

Review

The effect of various chemical activators on pozzolanic reactivity: A review

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Pozzolans are being extensively used as a partial cement replacement in the production of Portland cement concrete. The advantages of using pozzolans are lower costs and better durability, however it requires longer setting time and the strength development at the initial age is slower. Different methods have been developed to overcome these disadvantages and to enhance the reactivity of natural pozzolans. There are three ways which have been used to improve the pozzolanic reactivity; it includes mechanical method, thermal method and chemical method. The utilization of the chemical method as an activator of pozzolanic reactivity has received considerable attention in recent years. In this paper the effect of using different chemical activators on pozzolanic activity of a pozzolan is summarized by reviewing previously published work. It was found that proper chemical activators can be used as an addition to concrete containing pozzolans which later can increase the reaction rate of pozzolanic activity and compressive strength significantly.

Key words: Pozzolan, chemical activators, strength.

INTRODUCTION

For the past 25 years, the utilization of pozzolans admixtures as a partial cement replacement for use in mortars and concretes has increased significantly (Cordeiro et al., 2009). Although, it was recognized long time ago that the pozzolanic materials have been used successfully in many countries, finding new and improved ways to produce high strength concrete with new pozzolans is receiving much attention (Davraz and Gunduz, 2005).

ASTM C 125 defines an admixture as a material other than water, aggregates, hydraulic cements, and fiber reinforcement that is used as an ingredient of concrete or mortar and added to the batch immediately before or during mixing (Mehta and Monteiro, 2006). It is well known that certain admixture such as polymer has been successfully used for improving the bond strength between old and new concrete for making concrete pipes (Chandra and Flodin, 1987). It was reported that the cement hydration has been promoted and the mechanical properties of polymer-modified cement mortars were improved with appropriate addition of styrene-butadiene rubber into the cement system (Wang et al., 2005; Wang et al., 2006).

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According to Shetty (2008), suitable pozzolans used in appropriate amount, modify certain properties of fresh and hardened mortars and concretes, such as:

- a) Lower the heat of hydration.
- b) Reduce the alkali-aggregate reaction.
- c) Improve resistance from sulphate attack in soils and sea water.
- d) Improve extensibility.
- e) Lower susceptibility to dissolution and leaching.
- f) Improve workability.
- g) Lower cost.

The use of pozzolan materials as partial cement replacement in blended cements and concrete has become more attractive due to energy saving concerns and other environmental considerations, such as CO₂ emission related to the production of Portland cement clinker (Ashraf et al., 2009).

As we know, calcium hydroxide is formed as one of the products from cement hydration. This compound has no cementitious value and it is soluble in water and may be leached out by percolating water (Shetty, 2008). The use of Portland cement with pozzolans generates a reaction between calcium hydroxide produced from Portland cement hydration and the amorphous SiO₂ of the glass phase from pozzolans material. This leads to an increase in the calcium silicate hydrate, C-S-H gel formation and thus, increasing strength and density (Liu et al., 2005).

Pozzolanic materials are defined as siliceous or silica-aluminous materials which in itself possess little or no cementitious value, but in a finely divided form and in the presence of moisture chemically react with calcium hydroxide at ordinary temperatures to generate compounds possessing cementitious properties (ASTM C 618, 1999). Neville (1999) stated that pozzolanic activity results in increased concrete strength. Pozzolanic materials should have a high degree of specific surface area and containing high content of amorphous silica in order to generate a pozzolanic reaction (Velosa and Cachim, 2009).

Various reactive pozzolanas have been used as supplementary cementing materials in order to produce highly durable and high performance concrete. Examples such as silica fume (SF), metakaolin (MK), fly ash (FA), ground granulated blast furnace slag (GGBS) and rice husk ash (RHA) are being used as blended mineral admixtures in cement. However, the use of pozzolanic materials as supplementary cementitious materials have been discovered to have a negative effect as its early strength development is normally decreased (Shi and Day, 2001).

The theory and principle of pozzolan activation has been known since the 1940s (Pudon, 1940). Different techniques have been used to activate the pozzolanic reactivity and thus to enhance the mechanical strength of cement paste and concrete. Those techniques including calcinations of natural pozzolan, prolonged grinding,

elevated temperature curing and the addition of chemical activators. However, in previous published work, it has been found that the strength of lime-pozzolan cement pastes increased significantly when proper chemical activators are added. This technique was also found to be more efficient than grinding or subjected to elevated curing conditions (Shi and Day, 1993).

MECHANISM OF ACTIVATION

Calcium hydroxide is one of the soluble hydrates that formed from the reaction between Ordinary Portland Cement and water. It exists in the interfacial zone which promotes microcracks. The Ca(OH)₂ product can be reduced and the production of C-S-H which contributes to the strength can be further increased with the addition of pozzolanic materials. This is due to the reaction between pozzolans and the Ca(OH)₂ formed (Lee et al., 2003). It has been reported that the use of chemical activators namely sulfate activation and alkali activation may be utilized to accelerate fly ash reactivity. It was stated that sulfate activation can be studied by using several chemicals such as gypsum, CaSO₄·2H₂O and sodium sulfate, Na₂SO₄, where as NaOH and Ca(OH)₂ are used for alkali activation studies. The effect of using other types of chemical to accelerate pozzolanic reactivity such as CaCl₂·2H₂O and NaCl was also reported by previous researchers.

