



## An overview on comparative study of alternatives for Ordinary Portland cement

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Received: July 26, 2014

Accepted: October 8, 2014

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### ABSTRACT

Research on new alternatives for the conventional Portland cement is the primary need of the cement researchers and manufacturers due to the problems associated with, including the production of huge amount of green house gases, high cost of cement and durability problems in particularly aggressive environments. Moreover Portland cement is not the ideal binder for all construction applications, as its strength decreases at elevated temperatures due to chemical and physical changes. Similarly spalling of conventional concrete occurs in fire which causes a rapid layer-by-layer loss of concrete cover, potentially leading to the exposure of the main reinforcements within the concrete to fire. Several alternative binders for the Portland cement have been developed and other new ones are being developed and studied for different characterization. The present study discusses two such alternative cements to the Portland cement like super sulfated cement and calcium aluminate cement with respect to their history, composition, advantages and disadvantages, hydration and their reaction mechanism.

**KEY WORDS:** Portland cement, Environment, Production cost, alternative cement

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### INTRODUCTION

Among hydraulic binders common in our modern world, Portland cements remain the most used (Temuujin and van Riessen, 2009). However, production of Portland cement is a resource exhausting, energy intensive process that releases large amounts of the green house gas CO<sub>2</sub> into the atmosphere (Guo et al., 2010) Nevertheless, many studies are being carried out to design new hydraulic binders which can not only substitute Portland cements, but can also be produced in a way as to safeguard our environment.

For the build up of the strength in Portland cement, the alite and belite are the most essential phases which are formed above 800°C where alite is preferentially formed upon elevating the temperature and increasing amount of added burned lime, CaO. Out of these two phases alite (C<sub>3</sub>S) is responsible for short term strength development while belite (C<sub>2</sub>S) for the better long term strength development performances (Gartner et al., 2002)

In the present construction industry, Portland cement and its concrete has received great acknowledgment on account of its versatility, durability, economic value and relatively low embodied energy compared to other building materials and for its use of local materials, thereby reducing energy and pollution costs associated with material transport. In spite of all this, Portland cement is also facing a number of problems like the consumption of 10-11 EJ of energy on annual basis, during its clinkerization and production of huge amount of green house gases. Approximately one ton of carbon dioxide for every ton of cement is produced both from the calcinations of raw material and burning of fuel which accounts for 5% of manmade CO<sub>2</sub> emission. Therefore cement industry is trying to reduce both energy consumption and greenhouse gas emissions and is actively seeking alternatives to this familiar traditional binding material.

Production of Industrial wastes has become a global issue; many industries are going to find out the recycling techniques. Cement industry also play its role in this field which also address the two major problems associated with cement production process. Portland cement concrete accommodates a wide variety of waste materials used as supplementary cementing materials, including fly ash from coal combustion, ground granulated blast furnace slag from iron production, bagasse ash from sugar industries and silica fume from ferrosilicon production. However, the addressed problems are solved to a very lesser extent. The main interest of cement researchers is to create such binders made totally or almost entirely from the industrial waste materials and which fulfill the requirements of environmental friendly binder.

Additionally the exploration of alternatives to Portland cement can be derived from its shortcomings

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from certain applications and environmental point of view. For example rapid repair applications demand a quicker strength gain than the Portland cement concrete can provide. Secondly, environmental conditions with high acidity or high sulfate concentrations can cause substantial degradation of Portland cement concrete. For such conditions alternatives for Portland cement are demanded meeting the above shortcomings.

In order to reduce the environmental impacts of construction, improvement of concrete performance and utilization of waste materials in comparatively greater amount, new binders are being developed for concrete with a rapid pace. These newly designed binders are having considerably different approach from the traditional chemistry of Portland cement, and therefore do not benefit directly from the many years of research with respect to reaction mechanisms, property development and durability aspects. Moreover new materials are facing serious difficulty in finding acceptance in the construction industry, in which implementation in construction industry and market competition are considered as serious challenges. In this work some of the alternative binders are discussed which are attracting attention in research and practice, summarizing the present understanding, gaps in knowledge and challenges. Although there are many alternate binders for Portland cement, but in this work only few are addressed like calcium aluminate cement and supersulfated cement with respect to their properties and problems associated. This review study provides new directions to the cement researchers in solving the problem associated with the traditional ordinary Portland cement.

