The fundamentals of alkali activated binders biology essay

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1 - Introduction

1.1 - Basis for the Research

Annually, 11. 4 billion tonnes of concrete is used worldwide, a figure greater than that of the number of people on the planet (Mehta, 2002). Portland Cement (PC) is the predominant binder used in the production of concrete and this material has proven itself during its decades of existence. However, as it approaches the bicentenary of its conception, many questions have been raised as to its viability in the future, focussing mainly on the aspects of durability and sustainability. Conversely, alkali-activated binders (AAB) have only emerged as an alternative to PC fairly recently and have quickly gained widespread prominence worldwide. An AAB can offer higher compressive strengths and greater durability than PC as well as many other beneficial properties (Duxson, et al., 2007). Furthermore, an AAB can make full use of waste products such as fly ash and Ground Granulated Blast Furnace Slag (GGBS) without the need for additional PC. However, implementation into the construction industry would present problems due to the intrinsic nature of the chemicals involved in the reaction process. Activation of a fly ash or GGBS requires an alkaline solution. Research to date has focussed on producing high strengths and superior durability, resulting in the use of extremely caustic activating solutions, with no

consideration to end user safety at all. This report will focus on producing an implementable alternative to PC using a mixture of fly ash, GGBS, and a user-friendly alkali activating solution.

1.2 - Research Aims

The intention of this report is to produce a user-friendly AAB, and to determine whether it represents a viable option to be used as an alternative to PC. In order to thoroughly understand the research surrounding AABs, a review of the current literature will be carried out to understand what has been learnt to date, addressing the key points below: What is the existing practice regarding user-friendly cements? Why develop an alternative? What has been developed so far? Of the alternatives so far developed, how do the compressive strengths and durability of the products formed compare? Has the issue of ' user-friendliness' been addressed?

1.3 - Outline Methodology

Experiments will be conducted, testing mortar samples to determine compressive strength at 3, 7 and 28 days as well as durability with an attempt to answer the following questions: Can a user-friendly AAB produce a mortar under ambient conditions? Do AABs exhibit a strength and durability of any practical significance? Do AABs represent a viable alternative to PC?

2 - Literature Review

For this research to add to existing knowledge in the field of AABs, a review of the current literature is required. This study will consider the approaches currently used, the reasons for development and conduct a comprehensive review on the effects AABs have on compressive strength and durability. The investigation will also develop an understanding regarding user-friendly conditions that have been adopted both presently and in the development of alkali-activated binders thus far.

2.1 - Portland Cement

Portland cement (PC) is typically used in the production of concrete and is manufactured through a process known as Clinkering. Raw materials comprising of Lime (CaCO3), Silica (SiO2), Alumina (Al2O3) and Ferrous Oxide (Fe2O3) are milled and heated to temperatures of 1400-1500°C. Compounds including calcium silicates (2CaO. SiO2, 3CaO. SiO2), tricalcium aluminates (3CaO. Al2O3) and tetracalcium aluminoferrites (4CaO. Al2O3. Fe2O3) are formed with the resulting clinker being mixed with gypsum (CaSO4. 2H2O), to prevent flash setting of the final product (NZIC, 1998).

2.1.1 - Hydration Mechanisms

In the presence of water, the compounds mentioned above undergo exothermic reactions in which hydration products form. Initially, large amounts of heat are evolved, attributable to the reaction between tri-calcium aluminate and water, producing an aluminate-rich gel: 3CaO. Al2O3 + 6H2O 3CaO. Al2O3. 6H2O[2. 1]The presence of tricalcium aluminate in cement is undesirable as it contributes little to overall strength and once hardened, reacts with sulphates in the environment, causing degradation of the material (CCAA, 2002). Conversely, the silicate compounds react to form 3CaO. 2SiO2. 3H2O, also known as a C-S-H gel (or Tobermorite), and Calcium

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Hydroxide: 2(3CaO. SiO2) + 6H2O 3CaO. 2SiO2. 3H2O + 3Ca(OH)2[2. 2]2(2CaO. SiO2) + 4H2O 3CaO. 2SiO2. 3H2O + Ca(OH)2[2. 3]The C-S-H gel formed in equations [2. 2] and [2. 3] give concrete its inherent strength with 3CaO. SiO2 contributing to initial strength gain and 2CaO. SiO2 contributing to a later strength gain (NZIC, 1998). However, strength is only one of many factors that need to be considered when using a construction material such as PC.

2. 1. 2 – Ease of Use

One of the lesser appreciated advantages of PC is its user-friendliness, relative to many other materials and chemicals used in other industrial processes today. Dry PC is intrinsically hygroscopic, and can cause skin irritation, eye damage, and respiratory irritation. However, although sounding relatively aggressive, it is essential to realise that the substance is classified as merely an irritant. The regulation for classifying and labelling substances has recently been revised (Regulation EC No 1272/2008) and PC is classified into four hazard categories, reproduced in Table 2. 1 below (LaFarge, 2013). Precautionary guidance when using the substance advises wearing protective gloves, protective clothing, eye protection and face protection with general first aid measures being to wash the source of contact down with water. The user-friendliness of PC has enabled its insurmountable use within the construction industry with its irritability not even attempting to hinder its application.

2. 1. 3 – Limitations of PC

2.1.3.1 - Durability

PC has two main flaws regarding its durability. Firstly, its microstructure; large pores increase its permeability resulting in quicker carbonation rates, higher chloride penetration and higher sulphate penetration, leading to a faster deterioration of both the concrete and the steel reinforcement (Pacheco-Torgal, et al., 2012). Secondly, the hydration reaction of the silicate compounds creates calcium hydroxide. Although providing alkalinity to the concrete, protecting the steel further from corrosion, it does not provide any enhancement to strength and can react with impurities to form soluble compounds, further degrading the material (Pacheco-Torgal, et al., 2008). A report published in 2001 provides knowledge into the extent of durability of PC. It questions why before 1930 no examples of deterioration due to cracking were ever reported and suggests that in more modern times due to the high demand of high strength concrete, cement content has increased to the extent of detrimentally affecting the durability of the concrete. The suggestion that durability has been sacrificed to achieve greater strengths seems to concur with a vast majority of the literature implying that durability of PC concrete is one of the most serious problems facing the material (Mehta and Burrows, 2001).

