X-ray fluorescence technique. Sodium sulfate monohydrate (Na<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O) was used as solid activator while sodium silicate liquid 52°Baume having the composition of 15% Na<sub>2</sub>O, 30% SiO<sub>2</sub>, 55% H<sub>2</sub>O was used as a liquid activator.

**Table 1.** Chemical compositions of fly ash and OPC

	SiO <sub>2</sub>	reactive SiO <sub>2</sub> *	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	SO <sub>3</sub>
Fly ash	55.52	26.8	14.74	6.77	15.79	1.02	0.66	3.02	<0.001	0.75
OPC	20.92		5.49	65.21	3.78			0.97		2.22

\* reactive SiO<sub>2</sub> of fly ash was determined by gravimetric method



**Figure 1.** SEM image of fly ash (left side) and particles size pattern counted by Phenom's particle analyzer software (right side)

## 2.2 Methods

Fly ash, OPC, and sodium sulfate monohydrate activator were dry mixed. This blended cement-solid activator was reacted with two kinds of liquids: deionised water and solution of 1.1 M of  $\text{SiO}_2$ . The later was prepared by diluting sodium silicate liquid 52° Baume with deionized water. The  $\text{SiO}_2$  concentration was adopted from [18] for lower Na/Al mol ratio. Total water to total solid ratio (W/S) was arranged to get similar pastes flowability. Total water is the sum of deionized water and water in sodium silicate solution, while total solid is the sum of fly ash, OPC, sodium sulfate and the solid content of sodium silicate solution. Table 2 presents the detail mixtures.

**Table 2.** Proportion of hybrid alkaline cement pastes

Paste	Mass proportion			W/S	[ $\text{SiO}_2$ ], M*	Na/Al mol ratio*
	Fly ash	OPC	$\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$			
AS05	80	20	5	0.29	0	0.24
AS05-SS11	80	20	5	0.45	1.1	0.32

\*in reacting solution

The two resulting pastes were casted in 20mm x 40mm acrylic cylinders molding. These specimens were de-molded after 24 hours and stored under wet-sealed plastic films for the duration of the curing process. All pastes were tested for compressive strength at 3, 7, and 28 days. Setting time of pastes was tested by Vicat needle at 28°C in accordance to ASTM C191-08 [19]. Scanning electron microscopy (SEM) was used to analyze microstructure of the pastes. The degree of fly ash reactions of paste was gravimetrically measured by Takashima attack [12] followed by chloride acid (HCl) attack [20]. Takashima attack was conducted by reacting paste with a salicylic acid-methanol solution. Portland cement hydration product and unreacted Portland cement were disrupted by this treatment, while fly ash was not influenced. The residue of Takashima attack was mixed with water : HCl 37% solution (1:20). This solution dissolve reacted fly ash and left unreacted one. The ratio of soluble fly ash to total fly ash attacked by HCl was identified as fly ash reaction degree.

## 3. Result and Discussion

Table 3 shows setting time, the compressive strength of paste at 3, 7, 28 days and fly ash reaction degree at 7 days. As a usual behavior of cement materials, the compressive strength was increasing with curing time for all specimens. Surprisingly, specimen activated by a sodium sulfate - sodium silicate solution (AS05-SS11 paste) had shorter setting time than that with an only solid activator (AS05 paste) while the former composed of the mixture with higher water to solid ratio. Generally, increasing water to solid ratio correlated to longer setting time[21].

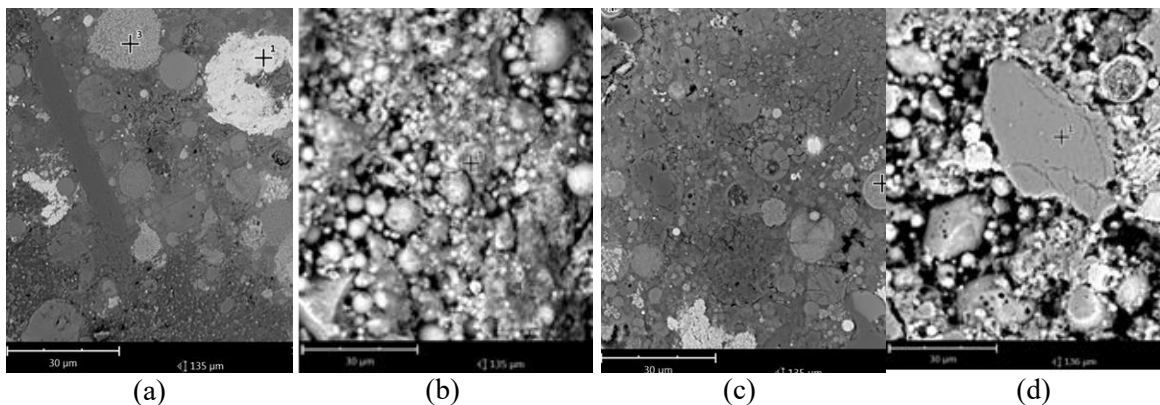
**Table 3.** Setting time and the compressive strength of hybrid alkaline cement paste