### **Super sulfated cement**

Super sulfated cements are binders containing mainly of blast furnace slag, calcium sulfate and an alkaline activator. Usually the alkaline activator is Portland cement, in small relative quantity.

Hans Kühl in 1909 discovered the possibility to activate blast furnace slag by sulfates. Basic slags containing high CaO and MgO content with a high Al<sub>2</sub>O<sub>3</sub> content (14-15%) were found to be suitable for the manufacture of supersulfated cements (Sahu and Majling, 1994) such materials exhibited a logical strength development. At the end of Second World War, a serious shortage of Portland cement was observed which increased the application supersulfated cement in several countries like Germany and the United Kingdom (Sherman et al.,1995; Li et al., 2007). Later on in Germany, due to changes in the iron manufacturing processes slags were produced which did not meet the minimum Al<sub>2</sub>O<sub>3</sub> content requirement (13%) anymore, and the use of the slags in blends with Portland cement (blast furnace slag cement). However, it has been shown that slags with lower Al<sub>2</sub>O<sub>3</sub> contents can be activated and used successfully as binders for rendering, injection and masonry mortars (Kondo and ueda, 1968; Garraut-Gauffinet et al.,1999) in aggressive environments like in the presence of high sulfate concentrations. Supersulfated cements attract new attention and are thought to have promising potential for industrial applications, due to the climatic debate, and more especially due to their very low heat of hydration and good durability in chemically aggressive environments (Livingston et al.,2001; Paglia et al.,2001). Various repair mortar applications have also been reported, such as rendering, injection mortars or masonry mortars (Pelletier et al., 2010; Wang and Yan, 2006) where especially the high sulfate resistance has been the main driving force to use supersulfated cement. The interest is illustrated by the fact that new products have recently come on the market and that a European standard for supersulfated cements (Jenning and Pratt, 1979) is now available.

### **Raw materials of supersulfated cements**

The major raw material of supersulfated cements are 70-90% ground granulated blast furnace slag, 10-20% calcium sulfate and generally low quantities of an alkaline activator (Jening and Pratt,1979; Kapralik and Hanic,1989). Usually slags with high CaO, MgO and Al<sub>2</sub>O<sub>3</sub> contents are suitable for the manufacturing of supersulfated cements (Palo and Majling, 1996; Gartner and Jennings,1987). The mixture composition for optimum properties is sensitive to the chemical composition of the slag. The slags containing high alumina contents require high calcium sulfate. The calcium sulfate is mainly anhydrite or hemihydrate gypsum (wang and yan, 2006; Jenning and Pratt, 1979) Phosphogypsum, flue gas desulfurization gypsum and fluoroanhydrite may also be used as secondary sources of calcium sulfate (Pera and Ambroise, 2004; Han et al., 1989). Apart from the Portland cement, other activators like calcium hydroxide (Wang and Yan, 2006), potassium hydroxide (Kapralik and Hanic, 1989) or sodium carbonate (Palo and Majling, 1996) have also been reported. Potassium hydroxide and sodium carbonate are favorable in the case of a low reactivity slag, because they increase the pH of the pore solution and thus enhance slag dissolution. However, an overdose of such alkaline activators leads to a significant loss of strength (Sung and Young, 2002). Excess of Portland cement clinker or calcium hydroxide has a negative impact on the

volume stability of the binder, as these components may cause expansive reactions deal with the formation of ettringite (winnefeld and Barlag, 2010).