2.1.3.2 - Environmental Impacts

It is now accepted that our global climate is changing. The Intergovernmental Panel on Climate Change (IPCC) was founded to increase knowledge in this area and to understand how our anthropogenic impact on the environment is changing the planet. Table 2. 2 below shows how carbon dioxide (CO2) has had the largest impact: The UK, as part of the European Union, committed itself into the Kyoto Protocol; a treaty whereby committed parties have agreed to reduce their greenhouse gas emissions by 5% in the period 2008-2012, relative to 1990 emissions (Viguier et al, 2003). This agreement was renewed during the 17th Conference of Parties (COP17) in South Africa (UNFCCC, 2012). An international change such as this requires research surrounding the predominant contributors to climate change, with a primary source being the production of PC. At least 5% of all CO2 emissions worldwide come from the production of PC, with estimates of this rising to approximately 10% in the near future (Habert, et al., 2011). In order to reduce the UK's CO2 emissions, a review of the cement industry is required, with the possibility of alternative cements being used.

2.1.4 - End of an Era?

Developing PC represented a milestone in the industrial world. It gave mankind a substance that possesses the essential constituents of creating a great building material. More recently however, the desire to progress as an industry is slowly altering the superiority of PC to one that is old-fashioned and out-of-date."...there would appear to be little doubt that alternative binders, less aggressive to the environment, must (at least partially) replace Portland cement." (Shi, et al., 2011)

2. 2 – Alkali-Activated Binders as an Alternative

One alternative with great significance in this field of research is alkali-

activated binders. AABs have been researched since 1940 when Purdon

studied the effect a sodium hydroxide solution had on slag. Glukhovsky further expanded on this work and determined the main product of hydration was comparable to that of PC, attributing the high strength of this material to the aluminosilicate calcium hydrate that formed. Davidovits also had a large significance in this area with the development of alkali-activated metakaolin and laying claim to the term ' Geopolymer' (Pacheco-Torgal, et al., 2008). However, it has only been recently that this area of research has gained much more significance. AABs have shown to produce mortars of high compressive strength, very good durability and possibly lower environmental impacts due to use of waste products in their production (Juenger, et al., 2011). Two of the most widely studied waste products used in this field of research are fly ash and GGBS. With only 20-30% of these materials currently being used in terms of enhancing the properties of concrete, they promise to be an accessible, sustainable and user-friendly alternative (Palomo, et al., 1999).

2. 2. 1 – The Fundamentals of Alkali-Activated Binders

Crudely, an AAB can be produced by activating fly ash or GGBS with an alkali solution. Approximately 300 million tons of fly ash and 22 million tonnes of slag are produced annually worldwide (King, 2005). Fly ash is created as a by-product in the production of electricity, forming due to heating and grounding hard coals at 1400°C. This extremely energy intensive process produces a siliceous, glassy fly ash known as a Class V fly ash with predominant constituents of Silica (SiO2) and Alumina (Al2O3). The composition is also made up of minimal amounts of Ferrous Oxide (Fe2O3)

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as well as a reactive Calcium Oxide (CaO) content of less than 10%. The quality of the fly ash produced is extremely variable due to the restraints in which it is produced. As electricity is fairly difficult to store, coal fired power stations regularly start and stop producing a varied fly ash. However, general trends in reaction mechanisms and products have been seen (Sear, 2001). Conversely, slag is produced as a by-product within the steel and iron industry and is formed due to the reduction of iron ore within a blast-furnace. GGBS is produced after employing rapid guenching and granulation on the slag. The composition of GGBS is generally a glassy, amorphous substance with the main oxides being that of Calcium Oxide (CaO), Alumina (Al2O3), Silica (SiO2) and Magnesia (MgO) (Li, et al., 2010). A variety of alkali solutions have been proposed in the alkali-activation of fly ash and GGBS including the hydroxides, silicates and carbonates of both sodium and potassium. However, the most common activators used seem to be sodium hydroxide and sodium silicate. Sodium hydroxide (NaOH) is produced through the electrolysis of brine (NaCl) by the chlor-alkali process. This process requires sources of electricity and heat to evaporate off excess water within the solution, both of which are provided by the burning of fossil fuels (ChemPaths, n. d.). Conversely, sodium silicate is formed by fusion of sodium carbonate (Na2CO3) and Silica (SiO2) at 1200°C to produce an amorphous ' cullet'. This cullet is reacted with steam and pressurised until it dissolves. This process is again, extremely energy intensive and requires very high temperatures through the burning of fossil fuels. The product formed, otherwise known as waterglass, is available in a variety of SiO2: Na2O ratios varying from 1.0 to 3.3. This ratio can be altered by addition of

sodium hydroxide with increased amounts of sodium corresponding to increased corrosiveness (NZIC, 2008).