Alkali activation

Martinez-Ramirez and Palomo (2001) defined alkali activation as a chemical process where the amorphous structure is being transformed into a skeletal structure that exhibits cementitious properties. Polymeric gel with variable composition is formed in the media of high alkalinity. The gel is produced when the solution of high alkalinity reacts with the starting materials. The main behaviour of the products formed via these conditions is having great mechanical properties at the early period of hydration.

Palomo et al. (1999b) investigated the way to activate fly ash by alkali activation method. They reported that the Si-O-Si and Al-O-Al covalent bonds collapsed and the (Si and Al) ions travel into the liquid phase. Condensation of structure occurred, then, forming a cementitious material with a disordered structure and it possesses a good strength properties.

According to Alonso and Palomo (2001), as the metakaolin is activated in the media of high alkalinity in the presence of Ca(OH)₂, it will produce sodium aluminosilicate that have amorphous structure with similar features to geopolymeric gel. The product formed is similar to the product obtained once metakaolin is activated in the absence of Ca(OH)₂ and it was found that the secondary product which is also known as C-S-H is

formed. Subjecting metakaolin to alkali activation is a way of producing cementitious materials with high strength (Palomo et al., 1990). However, the quantity of additives used must be limited. The addition of alkali in excess also results in cement paste degradation (Wu et al., 1990).

Wu et al. (1990) studied the activation of ground granulated blast furnace slag (GGBS) and reported that the activation of slag can be done by reaction with high alkalinity solution. This is because the bonds in the slag network structure are easily broken and enhances the slag hydration process. When the pH value of the solution reaches 12, the hydration of slag is most accelerated and the ettringite is formed stably. Sufficient hydroxyl should be provided in order to create an environment of high alkalinity in order to break the bonds in the glass structure and stabilizing the ettringite formed.

Palomo et al. (1999b) concluded that there are two alkali activation models which are based on the conditions of the starting situation. The first model is the activation of blast furnace slag (Si + Ca) with a mild alkaline solution and the second model is the activation of metakaolin (Si + Al) with a medium to high alkaline solutions. The content of reactive silica, amorphous phase and calcium are some of the most important reactivity parameters (Fernandez-Jimenez and Palomo, 2003).

Granizo and Blanco (1997) stated that a solid having an aluminosilicate network structure are possible to be produced. Mixing metakaolin with certain quantities of sodium hydroxide, NaOH solution (the concentration ranging from 7 to 12 M) and then cured at temperatures below 100°C have been suggested by them. Data obtained shows that this solid possesses interesting mechanical properties. This is due to the network structure formed, where it consists of a series of SiO₄ and AlO₄ tetrahedra linked by their corner and sharing all oxygen ions. The negative charge of the tetra-coordinated aluminium ions is balanced by the alkali ions from the activating solution present in the structure (Palomo et al., 1999a).

Ma et al. (1995) found that an additional material is required to enhance the hydration process of the lime-fly ash system. They reported that when the lime is mixed together with fly ash, the mechanical strength obtained at the early age is reduced. The way to activate the reactivity of this system is by adding a certain amount of Ca(OH)₂ or CaSO₄·2H₂O. It has been previously reported that in the presence of Ca(OH)₂, the amorphous SiO₂ in fly ash tends to dissociate much more easier (Lokken et al., 1990; Brown, 1986). The bonds are broken down and dissolution of the three dimensional network structure of the glass noticeably increases (Fraay et al., 1989; Roy and Silsbee, 1992). Puertas et al. (2000) have studied the effect of introducing specific amount of NaOH solution into pastes made from a combination of fly ash and slag. They found that fly ash is partially dissolved and participates in the reactive process with the most

important product which is C-S-H gel containing high quantities of tetra coordinated Al in its structure are formed.

Martinez-Ramirez and Palomo (2001) disclosed the results of Portland cement hydration in the high alkalinity medium. In their findings, the Portland cement hydration process tend to be retarded due to the effect of common ion: the increasing of hydroxide ion, OH⁻ concentration in the system causes the equilibrium to shift towards the left side in the hydration process of C₃S and C₂S. This phenomenon impeding the common evolution of the hydration process:



Therefore, they concluded that as the alkaline concentration of the hydrating solution increases, this reduces the degree of hydration of anhydrous silicates, for this reason, the compressive strength also reduced. Martinez-Ramirez and Palomo (2001) investigated the mechanical properties of pastes using NaOH solution in the hydration process. They concluded that mechanical strength of the pastes hydrated with NaOH solution drastically decreases compared to the one that is hydrated with waterglass, Na₂CO₃ and deionized water. Figure 1a) shows the SEM image of C-S-H gel produced when the sample hydrated with deionized water and Figure 1b) shows the formation of the hexagonal-like shape of Ca(OH)₂ when 10 M NaOH solution is used in the hydration process.

Neville (1995) also agreed with that reported by Martinez-Ramirez and Palomo (2001). He also found that when the hydration of cement is carried out in the media of high alkalinity and subjected to curing processes of less than 28 days, the strength is affected and he concluded that the strength reduces with increasing alkali concentration.