### **Hydration of supersulfated cements**

Supersulfated cements have clear hydration mechanism described in literature by many authors like (Gartner and Jennings, 1987; Winnefeld and Barlag,2009). The alkaline environment of the pore solution enhances the dissolution of the slag. The dissolved aluminum, calcium and silicon ions react with the added calcium sulfate and form ettringite and calcium silica hydrate (C-S-H) phases. Compared to Portland cement, a higher amount of ettringite forms, and is mainly responsible for early strength development. Apart from the main hydration products, being ettringite and C-S-H phases, minor hydrate phases like AFm phases or hydrotalcite also occur. Compared to the Portland cement system, the hydration degree of slag is lower. The degree of hydration of blast furnace slags in various supersulfated cements, determined from sealed samples at the ages between 28 and 90 days, is reported to be in the range of about 15-25% (Winnefeld and Lothenbach, 2010; Smroková et al., 1996). At this age, the small slag particles have reacted fully, whereas the bigger particles show only hydration rims (Wang et al., 1995). The kinetics of reaction of supersulfated cements have not been studied or modeled in a comparable way to Portland cement. The pH of pore solutions in supersulfated cements is normally much smaller than that of Portland cements. The pH of system activated by Portland cement or lime as the alkaline component during first hours of hydration is around 12.5, which at later ages drops to 11.5 (Gang and Kirkpatrick,1993). In case of KOH as alkaline activator, high pH values at early ages (13 to 8h), but decreases at later ages (12 to 28 days) (Garrault et al.,2005). Similarly the composition of the pore solution is changes with age, i.e. dominated by sulfate, calcium and alkali ions at early ages but at the later ages, sulfate and calcium concentrations do not significantly change, while the alkali concentration increases due to the decrease of the volume of pore solutions. With increasing the degree of hydration of slag, sulfide ions are released into the pore solution, which can act as a semi-quantitative indicator of slag dissolution. Si and Al concentrations in the pore solution are generally low, depending on the pH value of the pore solution, and increase with the increase of pH. Saturation indices with respect to the relevant hydrated phases can be calculated from the analysis of pore solution, (Krivenko, 1994) for which the pore solution is saturated and oversaturated with respect to gypsum and ettringite respectively. The microstructure of hydrated supersulfated cements is generally characterized by large ettringite crystals, which have precipitated from solution during the first hours of hydration and are responsible for setting and early strength development (Shietal, 2006; Husbands et al., 1994) Among the crystals of ettringite, fibrous or plate-like C-S-H phases occur on the surfaces of the slag particles, forming rims around the slag particles. Two C-S-H reaction fronts around the slag particles have been found with an inner layer exhibiting lower Ca/Si ratios (1.2) than the outer layer (1.4)(Husbands et al.,1994)

### **General Properties of Supersulfated cements.**

General parameters of Supersulfated cements are compared with Portland cement and other alternatives in table 1, while its advantages and disadvantages are compared in table 2. Some of the general properties are explained below;

#### **Setting Time**

The initial setting time of Supersulfated cements as per British standard specification EN 15743 should not be less than 75, 60, and 45 min for strength classes 32.5 N, 42.5 N, and 52.5 N, respectively, which are longer than that of Portland cements (Kirven et al.,2006) Setting time Values as reported in the literature are mostly between 1 h and 10 h (Kirven et al.,2006;Davidovits,2002), depending on the type and slag fineness and the mixture design of the Supersulfated cement. For hemihydrate as activator, the applications of retarders are very much necessary to prolong the setting times (Davidovits, 2002)

#### **Strength Development**

The early strength development of Supersulfated cement is slower than that of Portland cement while 28-day strengths are similar to Portland cements (Husbands et al., 1994; Novak et al.,2005). A prolonged moist curing is required for the slow hardening during the first few days to building materials based on Supersulfated cements (Cerulli et al., 2003). Apart from the poor strength, insufficient curing may also lead to dusting of the surface (Cerulli et al.,2003)

#### **Heat of Hydration and shrinkage**

Supersulfated cements exhibit a low heat of hydration. The heat of hydration after 7 days has been reported as 90 J/g. Supersulfated cement mortar and concrete shows the same shrinkage as that of Portland

cement (Trautmann and Knofel, 1994; Winnefeld and Knofel, 1998) provided that suitable curing is applied. Capillary porosity as determined by mercury intrusion porosimetry of supersulfated cements is very lower than that of Portland cement (Gartner and Jennings, 1987) which is favorable with respect to durability. Sulfate resisting property of supersulfated cements is quite satisfactory as compared to Portland cement (Kocaba, 2009; ORourke et al., 2009) Chloride Resisting Property