2. 2. 2 – Activation Mechanisms

2. 2. 2. 1 – Alkali-Activation of Fly Ash

Alkali-activated fly ash can be formed by the reaction between that of an alumino-siliceous solid and an alkaline solution. The product that forms from this reaction can be described as an alkaline aluminosilicate hydrate and has characteristics similar to that of PC; hardening and forming a solid mass (Shi, et al., 2011). Aluminosilicate hydrates were also given the nomenclature of ' Geopolymer' and by chemical definition, 'polysialate' by Davidovits. The chemical formula of a polysialate is: Mn $\{-(SiO2)z - AIO2\}n$, wH2O[2. 4]where different types of polysialate are attributed to different values of z and n, z being 1, 2 or 3 and n being the degree of polymerisation, see Figure 2. 1 overleaf. M can be any alkali cation, with sodium forming a sodiumalumino-silicate-hydrate, or N-A-S-H gel (Pacheco-Torgal, et al., 2008). Much research has gone into the alkali activation of fly ashes. A general model was proposed by Glukhovsky to attempt and explain the mechanism. Developed in the 1950's, The Glukhovsky Model describes the process in three main stages; (a) destruction - coagulation; (b) coagulation - condensation; (c) condensation - crystallisation (Duxson, et al., 2006). This model was further developed by Provis, see Figure 2. 2 overleaf. Initially, the solid aluminosilicate material undergoes alkaline hydrolysis, liberating aluminate and silicate species and integrating them into the aqueous phase medium. An activator with a high pH encourages this dissolution stage further,

resulting in a saturated aluminosilicate solution and the coagulation of polyhydroxy-aluminosilicate complexes. This coagulation (' gelation') stage releases the water consumed during hydrolysis and this becomes contained with the pores of the gel formed. Large networks are created in the gel which continually restructures, forming a large 3D, alkaline, aluminosilicate hydrate species, with chemical formula M2O. Al2O3. 2SiO2. nH2O and a structure bearing a high resemblance to that of a zeolitic precursor. When sodium is used as the alkali cation a N-A-S-H gel is formed. The [SiO4]4- and [AlO4]5anions arrange themselves tetrahedrally, with the alkali ion, such as Na+, balancing out the negative charged anions within the framework (Duxson, et al., 2006; Shi, et al., 2011; Pacheco-Togal, et al., 2008). The final zeolite crystallisation and hardening stage is a long term, theoretical stage (Fernández-Jiménez and Palomo, 2005). It is important to note that the stages within the mechanism, although shown separately, are coupled and run concurrently with one another. When compared to the mechanism of PC hydration, aluminosilicate activation produces a vastly different product. Alkali-activated fly ash forms an alkaline, aluminosilicate hydrate attributable to the lack of calcium in fly ash. The structure of the alkaline aluminosilicate hydrate can also vary significantly, being heavily influenced by a number of variables.

2. 2. 2. 2 – Alkali-Activation of GGBS

Slag, in comparison to fly ash, contains a much higher percentage of calcium altering both the reaction mechanism and final product when activated with an alkali solution. As cited by Juenger, et al. (2011), the composition of the gel formed is generally determined by the calcium content of the raw material, with binders containing high amounts of calcium, such as slag, forming a calcium aluminosilicate hydrate C-(A)-S-H gel. Wang and Scrivne

forming a calcium aluminosilicate hydrate C-(A)-S-H gel. Wang and Scrivner (1995) concluded that the predominant product formed through alkalination of a slag was a calcium silicate hydrate (C-S-H) gel. Furthermore, they state that C-S-H gel is always the main product of hydration, independent of the type of activator used, with hydrotalcite also forming as a minor product. They also indicate that the gel forms initially between the slag particles, suggesting a dissolution and precipitation model similar to that of fly ash. The formation of zeolites was not present, differing to the hydration of alumino-silicates. Davidovits presented one of the more detailed investigations into the activation of GGBS in 2011 (Davidovits, 2011). The main constituent of an amorphous slag is that of Melilite. This is comprised of three separate molecules; Gehlenite (Ca2Al2SiO7), Akermanite (Ca2Mg(Si2O7)) and Merwinite (Ca3Mg(SiO4)2). Through NMR spectroscopy it was determined that a variety of species form during the alkalination of GGBS, with the following mechanism proposed. Firstly, alkalination of Gehlenite produces ortho-sialate hydrates and liberates aluminium hydroxide (Al(OH)3). This step runs simultaneously with the yielding of Ca-di-siloxonate from Akermanite and Merwinite as well as the liberation of magnesium hydroxide (Mg(OH)2) and calcium hydroxide (Ca(OH)2). Subsequently, the ortho-sialate-hydrates and Ca-di-siloxonates yielded condense with one another producing ortho-(sialate-di-siloxo) molecules. The liberated hydroxides react with CO2 in the atmosphere to produce their respective carbonates. It is interesting to note the differing nomenclature for some of

these products; ortho-(sialate-di-siloxo) molecules can be written chemically as C3AS3 and Ca-di-siloxonate molecules written as C-S-H, the same compound formed during PC hydration. However, a shortcoming of this geopolymeric system is the structural formation of the molecules after alkalination. The positively charged alkali ions are not integrated within the structure but situated at non-bridging oxygen locations, enabling them to move and form potassium hydroxide and sodium hydroxide. This problem can be overcome by means of a ' user-friendly' system in which this integration is promoted with the formation of chemical bonds. Overall, the research describing alkali-activation of GGBS concludes the main product that forms consists of a calcium-silicate-hydrate (C-S-H) gel, corresponding to the same gel formed in hydration of PC. However, the following statement is worth considering regarding the activation of fly ashes and slag:" Both activation processes have advantages and disadvantages. From the knowledge of both materials [fly ash and slag], it is known that the disadvantages of one activation process can be balanced with the other one." (Puertas, et al., 2000)What can be drawn from this statement is that alkali-activation of a mixture of both GGBS and fly ash may work better than activation of the materials individually. One of the main reasons for this could be due to GGBS having a higher heat of hydration than fly ash. Although being lower than PC, the heat released due to the hydration of GGBS may allow for activation of fly ash at lower temperatures.