Paste	Setting time [h:m]		Compressive strength [MPa]			Fly ash reaction degree, 7days
	Initial	Final	3 days	7 days	28 days	
AS05	4:00	5:55	17	20	28	0.31
AS05-SS11	0:35	1:05	5	9	12	0.30

Observation by simple experiment on fly ash and OPC separately mixed with two kinds of activator was also has been carried out. It was found that pure OPC set quickly when it was reacted with sodium sulfate-soluble silicate solution activator. It is highlighted that soluble silicate is an aggressive species readily reacted with Portland cement. Furthermore, it is supposed that the reacted part of OPC has hardened immediately which in turn hinder further reaction. In other word, it is hypothesized that Portland cement was not completely reacted in AS05-SS11 system.

It was found also that activation of fly ash with solid-liquid activator decrease paste flowability than another one activated by a single activator, solid sodium sulfate. This condition leads to an increasing of water demand of AS0511-SS11 to get the same paste flowability of AS05. Usually, the strength of cement paste is decrease as water to solid ratio increase [21]. It is concluded that the lower strength of AS05-SS11 system than AS05 supposed resulted by uncomplete of OPC reaction and high water to solid ratio. The exact reason might be found by deep studying the effect of activators to each component of hybrid cement raw material separately.

Figure 2 presents backscatter scanning electron microscope (BS-SEM) image of paste specimens before and after Takashima attack. Before Takashima attack, specimen AS05 (a) is denser than AS05-SS11 (c) which conform to the compressive strength test results presented in Table 3, where AS05 paste has higher strength than AS05-SS11. Denser paste is produced by the higher portion of reaction product phase or lower water to solid ratio.



**Figure 2.** BS-SEM Image, (a) AS05 paste before Takashima attack, (b) AS05 paste after Takashima attack, (c) AS05-SS11 paste before Takashima attack, and (d) AS05-SS11 paste after Takashima attack

The strength of Portland cement paste is very likely contributed by C-S-H phase, while N-A-S-H phase is responsible for strength development of alkali activated fly ash. Both phases coexist in hybrid cement but interfere each other [17].

Figure 2 also shown that both of Portland cement hydration product and unreacted cement were dissolved by Takashima attack, while activated and unreacted fly ash were unaffected by this treatment. Figure 2 (b) and (d) illustrated bond of unreacted fly ash by activated one of AS05 and AS05-SS11 paste, respectively, which the former seem tighter than the later. This fact gives good confirmation of the higher compressive strength of AS05 than AS05-SS11. Fly ash reaction degree by

HCl attack at 7 days is presented in Table 2. Only about 30% of fly ash of the two systems are converted to reaction product at 7 days. It means that the strength contributed by fly ash reaction product is quite low. Criado [20] was found reaction degree of 55% at 7 days resulted by activation of fly ash having 50.44% reactive silica content. The possible reasons of low part of reacted fly ash in the hybrid cement mixture are inappropriate activator or low reactive silica content in fly ash, i.e 26.8%. This assumption might be proven by detail alkali activation experiments for numbers of fly ash with different reactive silica content.

#### 4. Conclusion

The following conclusions can be drawn from this study:

- The lower strength of AS05-SS11 system than AS05 supposed resulted by uncomplete of OPC reaction and high water to solid ratio. The exact reason might be found by deep studying the effect of activators to each component of hybrid cement raw material separately.
- Both systems have relative low fly ash reaction degree. The possible reasons are inappropriate activator or low reactive silica content in fly ash.

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