Chloride resistance and seawater resistance are usually high, which is related to the low porosity and the high content of aluminate phases in the hydrate assemblages, which are able to bind chloride (Gartner and Jennings, 1987; Shietal, 2006). Generally, good frost resistance can be reached in supersulfated cement based building materials (Winnefeld and Barlag, 2008; Winnefeld and Lothenbach, 2010)

### **Carbonation**

One of the most important issues of supersulfated cements is carbonation, and specially when curing is insufficient which causes a decomposition of the ettringite (Novak and Novak, 2004) and leads to a strong increase in capillary porosity (Thomas et al., 2009) and results a dusting or pulverization of the concrete skin (Garrault et al., 2005) To prevent skin formation the penetration of ambient air during early hydration (Thomas et al., 2009) or by using admixtures like polymer dispersions (FitzGerald et al., 1998) should be blocked.

### **Calcium aluminate cements**

Calcium aluminate cement represented as CAC is a special class of cement which contains calcium aluminate in the form of CA,  $C_{12}A_7$  or  $CA_2$ . Silica may also be present in small quantity in the form of  $C_2S$  or  $C_2AS$ . Small amount of iron may also be present in the form of a  $C_4AF$  solid solution with variable alumina to ferrite ratio (Bijen and Niel, 1981). Initially this cement was developed in the early 1900s, to resist sulfate attack by Jules Bied of the J. & A. Pavin de Lafarge company (Thomas et al., 2001). Concrete of calcium aluminate cement has several distinct advantages over traditional Portland cement concrete, which include rapid strength gain, and enhanced resistance to abrasion, sulfate attack and low production of  $CO_2$  as compared to Portland cement production. Presently CACs are mainly used in refractory and building applications, such as floor screeds and rapid-hardening mortars (Parkhurst, 1995). However, CACs are gaining renewed interest in the construction industry due to their rapid hardening and enhanced durability properties as compared to other cementitious binders.

### **Hydration of calcium aluminate cement**

The heat of hydration in calcium aluminate cement impact the phases and the rate of transition to stable hydrates from metastable state which may also be called as the conversion process. The metastable hydrates  $CAH_{10}$  and  $C_2AH_8$  are formed at low curing temperatures. At a temperature of  $15^\circ C$  the predominant metastable hydrates  $CAH_{10}$  is formed, while at  $30^\circ C$  curing temperature,  $C_2AH_8$  is also formed. The formation of  $CAH_{10}$  is however thermodynamically not favored and formation of  $C_2AH_8$  is slow as temperatures reaches  $30^\circ C$ . Both these hydrates convert to stable hydrates phase  $C_3AH_6$  along with the formation of  $AH_3$  gel and the release of some water. As a result of this phase conversion, the porosity of the paste increases and subsequently the strength of cement decreases. When temperature is as high as  $70^\circ C$ , the formation of stable hydrate  $C_3AH_6$  is predominantly occur (Matschei et al., 2005). The approximate temperature range for the formation of metastable and stable hydrates is shown in table 3. Research studies have shown that with the use of CAC concrete, lower converted strength rather than for maximum is achieved for eliminating long term post conversion. Therefore recent studies in CAC systems have focused less on strength development, but instead of characterizing and predicting dimensional stability so as to consistently predict field performance, as well as blending the cement with supplementary cementing materials in order to reduce the cost of CAC concrete. Similar findings have been reported by Juenger et al. 2010.

Using SEM (scanning electron microscopy) coupled and X-ray diffraction, (Pöllmann et al., 2008) investigated the microstructural development in early age. They observed the transformation of  $AH_3$  gel to crystalline  $AH_3$  phases at early ages after eight hours of mixing. From eight to fifteen hours, an increase in the density of  $CAH_{10}$ , and the crystallization of layered, hexagonal crystals of  $C_2AH_8$  was shown.