2. 2. 2. 3 – Mixtures of Fly Ash and GGBS

Little research has been conducted on the mechanisms of both fly ash and GGBS under alkali-activation. Further progress must be made first in understanding the mechanisms separately. However, some research has been attempted with their conclusions reviewed below. Fly ash/GGBS mixtures were considered in the 1970s by Smith and Osborne (1977). Investigations were undertaken on a 60: 40 mixture of GGBS and fly ash with a NaOH solution. Puertas, et al. (2000) also activated a mixture of fly ash/GGBS in different proportions with NaOH. Using a 10M NaOH solution, both materials fully dissolved; the fly ash dissolving more slowly than the slag. However, the significance of this research is that when analysing a 50: 50 mixture of slag and fly ash, no hydrated aluminosilicate product associated with the hydration of fly ash formed. The main product was a C-(A)-S-H gel with a degree of aluminium substitution for silicon. This differs to research conducted by Chi and Huang (2013) who also look at the reaction products formed from the alkali-activation of a 50: 50 mixture of fly ash and GGBS with sodium silicate. They provide us with 7 and 28 day SEM images to illustrate how the reaction progresses, see Figure 2. 3 below: At 7 days, they note the partially unreacted particles of fly ash surrounded by the product of slag hydration, a C-S-H gel. At 28 days however, a mixture of the 3D aluminosilicate from the hydration of fly ash as well as the C-S-H gel occurs. They also state that when considering mechanical strength development, the ratio between fly ash and slag is the most important factor to consider. Mechanical strength will be reviewed in a subsequent chapter.

2. 2. 3 – Ease of Use

To all extent and purposes, AABs are not user friendly. Fly ash and GGBS are themselves, relatively harmless. Conversely, the solutions required to activate them can be extremely aggressive. Material Data Safety Sheets suggest the use of tightly fitting goggles, face shield, waterproof gloves inspected prior to using the chemical, complete body suit protection and fullface, air-purifying respirators. Davidovits first looked at the development into user-friendly AABs in 2011. Information on relevant substances was gathered from their respective Material Safety Data Sheets (MSDS) which is reproduced in Table 2. 3 below: The table separates user-friendly materials from user-hostile materials, symbols of which can be seen in Figure 2.4 and an important piece of information is made clear; the majority of alkali activators used are corrosive and as stated by Davidovits:"...cannot be implemented in mass application without the appropriate safety procedures." (Davidovits, 2011)What is also brought to light from the research of Davidovits is that the vast majority of studies on AABs show that user-friendly systems are not considered at all. The information obtained when carrying out this report does tend to agree. Some user-friendly solutions have been adopted, including the work of Izquierdo, et al. (2009), who studied the effects a user-friendly solution had on fly ash. Their research also suggested that user-friendly conditions can differ depending upon the type of cation used in the activator with a user-friendly SiO2: K2O ratio of 1. 25 being used. However, in the majority of cases, user-friendly conditions are not the main focus of the research and are not considered. This represents a

huge boundary in attempting to implement this concept into the construction industry.

2. 2. 4 – Environmental Impacts

Much of the research surrounding this topic has concluded that an AAB has a lower environmental impact than PC. McLellan, et al. (2011) concluded that alkali-activated fly ash can have a 44-64% decrease in CO2 when compared to traditional PC. However due to the number of variables involved in achieving a set figure, the results can vary significantly. For example, Duxson, et al. (2007) concluded a reduction in CO2 emissions of greater than 80% can be achieved with AABs, attributing such a high figure to the lack of water and super-plasticising agents required. Habert, et al. (2011) considered the impacts that the raw materials have on the environment when conducting a Life-Cycle Assessment of Geopolymer Concrete. As pointed out in this research, although an AAB has lower CO2 emissions overall when compared to PC, this reduction is lessened when consideration of the 2008 EU legislation (2008/98/EC) regarding the designation of waste products is taken into account (European Commission, 2008). As the use of fly ash and slag is deemed to be certain and they can be used without further processing, they must be considered as by-products, not waste, and therefore have an associated CO2 allocation. Much of the research conducted before its implementation in 2010 had not attributed any CO2 emissions from fly ash or GGBS as they were considered waste products. The research also confirmed that the activating solution has a large impact when assessing the overall CO2 contribution AABs have on the environment, with

CO2 emissions being heavily influenced by the concentration and type of activator used. Using sodium silicate presented the worst case, increasing the amount of contamination in other environmental areas such as O-Zone depletion. From considering the information available on this topic, the general perception that AABs are much more environmentally friendly than PC is questionable, especially when taking into account the 2008 EU legislation. This has led much of the research pre-2008 to become out-ofdate and could potentially lead to distorted studies.

2.3 - Compressive Strength of Alkali-Activated Binders

The compressive strengths achieved in the alkali-activation of GGBS or fly ash can vary significantly. This suggests that there are a considerable amount of variables, including fineness of raw materials, open and closed curing conditions, fly ash: slag ratio, to name a few. This section will focus on two of the main variables associated with this investigation, namely the effects of the alkali solution and curing temperature.

2.3.1 - Effects of the Alkali Solution

2. 3. 1. 1 – Solution Type

Komljenović, et al. (2010) considered the reaction of potassium hydroxide with a siliceous fly ash. A potassium hydroxide solution containing 10% K2O by mass of fly ash produced poor results. The authors claim that the low compressive strengths obtained were attributable to a larger ionic diameter of the potassium ions affecting the final structure. Their results do however contrast with that of van Jaarsveld and van Deventer (1999) when studying the effect potassium has on activating a fly ash. They detected that when