Sulfate activation

The principle of sulfate activation also involves the dissolution of the network structure of the glass (Xu and Sarkar, 1991). This can be monitored by the addition of CaSO₄·2H₂O into pozzolan materials where the sulfate ions, SO₄²⁻ react with aluminate which comes from fly ash. Based on Li et al. (2003) cited by different researchers, previous studies have measured the mechanism of sulfate activation and can be summarized into the following points:

- i. Introduction of sulfate activators speed up the reduction of Ca(OH)₂ in the fly ash-cement system at the early stage of hydration (Shi and Day, 1995).
- ii. At early ages, the ettringite (Aft) generated in the fly ash-cement system are much more in the presence of activators and the network structure of the glass is broken down in an alkaline environment (Poon et al.,

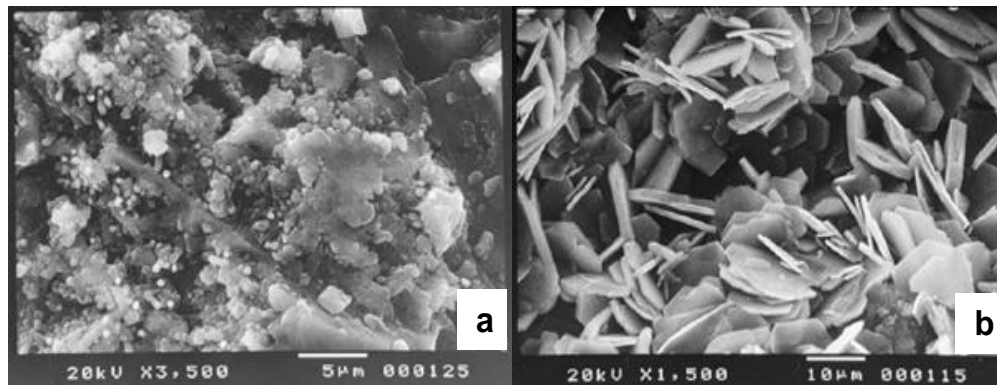


Figure 1. Cement pastes at 28 days examined by SEM. (a) Hydrated with deionized water (b) Hydrated with NaOH solution (Martinez-Ramirez and Palomo, 2001).

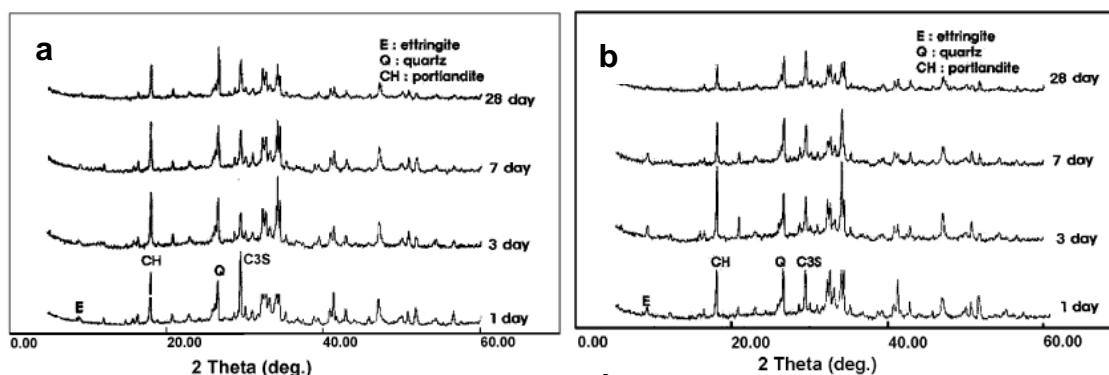


Figure 2. XRD patterns of pastes containing different types of activator (a) Without activator, (b) 1% Na₂SO₄ (Lee et al., 2003).

2001).

iii. Pore distribution in fly ash-cement pastes is affected by the presence of sulfate activators where the pore size becomes smaller and also reduced the porosity (Ma et al., 1995).

iv. The strength of fly ash mortar at an early age is enhanced with the presence of activators but at later ages the strength is almost similar to that fly ash mortar without activators (Xu and Sarkar, 1991).

The ettringite formed at the early stage of hydration in fly ash-cement pastes is increased with the addition of Na₂SO₄ and K₂SO₄ since the SO₄²⁻ ions will react with tricalcium aluminate, C₃A. At 7 days of hydration, ettringite is mostly formed and is later converted to monosulfates, C₄AH₁₃ and C₂ASH₈. This shows that, the production of ettringite is influenced by the addition of Na₂SO₄ and K₂SO₄ which contributes to early strength development of mortars consisting of fly ash and cement. Lee et al. (2003) used Na₂SO₄ and K₂SO₄ as activators in the fly ash-cement paste system. According to XRD

patterns, it was found that a small ettringite peak was observed when no activator is added to the fly ash-cement pastes. For the fly ash-cement pastes with the presence of chemical activators, a peak was observed at early stage of hydration (up to 7 days) resulting from the formation of ettringites. These hydration products were created by the reaction between SO₃²⁻ ions which come from the activators and the aluminates.

As the time increased, the ettringite is converted to monosulfate and other products, but, a small amount of ettringite still remains at 28 days. On the other hand, the major product generated from the hydration process is Ca(OH)₂ and its peak shows the highest intensity at 3 days of hydration, but decreases thereafter due to the pozzolanic reaction. These results tally with the research done by Poon et al., (2001) and Shi (1998). They point out that the production of ettringite is helpful for early strength development of the fly ash-cement pastes system consisting of a specific amount of sulfate activators with a reduction of Ca(OH)₂ content. Figure 2 shows the XRD patterns at different ages of hydration for

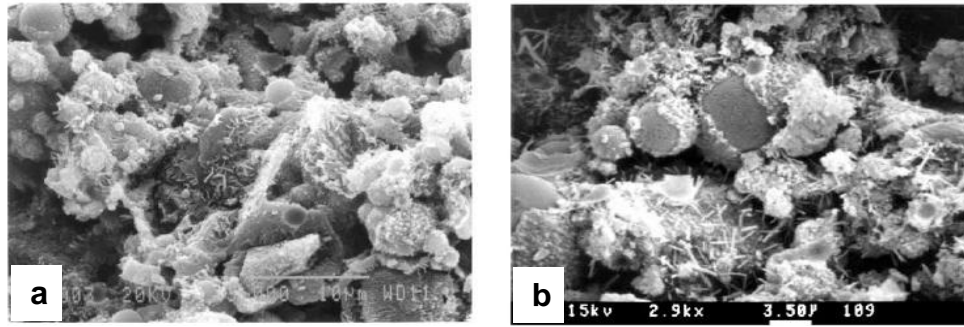


Figure 3. SEM images of fly ash-cement pastes containing different kind of activators at 3 days (Lee et al., 2003). (a) No activator (b) with Na_2SO_4 (1%).

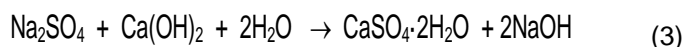
fly ash-cement pastes.

Figure 3 shows SEM images of C-S-H, $\text{Ca}(\text{OH})_2$ and ettringite produced from the pozzolanic reaction at 3 days of hydration. C-S-H and monosulfate products are mainly formed in the fly ash-cement pastes in the absence of a chemical activator, however, for the fly ash-cement pastes in the presence of sulfate activator, needle-shape hydration products which is ettringite were formed. These hydration products were created by the reaction between SO_3^{2-} ions which come from the activators and the aluminates (Lee et al., 2003).

Qian et al. (2001) investigated the mechanism of fly ashes by Na_2SO_4 . Amorphous aluminosilicate is the major component in the fly ash. $\text{Ca}(\text{OH})_2$ is hydrolyzed first when water without an activator is mixed with lime-fly ash cement, and the pH value of the solution reaches almost 12.5 at 20°C very rapidly:



In the solution with high alkalinity, various ions that are present in the fly ash are quickly dissolved into the liquid phase. Examples of the ions are Ca^{2+} , K^+ and Na^+ . This condition also causes the silicate or aluminosilicate structure to dissociate and dissolve into the solution. As the dissolved monosilicate and aluminate react with Ca^{2+} ions, the formation of C-S-H and calcium aluminate hydrate, C_4AH_{13} are promoted. As Na_2SO_4 is added to the system, there is a reaction between Na_2SO_4 and $\text{Ca}(\text{OH})_2$ and this can be expressed in the equation:



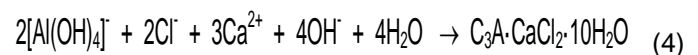
The pH value of the liquid phase is increased by this reaction hence the resulting fly ash dissociates and the $\text{Ca}(\text{OH})_2$ tends to react much more with the fly ash. Simultaneously, the SO_4^{2-} ion concentration increases with the presence of Na_2SO_4 thus producing additional ettringite (AFt). For this reason, the structure becomes denser and results in the increase of the early strength of pastes (Qian et al., 2001).

Other type of activation

The addition of chemical activators in concretes with various natural and artificial pozzolans has been examined by previous researchers. Many types of activators can be used to accelerate the reactivity of pozzolan materials. Shi and Day (1993) found that there are significant effects on the pozzolanic activity over a period of time with the presence of CaCl_2 in the pozzolanic materials. Referring to Shi and Day (2000b) which is from Guo (1986), the $\text{Ca}(\text{OH})_2$ dissociates very slowly. The introduction of CaCl_2 reduced the $\text{Ca}(\text{OH})_2$ solubility, however, the dissolution rate of $\text{Ca}(\text{OH})_2$ was increased significantly.

Shi and Day (2000b) used CaCl_2 to study its consequence on the lime-pozzolan blend system. The presence of 4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ caused a decrease in alkalinity of the liquid phase from pH value of 12.5 to 11.75. However, the detailed mechanism of the hydration process of cement with the addition of CaCl_2 is still unclear. For the lime-pozzolan system with the presence of CaCl_2 , the reaction can be summarized according to the following mechanisms:

When the CaCl_2 solution was added into the lime-pozzolan blend, the resulting $\text{Ca}(\text{OH})_2$ dissolves and reduces the solution alkalinity. A reduction of the alkaline environment shows the negative effect where the pozzolan dissolution process tend to be retarded. The addition of CaCl_2 leads to a greater Ca^{2+} content but the amount of dissolved monosilicate and aluminium species are much less in the activated pastes solution as compared to the control paste. This causes the production of $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ to form very rapidly.



The solid solution of $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ - $\text{C}_3\text{A} \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ was formed easily as both products $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ and $\text{C}_3\text{A} \cdot \text{Ca}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ comprised of an identical structure. Through this solid solution

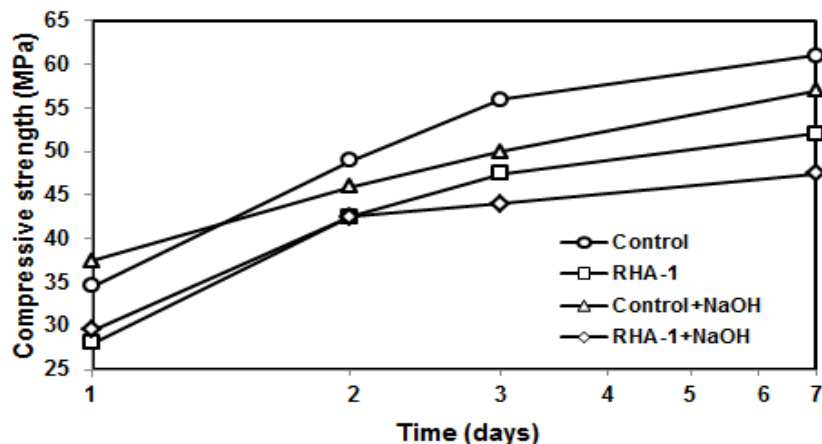


Figure 4. Development for mortars with sodium hydroxide solution (Paya et al., 2000).

formation, the reaction increases the consumption of the dissolved monosilicate and aluminate. The product produced is precipitated away from the pozzolan particles so that a further reaction can take place. The solid volume increased greatly with the formation of $C_3A \cdot CaCl_2 \cdot 10H_2O$. The solid volume produced by this product is higher than those of the C-S-H and $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ formation. Therefore, the paste structure become denser and high in strength compared to the control pastes at certain periods of time.

STRENGTH DEVELOPMENT USING VARIOUS CHEMICAL ACTIVATORS

Strength development of mortars containing various chemical activators has been reviewed for the evaluation of the pozzolanic activity of each sample studied by previous researchers.

Alkali activation

Alkali activation is also known as a method that transforms a glassy network of structures into a very compact well-cemented composite (Palomo et al., 1999b). The addition of alkaline activators breaking the Si-O and Al-O bonds in the slag glass structure and thus accelerates the rate of dissolution of Si and Al ions into the liquid phase. Some of the chemicals that are commonly used by previous researchers for alkaline activation are $Ca(OH)_2$, NaOH and KOH solutions (Wu et al., 1990).

NaOH

Puertas et al. (2000) used NaOH solutions as an activator

in the fly ash/slag pastes system. They found that the addition of 10 M NaOH solution into the mixture consisting of 50% fly ash/ 50% slag and subjected to curing temperatures of 25°C produce a compressive strength of about 50 MPa at 28 days of hydration. Paya et al. (2000) studied the rice husk ash (RHA) activation using the NaOH solution and it was noticed that the presence of NaOH caused the compressive strength to increase slightly at 1 day of hydration. However, between the 2 to 7 days period, the compressive strength values were lower than those for mortars without this addition, indicating the negative role of the addition and the none activation of RHA. This shows that NaOH did not act as an effective pozzolanic activator for crystallized RHA. The compressive strength developments for mortars with and without the NaOH additions were presented in Figure 4.

$Ca(OH)_2$

Ma et al. (1995) noticed that the SiO_2 solubility in the fly ash increased with the presence of $Ca(OH)_2$. As the $Ca(OH)_2$ activator was added into the fly ash, this resulted in a reaction between the most part of $Ca(OH)_2$ and the silicate, forming a C-S-H gel and ettringite (Li et al., 2000). At 7 days of hydration, he found out that a lot of needle-like shaped ettringite were formed hence improving the properties and mechanical strength of cement at an early age. Paya et al. (2000) carried out research on the activation of the rice husk ash (RHA)/ cement system by replacing 5% of the cement by powdered $Ca(OH)_2$ in order to investigate the strength development of mortars containing RHA with a 15% cement replacement. However, they found that the compressive strength increased slightly at 1 day and was lower than those mortars without the chemical addition at

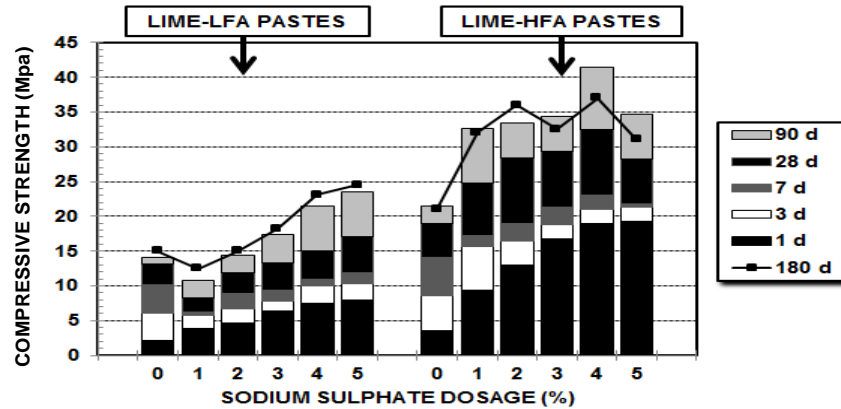


Figure 5. The strength development of pastes containing fly ash with addition of Na_2SO_4 activator (Shi and Day, 1995).

2 to 7 days.

Quicklime

Antiohos and Trismas, (2004) studied the activation of fly ash/ cement (FC) systems by quicklime. Fly ash from class C which consists of high calcium content was used. The fly ash mortars were used to determine the mechanical strength and any changes in the fly ash during the hydration process was measured. It showed that the compressive strength of mortars containing a replacement of 3 and 6% by quicklime was slightly accelerated as compared to fly ash mortar without quicklime at the early testing period.

Sulfate activation

Alkaline-slag cement has been widely used for a long time and possesses significant properties of high strength. Other behaviours such as porosity, permeability and heat evolution is markedly low instead of having a high resistance to chemical attack (Wu et al., 1990). However, alkali such as NaOH is expensive and potentially harmful to the operators while handling it, therefore, neutral salts such as Na_2SO_4 and others that provide similar consequences can be used to substitute the alkali activators since it is less harmful in addition of less expensive.

Na_2SO_4

The activation of lime-pozzolan cement (LPC) using a chemical activator was reported by Shi and Day (1993). The addition of 4% Na_2SO_4 activator considerably enhanced the strength of LPC at early age. The LPC is a

mixture of 20% hydrated lime and 80% natural pozzolan and chemical activators added based on the mass of LPC. They also found that the strength of hardened LPC pastes were also enhanced at later age with the Na_2SO_4 addition, however, the effect is more apparent at early ages as compared to the later ages.

Lee et al. (2003) investigated the use of Na_2SO_4 to accelerate the strength of mortar containing fly ash at an early age. 40% of the fly ash used in the mortar mix consisted of 1% Na_2SO_4 addition based on the weight of the cementitious materials. The compressive strength increased noticeably for mortars containing 1% and more Na_2SO_4 at 1 day but the strength was similar to that mortar containing 40% fly ash without the presence of Na_2SO_4 at 28 days.

Shi and Day (1995) also studied the effect of using Na_2SO_4 as an activator on the strength development using two different kinds of fly ash (low calcium content, LFA and high calcium content, HFA) on lime/ fly-ash pastes system. The reactivity of ashes was studied based on the strength development of the mixtures consisting of 80% fly ash and 20% hydrated lime. The results obtained show that the pozzolanic reactivity of pozzolans for both forms of ash increased with the addition of Na_2SO_4 . This was shown by significant improvement in strength. Na_2SO_4 mainly influences the strength development during early age of hydration whereas the effect on later ages differed depending on the type of fly ash used. The results are shown in Figure 5.

An experiment on the strength of lime-fly ash mortars was carried by Qian et al. (2001). They reported that the lime-ungrounded fly ash mortars without an activator did not show any strength development (Figure 6). However, the strength of lime-fly ash mortar increased considerably when the fly ash used was subjected to the grinding process. On the other hand, they found that grinding is an energy intensive process and requires a complex instrument. The strength of the lime-fly ash mortars

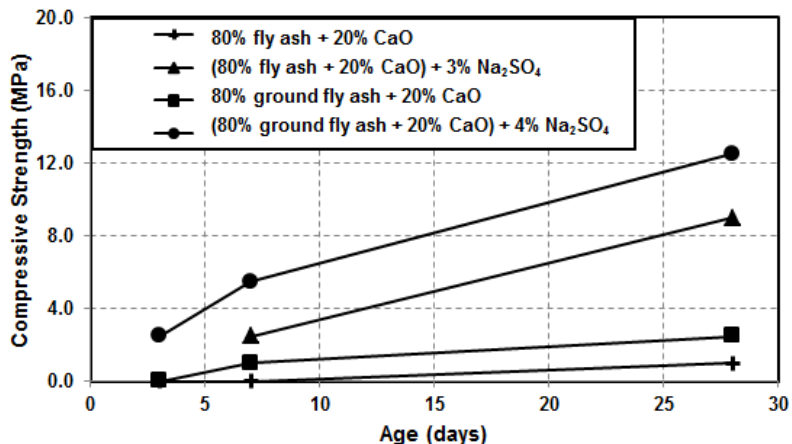


Figure 6. Development of compressive of mortars for lime-fly ash system (Qian et al., 2001).

containing Na_2SO_4 also increased significantly and was greater than of grinding effect. By comparing the different activation techniques according to the price for one unit strength, Shi and Day (2001) concluded that the most helpful technique is the chemical activation.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum)

Xu and Sarkar (1991) mentioned that when an activator such as gypsum is being used, it produces sulphate ions which are able to react with aluminate causing the dissolution of the glass structure. The increase of compressive strength for pastes containing fly ash (Class F: low calcium content) is around 30 to 60% which is caused by the presence of 3 to 6% gypsum as compared to pastes without the addition of gypsum that produces a lower compressive strength.

CaSO_4 (Calcium sulfate anhydrite)

Poon et al. (2001) investigated the use of an anhydrite to activate the fly ash cement system. The mortar was subjected to steam curing at a temperature of 65°C for 6 hours before normal curing at room temperature. He made a comparison between the mixture with the absence of an activator and the mixtures containing various anhydrite contents. A 10% anhydrite was found to be the maximum addition for mortars containing fly ash with a replacement of up to 35%.

An evaluation was done between gypsum and anhydrite to compare their roles in activating the fly ash reactivity. It shows that the compressive strength resulting from the fly ash mortar with a 35% cement replacement containing 10% anhydrite is greater than 10% gypsum (Poon et al., 2001).

$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (Hemihydrate gypsum)

Shi and Day (1993) used various dosages of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ as an activator to study its effect on the development of strength of lime-pozzolan cement (LPC) pastes. They discovered that the strength was highest with the addition of 6% $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. Although at later ages of hydration, the strength of pastes increased with an addition of 6% $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, however, its effect is lower than those activated pastes with the addition of 4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

Other types of activation

According to Shi and Day (1995), the addition of other chemicals which do not belong to the alkali or sulfate group such as CaCl_2 has a considerable influence on the strength at an early age and at the intermediate ages. It was discovered that the strength of pastes containing a 3 to 5% CaCl_2 activator were noticeably enhanced at 90 and 180 days of hydration.

Flake Calcium Chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)

Shi and Day (1993) also utilized various dosages of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ activator in the LPC system in order to study its effect on the compressive strength development. An insignificant effect on the development of compressive strength of LPC pastes containing CaCl_2 was found at 3 days of hydration. At all ages, the strength of the LPC pastes was reduced with the addition of 1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, however, the strength increased when increasing the amount of dosage used. The strength was enhanced with the addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ above 3%. Their results led them to conclude that the addition of a CaCl_2 activator is

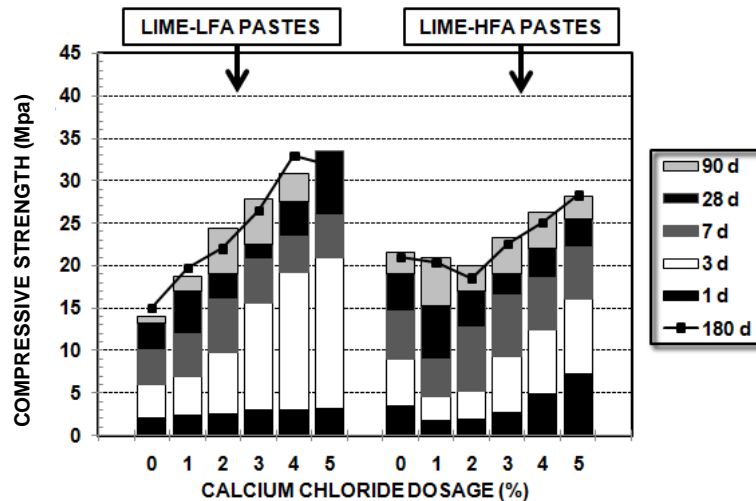


Figure 7. Strength development of pastes with CaCl_2 activators (Shi and Day, 1995).

not effective on the early strength development, however, the later strength is much more accelerated using this chemical activator. The pastes containing a 4% CaCl_2 activator resulted in a greater strength at later ages as compared to pastes containing a 4% Na_2SO_4 (Shi and Day, 1993).

The effect of using a CaCl_2 activator on the strength development of fly ash (low calcium content) LFA and (high calcium content) HFA pastes (Figure 7) was investigated by Shi and Day (1995). An insignificant effect had been observed with the addition of CaCl_2 on 1 day strength for both types of the pastes and this effect is found to be the same to that strength resulting from the lime-pozzolan pastes without an activator. However, after 1 day and thereafter, the improvement on strength of LFA pastes was observed with the addition of CaCl_2 from 1 to 5% dosage. However, the improvement of strength for HFA pastes is only helpful with the addition of 3 to 5% CaCl_2 dosage. Therefore, they concluded that, CaCl_2 activators are much more activate in the LFA pastes than in the HFA pastes.

NaCl

The strength development of LPC pastes containing certain amounts of NaCl was studied by Shi and Day (1993). It was found that as NaCl was added into the system, it does not contribute to the strength development of the pastes with an addition of up to 5% and at 180 days of hydration.

Shi and Day (1995) also studied the influence of 0 to 5% NaCl addition on the development of the strength of HFA pastes. They also found that the addition of a NaCl activator had an insignificant effect on the development of

strength of HFA pastes. A similar observation was obtained when pastes consisting of lime-natural pozzolan blends were tested in 1993. Even though the tests using NaCl as an activator on LFA pastes were not performed, it can be concluded that the same observation would be obtained since there is a similarity between the chemical composition of LFA and natural pozzolans which had been tested before.

$\text{Ca}(\text{OH})_2$ content

$\text{Ca}(\text{OH})_2$ is not a desirable product in the concrete structure. It is soluble in water, hence, may be leached out making concrete porous and is harmful for the concrete strength (Shetty, 2008; Yang et al., 2000). The use of pozzolan materials such as fly ash, silica fume and other pozzolanic materials are the steps to reduce the amount of $\text{Ca}(\text{OH})_2$ in order to improve the microstructure and quality of concrete.

The amounts of $\text{Ca}(\text{OH})_2$ present in the samples can be determined by thermogravimetric analysis, TGA (Bhatty and Reid, 1985; Vessalas et al., 2009). Degree of reaction of $\text{Ca}(\text{OH})_2$ in lime-pozzolan pastes was studied by Shi and Day (2000a). They found that the remaining $\text{Ca}(\text{OH})_2$ in Na_2SO_4 -activated pastes was less than that of the control pastes. Similar observations were also made by Lee et al. (2000). Lee et al. (2000) determined the amount of $\text{Ca}(\text{OH})_2$ produced with and without the presence of chemical activators for the fly ash-cement pastes system (Figure 8). They showed that the amount of $\text{Ca}(\text{OH})_2$ in the cement paste containing 40% fly ash was nearly 50% less compared to the cement paste without fly ash. The addition of chemical activators resulted in similar trends to cement pastes containing

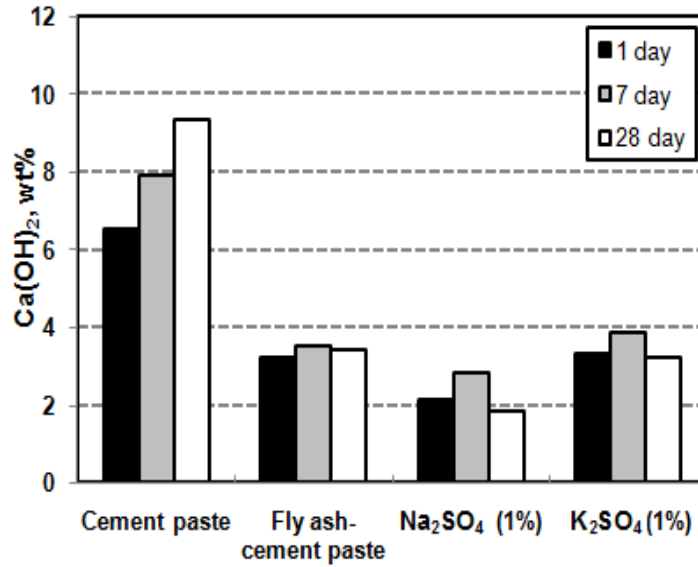


Figure 8. Amount of Ca(OH)₂ of cement paste, fly ash-cement paste and chemically activated fly ash-cement pastes at 1, 7 and 28 days (Lee et al., 2003)

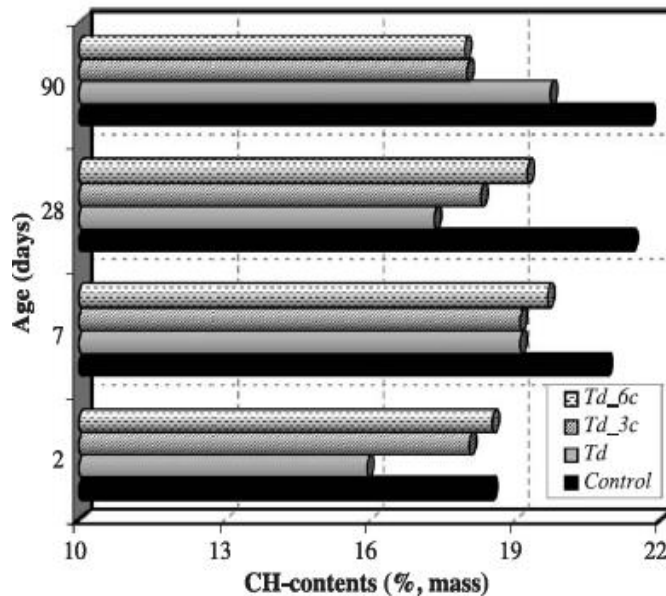


Figure 9s. CH contents of the cement, cement-Td fly ash, and quicklime activated Td pastes with hydration age (Antiohos and Trismas, 2004).

40% fly ash. However, it was found that Na₂SO₄ was the most effective in decreasing the level of Ca(OH)₂ at early age.

Antiohos and Trismas (2004) have shown that cement paste without fly ash is constantly producing Ca(OH)₂ throughout the hydration period. On the contrary, the specimens with fly ash were explained by the

simultaneous production and consumption of Ca(OH)₂. However, small replacement of fly ash by 3% lime accelerated the Ca(OH)₂ depletion from the early period of hydration. The Ca(OH)₂ contents of the high-calcium (class C) fly ash designated as T_d with 3 and 6% fly ash replacement by quicklime with hydration age are shown in Figure 9.

CONCLUSIONS

Numerous species serve as activators and accelerators. By reviewing previously published work, it can be concluded that for maximum benefits, choosing a suitable activator and the type of material to be activated is very important. The rate of pozzolanic reaction, mainly the early strength development, together with the pozzolanic reactivity can be improved using suitable chemical activators instead of using other techniques such as the thermal and mechanical methods. The reaction of pozzolanic materials with a solution in high alkaline environments was found to be one of the principal ways in which the pozzolanic materials can be activated. This involves breaking down the bonds in the network structure of glass and hence, accelerating the rate of hydration of the pozzolan. However, many aspects should be considered in selecting proper activators especially those including the financial and practical processes of handling the chemicals.

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