The insightful effect of curing temperature on the volume change of early-age was demonstrated by Ideker (Ideker, 2008) the formation of metastable hydrates like  $CAH_{10}$  under isothermal curing was linked to shrinkage. On the other hand the formation of stable phases like  $C_3AH_6$  was related to the expansion of cement. The mechanisms of these volume changes are not obvious. Simple calculations regarding changing in volume of the hydrates for conversion from  $CAH_{10}$  and  $CAH_{10}$  to  $C_2AH_8$  and  $C_3AH_6$  show volume increases of 4.4% and 2.4%, respectively. This includes the release of water from  $CAH_{10}$ , which move within the pore structure, resulting in the expansion due to increased hydraulic pressure (Matschei et al., 2005; Ideker, 2008).

The improved performance of Calcium aluminate cement compared with ordinary Portland cement in sewer tunnel linings was studied Alexander et al., 2008. As higher concentrations of aluminum ions in CAC systems is present associated with low pH level established in wastewater transportation were shown to inhibit bacterial growth, thus reducing damage in CAC-based mortar linings.

The reaction kinetics and long-term properties of Portland cement and calcium aluminate cement flooring mortars were investigated by Kighelman et al.(Kighelman et al.,2008), who found that Calcium aluminate cement systems were more stable volumetrically due to early strength gain and formation of denser microstructure. They also investigated that the CAC systems showed improved abrasion resistance compared to OPC systems.

**Problems associated with calcium aluminate cement**

In spite of many advantageous characteristics, it is not used as extensively as Portland cement; the widespread use of the CAC is limited due to two challenges. First, conversion process occurs in hydrated CAC over time, whereby metastable hydrates convert to stable hydrates, leading to an increase in porosity and subsequent decrease in strength. A number of building collapses have occurred in the 1970s, which were attributed to CAC conversion and the use of this cement was banned. Later on, investigations revealed that in one of the collapse, improper structural detailing was to blame, and other failures were a result of improper usage of material despite manufacturer recommendations. Since this time, intensive research has provided a greater understanding of CAC chemistry and behavior. A report by the Concrete Society in 1997 provided improved guidance for predicting long-term properties, and, as a result, the technical concrete market has seen a Renaissance in the interest and use of this alternative cementitious binder (Matschei et al., 2005). Secondly, CAC is expensive compared to Portland cement, with the cost related directly to the limited supply of bauxite, the main source of alumina in CAC production.

**Table 1. Comparison of different parameters of Alternative Cementitious Material with Portland cement**

Parameters	Supersulfated cement	Calcium aluminate cement	Portland cement
Primary phases/materials	Slag, CS/CSH <sub>2</sub>	CA	C <sub>3</sub> S
Secondary phases/materials	Alkali/Portland cement	C <sub>12</sub> A <sub>7</sub> ,CA <sub>2</sub> ,C <sub>2</sub> S, C <sub>2</sub> AS, C <sub>4</sub> AF	C <sub>2</sub> S, C <sub>3</sub> A, C <sub>4</sub> AF, CSH <sub>2</sub>
Hydrates	Hydrotalcite	CAH <sub>10</sub> (m*), C <sub>2</sub> AH <sub>8</sub> (m), C <sub>3</sub> AH <sub>6</sub> , AH <sub>3</sub>	C-S-H, CH, Aft AFm
Raw material CO <sub>2</sub> (g/g)primary phase	0	CA=0.279	C <sub>3</sub> S=0.578
Clinkering temperature	Nil	>1450 °C	~1450 °C
Grinding energy (kWh/t)	Slag: 50	>30	30

**Table 2. Comparison of advantages and disadvantages of Alternative Cementitious Material with Portland cement.**

Parameters	Supersulfated cement	Calcium aluminate cement	Portland cement
Advantages	<ul style="list-style-type: none"> <li>➤ Low heat of hydration</li> <li>➤ Durable in aggressive environments</li> </ul>	<ul style="list-style-type: none"> <li>➤ Rapid strength</li> <li>➤ No alkali-silica reaction</li> <li>➤ Abrasion resistant</li> </ul>	<ul style="list-style-type: none"> <li>➤ Long history</li> <li>➤ Standard Compositions</li> </ul>
Disadvantages	<ul style="list-style-type: none"> <li>➤ Slow strength</li> </ul>	<ul style="list-style-type: none"> <li>➤ Strength loss on conversion of metastable to stable hydrates</li> </ul>	<ul style="list-style-type: none"> <li>➤ High energy</li> <li>➤ High CO<sub>2</sub></li> <li>➤ Limited early strength</li> <li>➤ Poor in aggressive environments</li> </ul>

**Table 3. Approximate temperature range of metastable and stable hydrates**

Temperature range	Chemical reactions
Up to 30 C°	6CA+6OH → CAH <sub>10</sub>
Up to 70 C°	6CA+6OH → C <sub>2</sub> AH <sub>8</sub> +AH <sub>3</sub> +27H
Above 70C°	6CA+6OH → C <sub>3</sub> AH <sub>6</sub> +AH <sub>3</sub> +36H

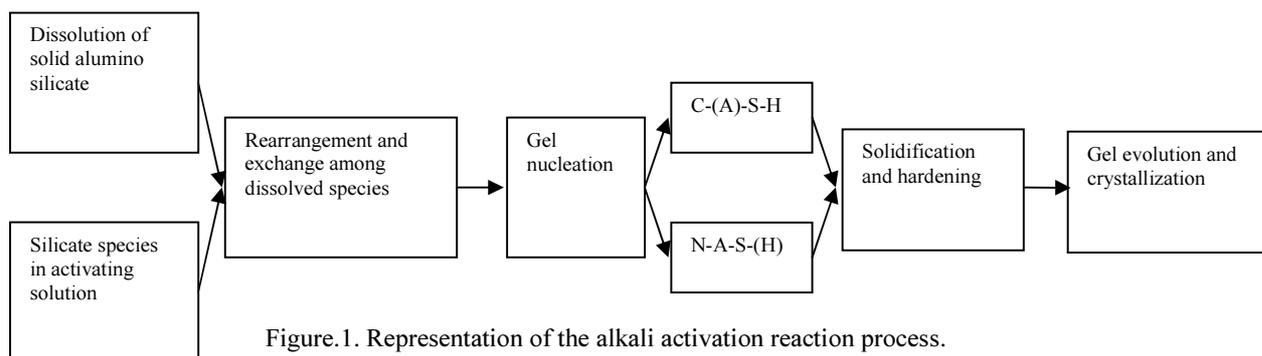


Figure.1. Representation of the alkali activation reaction process.

### Conclusions

Both the alternative binders discussed so far in this study are similar in many respects like composition, energy use, greenhouse gas emission, and performance, at the same time there are also obvious and substantial differences between these materials, remarkably they all have a period of fluidity to enable mixing and substantial strength gains in the absence of applied heat. In the recent years dramatic improvements have been brought in the performance of alternative cementitious binders with respect to reaction mechanisms and property development. The only problem with these alternative binders is their higher costs as compared to Portland cement and the prescriptive nature of specifications for binders in concrete. It is likely that the use of alternative binders will increase, as the performance-based specifications become more prevalent.

Supersulfated cements also have the advantage of being made from waste materials, with low heat production and good durability in aggressive environments but still suffer from poor early strength development. With adequate curing they can reach to the strength of Portland cement concrete by 28 days and have excellent durability.

Calcium aluminate cements offer rapid strength gain and good durability in high sulfate environments; still they are not so familiar because of the loss in strength which occurs over time due to the conversion of metastable hydration products to more dense stable hydration products, which cause an increase in the porosity. However, their uses in combination with supplementary cementing materials and chemical admixtures have resulted in a lower cost material that effectively eliminates the formation of metastable hydrates, eliminating the conversion problem.

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