using a potassium cation, the product formed possessed a higher molecular weight than that of the product formed with sodium silicate, suggesting a greater degree of condensation, and therefore creating a structure with higher compressive strength. Nonetheless, the majority of research has focussed on using sodium as the cation in the alkali activator. Research has concluded that the highest compressive strengths of activation of fly ashes were achieved using sodium silicate solutions. Palomo, et al. (1999) noticed that a solution of sodium silicate gave higher reaction rates when compared to sodium hydroxide and sodium carbonate solutions. This was attributable to sodium silicate causing dissolution of silica and alumina into the solution to happen more briskly, resulting in a quicker development of mechanical strength suggesting that an increase in silica content increases the rate of reaction. Furthermore, Fernández-Jiménez, et al. (2007) achieved higher compressive strengths when using a sodium silicate solution than when using sodium hydroxide solely. When considering a sodium carbonate solution however, the carbonate ions acidify to produce a soluble sodium bicarbonate in the final product, leading to lower mechanical strengths (Fernández-Jiménez and Palomo, 2005). A similar trend seems to occur with alkali-activated slag. Fernández-Jiménez, et al. (1999) in their work on slag activation concluded that a sodium silicate solution gave better compressive strengths than that of sodium carbonate and sodium hydroxide solutions. However, this contrasts with research conducted by Haha, et al. (2012) who concluded that the activation of GGBS using sodium hydroxide solutions gave higher compressive strengths. Then again, this was only at earlier stages of development, and later compressive strengths reduced due to

larger pore sizes when compared to sodium silicate. Smith and Osborne (1977) considered the effects a NaOH solution had on a mixture of 40% fly ash and 60% slag. Compressive strengths within the region of 8. 0-13. 5MPa were achieved after seven days with a noticeable retardation in strength gain occurring between three and seven days. A two stage hydration mechanism was suggested in which the fly ash contributes more to strength at later ages. Shi and Day, (1999) when considering the activator type on mixtures of fly ash and slag concluded sodium silicate to be the most effective solution for activating GGBS.

2.3.1.2 - Molar Ratio of SiO2: Na2O

The SiO2: Na2O molar ratio of the activating solution has one of the greatest impacts on how the reaction will progress and inevitably produce the final product, with Silva de Vargas (2011) suggesting it plays the most important role on compressive strength in alkali-activated fly ash. The main conclusion drawn is that lower molar ratios achieve better results. This research experimented with sodium hydroxide solutions at very high SiO2: Na2O molar ratios from 2. 5 - 5. 0, resulting in low compressive strengths, varying from 1. 76MPa to 5. 25MPa at 7 days. Komljenović, et al (2010) studied the reactions of sodium silicate with varying molar ratios on a siliceous fly ash. 7 day optimal compressive strengths were reached under the conditions of SiO2: Na2O = 1. 5 which corresponds well with work done by Ma et al (2012) who observed an optimal SiO2: Na2O molar ratio of 1. 0 – 1. 5. However greater mechanical strengths seem to be achieved using more user-hostile conditions. Fernández-Jiménez and Palomo (2005) managed to produce

higher mortar strengths of up to 91. 6MPa using a much lower SiO2: Na2O ratio of 0. 118. Atiş, et al. (2009) concluded an optimum molar ratio of 0. 75 for alkali-activated slag however less research has been conducted on how the molar ratio explicitly affects the activation of both slags and mixtures of slags and fly ashes. However it has been explored through the concentration of alkali used.

2.3.1.3 – Alkali Concentration

In similar respect to the molar ratio, the concentration of Na2O within the solution is also of relevance when discussing compressive strength. When considering alkali-activated slag, Atis, et al. (2009) suggest that the compressive strength is dependent not only on the activator type but also the concentration of alkali within the solution. They concluded that as the percentage of sodium increased within the activator, the compressive strength of the mortar increases. This was further developed by Wang, et al. and Fernández-Jiménez, et al. who, as cited in Pacheco-Torgal, et al. (2008), concluded that values of Na2O by percentage mass of slag should lie within the range of 3-5. 5% and 3-5% respectively to achieve optimal results. With the activation of fly ashes on the other hand, Katz (1998) concluded that reaction rates are increased when using a higher concentration of activator. This work agrees well with Komljenović, et al (2010) who achieved greater compressive strength when increasing the concentration of Na2O from 8% to 10%. An optimal strength of sodium silicate solution was also achieved at the percentage of 10%. This research is similar to the work of Ma, et al (2012) who stated a percentage of 9.3% to be optimal. Fernández Jiménez and

Palomo (2005) researched the alkali activation of fly ash under different concentrations of Na2O. The results they achieved gave interesting results. They concluded that although the percentage of Na2O is an important parameter, the solution-binder ratio also plays an important role illustrating that an increase in Na2O content may have adverse effects on compressive strength. Research with a mixture of fly ash and slag concluded that the concentration of the activator solution is very significant. A 10M solution had a better effect on compressive strength than a 2M solution (Puertas, et al., 2000). Chi and Huang (2013) studied the effect that a mixture of sodium silicate and sodium hydroxide solutions had on a mixture of different proportions of fly ash and slag. Their results illustrated that a higher concentration of Na2O within the mix had positive effects on the compressive strength, with a ratio of 50% fly ash - 50% slag and a 6% Na2O concentration being concluded as optimal. Smith and Osborne (1977) noted little effect when increasing NaOH concentration above 5% in their investigation using a 40% fly ash and 60% slag mixture. These investigations showed that a higher content of slag reduces the need for high concentrations of alkali.

2.3.2 – Curing Temperature

It is important to consider the conditions under which the majority of previous mortar samples cured. Xie and Xi (2001) compared two sodium silicate solutions with SiO2: Na2O molar ratios of 1. 64 and 1. 0 and again confirm that as the ratio decreases, a higher mechanical compressive strength is achieved. However, they make an important statement:" Previous experiments showed that the activation reactions do not proceed in a sufficient rate to produce high strength paste under ambient temperature. Elevated temperatures are necessary to accelerate the reactions." (Xie and Xi, 2001)This statement is also corroborated by Duxson, et al. (2006) who suggested that temperature affects the mechanical strength of aluminosilicates greatly. Very few sources studied the curing of alkaliactivated fly ash at ambient temperature (Somna, et al., 2011). When considering the effect temperature has on alkali activated slags, Bakharev, et al. (1999) concluded that at elevated temperatures, higher early compressive strength is attained. However, when compared to later ages, ambient temperature seems to produce better results. This is in agreement with Altan and Erdoğan (2012), demonstrating that at later ages, ambient temperature can promote compressive strength gain. Early strengths however are much lower. This represents a huge barrier when trying to integrate their use into mainstream construction.

2.4 - Durability

As established in Juenger, et al (2011), durability represents the primary concern when assessing the viability of an AAB. Research in this area has tried to determine how the many variables throughout the reaction affect the final product. This has been attempted by conducting chloride diffusion/penetration tests, alkali-silica reaction tests and carbonation tests, to name a few. This research will try and consider how durability is affected by a) the type of material to be activated, b) the type of alkali activator used and c) solution-binder content. However, the research in this area is sparse. Very few direct comparisons have been made between how different activators affect the durability of alkali-activated fly ash and alkali-activated slag. Moreover, alkali-activated fly ash/slag mortars have not been tested for durability at all. For this reason, the majority of comparisons will be drawn between PC.

2.4.1 – Material Effects

Bakharev (2005) researched the effects acids had on alkali-activated fly ash, determining that degradation of alumino-silicate materials is the result of depolymerisation of the structure and substitution of the alkali cations with either hydrogen or hydronium, see Figure 2. 5. Fernández-Jiménez, et al. (2007) also suggest that the Si-O-Al bonds in the aluminosilicate are broken by the acid, producing Si-OH and Al-OH bonds with the end result being a loss of mass. The susceptibility of deterioration is also the result of the structural order of the gel as well as the amount of crystalline or amorphous material within the product formed. Degradation of alkali-activated fly ash is also considered by Chindaprasirt, et al. (2007) who conducted a Coulomb Charge Test to determine chloride permeability of alkali-activated fly ash. All the fly ashes tested independent of their fineness, performed better than PC under the same conditions. Furthermore, an increase in fly ash fineness improved the penetrative resistance. El-Didomony, et al. (2012) stated that high durability and resistance to chemical attack can be achieved with alkaliactivated slag. Immersion in sea water for 12 months did not halt compressive strength increase, confirming that alkali-activated slags have high resistance to chloride penetration. Carbonation tests however, seem to

achieve the opposite. Due to the lack of calcium in alkali-activated slag (roughly half that of PC), and an increase of soluble sodium, the pH reduces very quickly on the surface, leading to concrete softening and C-S-H calcification. It was determined that alkali-activated slags are more susceptible to carbonation when compared to PC (Bakharev, et al., 2001).

2.4.2 - Effects of the Activator

As previously mentioned, few comparisons have been made between how different activators affect the durability of alkali-activated fly ash and slag. Fernández-Jiménez, et al. (2007) suggested that different activators produce variations in durability due to the structural differences within the final product. The observations in this research concluded that fly ash activated with sodium hydroxide and sodium silicate produced no significant deterioration when exposed to seawater, de-ionised water and sulphuric acid, with no surface deterioration being observed even after 12 months. However, sulphates were observed within the pores suggesting some permeation. An accelerated alkali-silica reaction test also produced fairly good results with no surface cracking observed, attributable to low calcium contents and unlikely formations of sodium-calcium silicate gels. Bakharev (2005) considered how alkali-activated fly ash is affected by the activator typology using the same percentage of Na2O (8%). A range of techniques used led to the conclusion that durability was firstly related to the porosity, and secondly, to the pore diameter of the mortars produced. The fly ashes activated with sodium silicate had much lower porosity (0. 36%) when compared to those activated with sodium hydroxide (1. 98%) and

sodium/potassium hydroxide (17. 5%). However, average pore diameter was 63, 45 and 116Å respectively. When tested under sulphuric acid attack, the fly ash activated with the hydroxide activator, although being slightly more porous than the ash activated with the silicate activator, performed better due to the lower average pore size. Conclusions drawn were that average pore size was considered to be more of a dominant factor than porosity. Ma, et al. (2001) concluded that increasing the amount of SiO2 or Na2O within the activator led to a denser matrix of gel, with smaller pore diameters. These results, when compared to those of Bakharev above, tend to suggest a greater durability would also occur. However, when compared to the work by Silva de Vargas, et al. (2011), micro-cracking formed in mortars with very high SiO2: Na2O molar ratios suggesting an optimal amount. In the same research by Bakharev (2005), further results concluded that under acid attack, the stability of the structure was dependent on the structural order within the gel formed. Sodium hydroxide produced a more crystalline gel than sodium silicate and sodium/potassium hydroxide, therefore producing better durability results. This compares well to the work of van Jaarsveld and van Deventer (1999) who concluded that the final structure was more stable when sodium hydroxide solution with molar ratio 0.35 was used as the activator. This further agrees with the citation in the previous research by Fernández-Jiménez, et al. (2007), stating the degree of crystallisation is reduced if an activator contains soluble silicates. When considering how the molar ratio affects the durability of an alkali-activated cement, Al-Otaibi (2008) considers the difference sodium metasilicate (SiO2: Na2O = 1.0) and sodium silicate (SiO2: Na2O = 1.65) solutions have on a slag. By considering

rapid chloride penetration testing, solutions with higher molar ratios produced lower values with the same Na2O concentration. This was true at both 4% and 6% concentration, suggesting a higher molar ratio led to a lower permeability. Carbonation testing revealed that the molar ratio had little effect: however an increased Na2O concentration did reduce carbonation depth. The concentration of a particular type of activator has also been considered. Chi (2012) looked at how the concentration of Na2O within the activator affected the durability of alkali-activated slag by conducting rapid chloride penetration tests and sulphate attack resistance tests. The results obtained concluded that the quantity of Na2O within the activator radically affected the durability, with all the results of alkaliactivated slag being greater than PC. The sulphate attack resistance test illustrated that less mass was lost in the alkali-activated slag complexes suggesting a less permeable, more durable structure. However, the accuracy of the experiment conducted is guestioned as an increase in compressive strength was achieved after the sulphate attack test. Finally, a review of the durability of binders presents its findings on both acid corrosion and alkalisilica reaction from many researches. One of the main conclusions drawn from this review was the resistance to chemical attack is higher in alkaliactivated cements than compared to PC, however this is attributed more to the lack of calcium within the gels formed (Pacheco-Torgal, et al., 2012). This compares well with the earlier research conducted by Fernández-Jiménez, stating that regardless of the activator, alkali-activated fly ash is more durable than PC.

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2.4.3 – Solution-Binder Ratio

As previously mentioned, pore structure is an important factor when considering the durability of alkali-activated cements and the solution-binder ratio highly determines the composition of the pore structure, suggesting it to be an important factor to be considered (Juenger, et al., 2011). Ruiz-Santaguiteria, et al. (2012) considered the solution-binder ratio in alkaliactivated fly ash using both sodium hydroxide and sodium silicate as activators. The results concluded that increasing this ratio tended to affect both the reaction mechanism and final product. N-A-S-H gels with greater aluminium contents were formed at higher ratios along with increased zeolite formation. However, increasing the ratio further increased the amount of OH- ions within the solution, slowing the polymerisation process and producing a less ordered structure. By keeping the solution-binder ratio constant, Bernal, et al. (2010) considered the effect that an increase in binder content would make on the end product. A water absorption test of an alkali-activated slag gave results that were slightly lower but comparable to PC. Higher binder contents acted advantageously up to a certain amount, lowering the water absorption and acting in a similar way to PC. Carbonation tests however revealed that again, AABs behaved poorly when compared to PC.

2.5 - Summary

Much of the research conducted has shown that there is a lot of variety in this area of study. Fly ash is less reactive than slag due to the lack of calcium available to react and form a C-S-H gel, as in the activation of slags. For this

reason an alumino-silicate hydrate forms. However, these products can vary significantly depending on a large number of variables, consequently affecting the physical properties of the materials formed. Additionally, much of the research thus far has focussed on producing binders which exhibit a high compressive strength and a high durability. Compressive strength is attributed to the formation of either a N-A-S-H gel in fly ashes, or a C-(A)-S-H gel in slag, with C-A-S-H gels forming depending on the availability of aluminium to substitute silicon. Variability in strength was attributed to the amount of gel formed with increased amounts of silica in N-A-S-H gels further appearing to increase mechanical strength. A decrease in molar ratio and an increase in concentration of the activator also added to mechanical strength. Durability is affected primarily by pore structure, with sodium hydroxide solutions outperforming sodium silicate and sodium carbonate solutions. Overall however, what seems to have only been highlighted recently is the practical application of these alternative cements; the corrosive nature of the chemicals involved makes their integration into the construction industry very difficult. Moreover, many researches tend to summarise the most important factor to consider in the experiment, with a large variety of conclusions being drawn. This further reiterates that the number of complex variables involved and how they affect the final product is yet to be fully understood.

3 – Experimental Investigation

Aim

To develop a user-friendly, alkali-activated binder that could represent a viable alternative to Portland cement.

3.1 - Objectives

Objective 1:

To determine the compressive strengths achievable using a user-friendly mixture of sand, fly ash, slag and alkali activator. Four activators with varying molar ratios will be used with a constant mix ratio.

Objective 2:

To determine whether an increase in binder content affects the compressive strength of the specimens. This will be investigated using a single solution and varying the sand-binder ratio.

Objective 3:

To assess the durability of the specimens using an absorption test. A test to determine porosity will also be conducted.

3. 2 – Materials & Methodology

3. 2. 1 – Preparation of the Alkali Solutions

Four solutions with differing SiO2: Na2O molar ratios (1. 50; 1. 70; 1. 90; 2. 10) were produced. This classifies them as irritants rather than corrosives and can be used safely in the Civil Engineering Department (Davidovits,

2011). The composition of the Na2SiO3 solution by percentage weight was

27. 80% SiO2, 8. 50% Na2O, and 63. 70% H2O. The composition of the NaOH by percentage weight was 50% NaOH and 50% H2O. A ratio by weight of SiO2: Na2O was calculated using percentages of SiO2, Na2O and H2O. This was converted to a molar ratio using respective molar weights. See Appendix A for a breakdown of the calculations. The following chemical equation was used to determine the number of moles of Na2O in NaOH. 2NaOH Na2O + H2O[3. 1]It was observed that in order to reduce the molar ratio of SiO2: Na2O, the concentration of the solution increased due to the amount of sodium present. The proportion of distilled water was therefore altered so as to keep a 10% concentration of Na2O within each of the mixes. This enabled a fair comparison between molar ratios and not Na2O concentration. The literature concluded an optimal concentration of roughly 10% to be used for solutions activating siliceous fly ashes. Solutions of molar ratio 1. 50, 1. 70, 1. 90 and 2. 10 were produced and are shown in Table 3. 1 below by percentage weight. See Appendix A for more detailed information.

Materials

Na2SiO3 solution with SiO2: Na2O molar ratio = 3. 3NaOH solution, 50% concentrationDistilled Water5L conical flaskMagnetic StirrerGlass BeakersAppropriate safety equipment including gloves, eye protection and fume cupboard.

Safety Information

NaOH should be added slowly to Na2SiO3 to avoid excessive heat gains. Due to the extremely aggressive nature of the NaOH, the solutions were produced under supervision in the pharmacology department. For the same reason, safety is of utmost importance. The use of eye protection, gloves, lab coat and a fume cupboard was necessary at this stage. After the solutions are prepared, classifying them as irritable only, they can be safely relocated to the Civil Engineering department. A small amount of heat was produced when mixing the chemicals. For this reason the bottles were left to cool in the fume cupboard for 5mins. The lid was then secured tightly and bottle safely stored.

3. 2. 2 – Preparation of Mortar Samples

Mortars were prepared following BS EN 196-1. Portland cement was replaced with a binder comprising of 90% FA and 10% GGBS. See Table 3. 2 for mix proportions. A solution to binder ratio of 0. 67 and sand-binder ratios of 3. 0, 2. 0 and 1. 0 were used. Moulds were half filled with the mix and jolted 60 times using the jolting apparatus. The moulds were then filled, jolted a further 60 times, levelled off and a glass plate applied. Specimens were placed in the environmental room at 20°C and 60% RH until testing at 3, 7 and 28 days. Samples were clearly labelled to avoid potential errors. Compressive tests were conducted on each half of the mortars, with an average strength being recorded.

3. 2. 3 – Sorptivity Testing Method

Rate of absorption was determined following ASTM C1585-04 using half of a $40 \times 40 \times 160$ mm mortars, prepared in the same way as above. At specified ages, samples were placed in an oven at 50°C. Samples were weighed until their dry mass was determined to within +/-0. 1g. Samples were then removed to acclimatise to the ambient temperature and humidity for a

further day. The four longitudinal sides were wrapped in electrical tape and a sealable plastic bag placed over one end to ensure no loss of water via evaporation. Samples were placed on their ends in approximately 2-3mm of water at 20°C and weighed at 1min, 5min, 10min, 20min, 30min, 60min, and every 60mins until 360mins. A plot of absorption, I vs. √time was used to determine absorption.

3. 2. 4 – Determination of Porosity

The samples used in 3. 2. 3 were used to determine porosity. Dry Weight, saturated weight and weight in water of samples were determined to within +/-0. 1g.

3. 2. 5 – Scanning Electron Microscopy (SEM) Preparation

Samples approximately 1cm3 were placed in an oven at 50°C for 48hrs. Samples were then secured with carbon tape and electrically earthed with silver paint before being placed in a desiccator for 24hrs to remove any excess moisture. Samples were finally scattered with 10nm coating of chromium to finalise the preparation.

3.3 – Results and Discussions

3. 3. 1 – Preparation of Alkali Solutions

Preparation of the alkali solutions is described above. The Na2SiO3 was fairly viscous which caused slight inaccuracies in some of the measurements. The NaOH, being the most caustic solution, was added slowly to the Na2SiO3 so as to avoid an excessive heat gains. The conical flask became slightly warm, with decreasing molar ratios expelling more heat. Water vapour was given off with condensation appearing on the inside of the conical flask, see Figure 3. 1. It should also be noted that eye protection, gloves, lab coat and a fume cupboard were used at this stage due to the severe caustic nature of the NaOH.

3. 3. 2 – Preparation of Mortar Samples

Following BS EN 196-1: 2005, the resulting mortars created were too dry and very unworkable. This was attributed to a lack of water in the mixture as a proportion of the solution contained Na2SiO3 and NaOH. For this reason, the amount of solution added to the mixtures was gradually increased to produce a workable mix. Approximately 300g of Solution #1 was required for the mix to become workable resulting in a solution: binder ratio of 0. 67. See Figure 3. 2 below for comparison. However, mortars proved to be less viscous at lower molar ratios with the same solution-binder ratio. This decrease in viscosity was attributed to an overall increase in water content within the mixtures from the solutions. This represented a workability problem with the mortars being cast. Using a ratio of 0. 67 allowed all four solutions to be used. Consequently the moulding, testing and consideration of all mixtures was possible using the same solution-binder ratio to ensure a fair comparison. Workability also caused a large issue when altering the sand-binder ratio. Reducing this ratio from 3: 1 through to 1: 1 had a similar effect to reducing the molar ratio. The mix became less viscous with an increase in fly ash/slag content. A ratio of less than 2: 1 resulted in a mix that was fairly fluidic however setting times were reduced as a consequence. Additionally during casting, a noticeable amount of effervescence occurred.

This could be attributed to the reaction between the alkali solution and the fly ash/slag or possibly as result of air entrainment during mixing. Furthermore, whilst casting the mortars, ' crystals' seemed to form on the surface of the specimens, occurring more prevalently in areas where there seemed to be more solution, see Figure 3. 3. An increase in these ' crystals' was also noticed with decreasing molar ratio. During de-moulding, a black residue was left on surfaces. This occurred with more significance with specimens using lower molar ratio solutions and could be attributed to the higher water content within these specimens. This residue was still apparent up to 28 days with addition of moisture and friction allowing a slow but steady degradation of the surface. Mortars tended to become paler in colour as they aged with a final colour not too dissimilar to that of PC concrete.

3. 3. 3 – Addition of Superplasticisers

Proposals to use superplasticisers were considered to try and help relieve the workability issues so far raised. The same proportions of fly ash, GGBS and sand were used but with reduced solution to binder ratios of 0. 5 and 0. 6. The superplasticiser used was Glenium Sky 544. The recommended dosage by weight of Glenium Sky 544 is 0. 20 – 1. 50kg per 100kg of cement equating to 0. 2 – 1. 5 wt% of binder. Mixes indicated a possible lack of compatibility with the superplasticiser and fly ash/slag. Dosages much higher than the recommended were required, seemingly just to increase the amount of liquid within the mixture rather than thinning the mixture down. For this reason, superplasticisers were not used within this investigation. However, a superplasticiser that is compatible may facilitate the production

of mortars using a lower solution-binder ratio, possibly increasing their strength and durability.

3. 3. 4 – Compressive Strength Testing

Preliminary testing showed that the compressive strength of samples reduced between 3 and 7 days when cured in a water bath. This was corroborated with a crude hardness test with samples cured in water being less hard than those cured in air at 20°C, see Figure 3. 9 below: An understanding of underwater curing may provide an explanation for this. PC mortars are cured in water baths to prevent drying shrinkage of the specimens. However, for an alkali-activated binder, it seems that excess hydroxide (-OH) ions may adversely affect the strength gain of the specimen. For this reason, air curing of specimens was conducted with Figure 3. 5 below illustrating how the compressive strength of specimens varied over a 28 day time period: