O. Kayali developed and patented a sintered fly ash based lightweight aggregate, named Flashag. When mixed with Ordinary Portland Cement these aggregates produce concrete with lighter weight and superior strength compared to concrete produced with regular aggregates[1]. However, the utility of Flashag with geopolymer cements is limited by Flashag’s relatively low strength. This paper investigates the potential of increasing the strength of Flashag by causing a limited degree of polymerization prior to sintering. Whilst aggregates have been produced through both sintering and geopolymerisation, no prior research has been conducted in combining both effects in a hybrid aggregate. The research was successful in developing a method for the production of such aggregates. It was found that the addition of chemicals necessary for polymerization combined with the elevated temperatures required for sintering encouraged the formation of ferro-silicates. The formation of ferro-silicates was found to limit the degree sintering and the utility of the aggregate produced. To better understand the utility of hybrid aggregates further research is required to determine the relationships between the input variables, temperature and the quantity of additives, and the output variables, the degrees of sintering, polymerization and ferro-silicate formation.

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I. Introduction

Light weight aggregates have numerous structural and environmental advantages over regular weight aggregates [1]. Structurally, they lower the self weight of concrete members, allowing for a reduction in size of columns, beams and footings. Lighter members can be more easily handled and transported, and being smaller leave more usable space on the interior of structures [2]. Light weight concretes also exhibit superior thermal and fire resistant properties to their regular weight counterparts. The environmental benefits of light weight aggregates are also numerous. Lighter members also require the use of less cement. The environmental burden of the cement industry has been well documented, and is considerable. The forfeit of regular aggregates also spares river beds, beaches and other areas from the damages associated with aggregates mining [3].

One viable material for the production of light weight aggregates is fly ash. Fly ash is the primary waste product of the combustion of pulverized coal [4]. In 2000, the estimated global production of fly ash was 600 million tones. Only 9% of this quantity was recycled. More locally, in 2004 Australia and New Zealand produced 12.5 million tones of fly ash, of which 35% was recycled [5]. Fly ash which is not recycled is disposed of, often at great financial cost. It can be deduced from this that the production of fly ash based light weight aggregates has an additional environmental benefit - it provides a use for an abundant waste material that would otherwise be disposed of. This is of particular interest for regions such as the Middle East, with an excess supply of fly ash and a deficit of good quality natural aggregates.

Fly ash based aggregates are produced in several industrial nations, including the USA, UK, Japan and India. These aggregates are typically pelletized through a process of granulation or milling, prior to sintering at temperatures as high as 1300°C [1]. The process is energy and time intensive. Despite the requirement for stringent controls, it produces aggregates of inconsistent size and density. These qualities are reproduced in concrete produced with these aggregates, limiting their utility for high strength or structural concrete.

‘Flashag’ is a fly ash based light weight aggregate, developed by O. Kayali and K. Shaw. The aggregates are sintered, but non-pelletized - instead produced in bricks or briquettes which can then be crushed down to aggregates of the required size. Most importantly, the production of Flashag is less energy and man hour intensive than other commercially available fly ash aggregates [1]. The benefits of the use of fly ash have been documented by O. Kayali. Flashag can be used to produce high strength concrete, with a compressive strength in excess of 70 MPa. Furthermore, said concrete is 20% stronger and 20% lighter than concrete produced with regular aggregates, at equal cement content. Cement produced with Flashag also display less drying shrinkage.

Another use for fly ash is the production of Geopolymer Cement (GPC). The term cement is perhaps a misnomer, as bonding is achieved not through a hydration reaction, but by the polymerization of aluminosilicates. The benefits of GPC are also well documented [6] [7] [8]. Like Flashag, it provides an avenue for the reuse of fly ash. It exhibits excellent resistance to sulfate and chloride degradation [9]. The polymer bond displays excellent resistance to high temperatures. Concrete produced with OPC will retain only 9% of its residual strength after heating to 1000°C [10]. This is significant as it means that, after a serious fire incident, concrete structures can be rendered structurally unsound, requiring a partial or complete knock down and rebuild. Geopolymer concretes made with regular aggregates or Flashag exhibit residual strengths of 45% and 85% respectively [6]. It is feasible that at higher temperatures, geopolymer concretes with fly ash aggregates could exhibit residual strengths of over 100%.

Due to the relative strength and stiffness differences between GPC and OPC, and Flashag and regular aggregates, GPC and Flashag cannot be used to produce high strength concrete; maximum strength achieved is in the order of 40 MPa. The limiting factor is the strength of the Flashag.

II. Project Outline

A. Project Aim

This research aims to pioneer a method to increase the strength of Flashag. It attempts to achieve this by introducing geopolymer bonding to the fly ash mixture prior to sintering, producing an aggregate with both polymeric and sintered bonding.

The initial report submitted for this research detailed numerous aims - including the trialing of three different mix designs, and a full evaluation of the aggregates yielded by each mix design. Unforeseen difficulties in the production of hybrid aggregates left these aims untenable. These difficulties are described in detail and form the basis of this report.

The project aims were revised to the following outputs:

1) Determine if the production of hybrid aggregates is feasible, and
2) Produce a method for the production of hybrid aggregates usable for follow on research.
B. Significance of Work
The strength of cement produced with GPC and Flashag is the ceiling strength of Flashag. Increasing the strength of Flashag could lead to the production of high strength, geopolymer concretes consisting of entirely fly ash based products. Concrete such as this would be suitable for a wide variety of applications, with a significantly smaller environmental footprint.

Furthermore, high strength concrete produced with improved Flashag and GPC would likely retain the excellent residual thermal properties exhibited by current products. This would have an application in critical infrastructure, where a ‘knock down and rebuild’ approach after fires is either uneconomical, or significantly impair critical functions.

C. Report Structure
Due to the iterative nature of the research conducted, the report lends itself poorly to a traditional ‘method - results discussion’ structure. Instead, the methodology will describe the common aspects of the methods used, including the mix designs, materials and general processes. The key iterations will then be discussed in detail, each with their own brief methodology, results and discussion.

III. Literature Review
A. Outline
The literature review will provide detail to substantiate many of the claims made in I. Background, as well as serve as a source of references for further reading.

B. Why concrete fails
This section provides a background to the different failure methods in regular and light weight concretes. This is important in justifying why the strength of geopolymer concretes is limited by the strength of Flashag.

1. Regular Concrete
Regular concrete is usually modeled in three phases – the aggregate, the cement matrix and the interfacial zone in between them [11]. The stress transfer in regular concrete occurs largely through the more rigid aggregates. The stress concentration lines in normal aggregate concrete can be seen in Fig 2. However, because the tensile strength of normal aggregates is higher than that of the surrounding cement matrix, failure usually occurs at the weaker interfacial zone, and propagates through the cement matrix and around the aggregates [12].

The interfacial zone is weakest due to the chemical nature of cement binder in the region immediately adjacent to the aggregate. Due to the thin film of water that develops around large aggregates during mixing, there is a tendency for the development of a 10 – 15 μm ‘transition zone’ around the aggregate. The transition zone is characterized by larger quantities of Ettringite than the bulk of the cement matrix [13]. As a result, the transition zone is the weakest point in the concrete.

2. Light weight Concrete
The failure mechanisms in light weight concrete are far more variable. First of all, light weight aggregates typically form strong bonds with the surrounding cement matrix. Therefore, light weight concrete is modeled in two phases [14] – simply the aggregate and the surround matrix [15]. Also, unlike normal aggregates, it is typical for the light weight aggregates to have a lower stiffness than the surround cement matrix. As a result, the majority of the stress is carried by the matrix. This is represented pictorially in Fig 1.

According to the FIP Manual of Light Weight Aggregate Concrete, the behavior of light weight concrete under axial loads can roughly be depicted by Fig 2[16]. When the aggregate stiffness is much higher than stiffness of the matrix, the failure will occur in the matrix. This is represented by region 1 and 1 in Fig 2, and the compressive strength of the concrete is approximately equal to the compressive strength of the mortar [17].

If the aggregates are less stiff than the matrix, the matrix will absorb proportionally more stress than the aggregate, and the concrete will have less strength than if it comprised of solely concrete. This is represented by region 2 in Fig 2. The transition between regions 1 and 2 occurs where the stiffness of the aggregate and that of the matrix are approximately equal. This threshold is termed the ‘limit strength’ denoted by $f_L$, and is achieved when the strength of a concrete sample is the same as an identical sample comprised of solely cement.
When the limit strength is exceeded, the concentration of stress around the aggregates will lead to the development of tensile stresses above and below the aggregate. This is depicted in Fig 1. These tensile stresses are assumed to be resisted by the interfacial bond between the aggregate and the concrete. If the interfacial bonds are weak, cracks will begin to propagate here and continue along the interfacial zone, leading to bulk failure. This is represented by region II in Fig 2.

If the interfacial bond is sufficiently strong to resist these tensile forces, the loading on the concrete can continue, with the aggregate assuming the majority of the tensile forces. If the aggregates are weak, the tensile stress of the aggregate will be reached before cracks in the matrix reach their maximum length, which is assumed to be the distance between adjacent aggregates in the matrix. Reaching the maximum tensile stress in the aggregate will lead to aggregate failure, and the failure of multiple aggregates will lead to failure of the concrete, denoted by region III in Fig 2. For stronger aggregates, the cracks in the matrix will reach adjacent aggregates, also causing bulk failure, denoted as region IV in Fig 2.

For very high strength matrixes, the maximum tensile stress in the aggregate will be reached before cracking in the matrix begins. In this case, the concrete is said to have reached its ‘limit compressive strength’ [16], denoted by $f_{cc}$. At this point, the strength of the concrete is governed by the strength of the aggregate. This is denoted by regions 3 and V in Fig 2.

C. Geopolymer Bonding

This section provides a description of the processes required for the polymeric binding of fly ash. This is important in justifying the methods used in the production of hybrid aggregates.

1. Geopolymerisation

Geopolymer cement (GPC) is the generic term used to describe the product of a reaction between aluminosilicates and alkaline liquids, or the polymerisation of a source material that is geological in nature [18]. This report focuses on geopolymers which use fly ash as the primary source of aluminosilicates. The reaction occurs in three phases – (1) dissolution of Si and Al from the source material, (2) hydrolysis or gelation and (3) condensation into a polysilicate 3D network, or ‘geopolymer backbone’. The general equations for the formation of geopolymer cement can be seen below [19].

\[
\text{Si-Al source} + \text{Silicates} + \text{Water} + \text{Alkaline Liquid} \rightarrow \text{Geopolymer Precursor}
\]

\[
(Si_2O_5, Al_2O_3)n + nSiO_2 + nH_2O \xrightarrow{\text{NaOH, KOH}} n(OH)_3 - Si-O-Al-O-Si-(OH)_3
\]

\[
\text{Geopolymer Precursor} + \text{Alkaline Ions} \rightarrow \text{Geopolymer Backbone}
\]

\[
n(OH)_3 - Si-O-Al-O-Si-(OH)_3 \xrightarrow{\text{NaOH, KOH}} (Na, K)^{+} - Si-O-Al-O-Si-O- + nH_2O
\]

2. Requirements for Polymerisation

Fly ash typically provides much of the silicates, and all of the alumina required for the polymerisation reaction to occur. Additional silicates are provided through the addition of Sodium Silicate. The alkaline environment is provided by both the silicates and hydroxides. Finally, although water is not 'consumed' in the
polymerisation process, it is still necessary for the reaction to progress. Further information regarding geopolymer mix designs can be found in the following references [7] [20].

Heat curing is generally recommended to improve the rate and quality of polymerization. Both curing time and temperature have an impact on the degree of polymerisation, and hence the compressive strength of the resulting geopolymer. The majority of the potential strength gain occurs during the first 24 hour period. Beyond 100 hours of curing, the strength gains are minimal [7]. Similarly, the compressive strength of samples increases rapidly as curing temperature is increased from 30 - 60 degrees. Strength increases past this point occur at a reduced rate. The equivalent of 28 day OPC strength is achieved by three days of curing, at 80°C.

3. Thermal Properties
OPC is known to lose over 90% of its compressive strength after heating to 1000°C. This is because heating causes the loss of free water caught within the cement matrix, and the dehydration of water chemically bound as calcium hydroxide within the cement binder. In addition to undermining the concrete’s chemical structure, the escaping water vapor damages the macrostructure, causing the ‘spalling’ effect [21]. Furthermore, disparity in the rates of expansion between the cement and the aggregates leads to internal microfractures, which also degrade the strength of the concrete.

GPC is, dependent on the aggregate used, capable of retaining between 50 - 85% of its compressive strength. This is mostly because there is no water chemically bound within the polymer matrix. The majority of the water is evaporated from the matrix during the curing phase. The geopolymer structure is also naturally littered with voids, which allow for water vapor to egress with minimal damage to the overall structure [6]. The strength of the structure is increased at high temperatures, as un-polymerised fly ash is sintered together. Finally, if GPC is used with fly ash aggregates, there is no disparity in rates of thermal expansion, and hence no internal microcracking.

D. Flashag
This section provides a brief outline of the material properties of Flashag.

1. Physical Properties
Flashag is a non pelleted, sintered aggregate. Unlike typical fly ash aggregates, which are smooth and rounded, Flashag is rough and angular. The surface is heavily pitted with small pores, each no larger than 0.2 mm. These pores are not continuous, and were likely formed from small bubbles dispersed through the aggregate during the manufacturing process. The aggregate properties of Flashag are compared to commercially available, pelleted and sintered fly ash aggregate and regular granite aggregates in Table 1.[1]

<table>
<thead>
<tr>
<th>Property</th>
<th>Flashag</th>
<th>SP</th>
<th>Granite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent specific gravity (SSDC)</td>
<td>1.69</td>
<td>1.72</td>
<td>2.77</td>
</tr>
<tr>
<td>Apparent specific gravity (oven dry)</td>
<td>1.61</td>
<td>1.4</td>
<td>2.74</td>
</tr>
<tr>
<td>Dry rodded bulk density (kg/m³)</td>
<td>848</td>
<td>831</td>
<td>1478</td>
</tr>
<tr>
<td>Crushing value</td>
<td>0.28</td>
<td>0.35</td>
<td>0.17</td>
</tr>
<tr>
<td>Absorption Capacity (24 hour)</td>
<td>0.034</td>
<td>0.107</td>
<td>0.027</td>
</tr>
</tbody>
</table>

It can be seen that the specific gravity of Flashag is comparable to the SP, both approximately 60% of the regular aggregate. However, the crushing value of Flashag is considerably better than that of SP. The difference in absorption capacity between Flashag and SP indicates that the voids in SP are likely continuous throughout the structure. This likely a byproduct of the pelleting process.

2. Failure of Flashag
Fig 4 shows the fracture surface concrete samples produced using Flashag and OPC (top) and GPC (bottom). In the top image, a crack can be seen running horizontally along the width of the aggregate. In the bottom image, the grey spots are in fact half aggregates. In both situations, the failures have been restricted to the aggregates, and have been arrested at the interfacial boundary. There is no obvious cracking or distress in the binder matrix. This is indicative of a ‘type 5’ failure described in B. Why Concrete Fails. At this type of failure, the ceiling strength of the concrete is limited by the strength of the aggregate. Hence, by improving the strength of the aggregate, the strength of the resulting concrete will also be improved.

![Figure 4. Fracture surfaces](image)
IV. Experimental Method

A. Methodology

The basis of this research was the development of a process for the production of hybrid aggregates. The experimental program was not predetermined. Different sample designs were chosen, based off of the additives required for polymerisation.

A 'control sample' of the original Flashag mix was also used to provide a point of reference; it was initially envisaged that the process would be modified until the original Flashag had been reproduced, then modified further if required to produce the hybrid aggregates.

The variation in water content is discussed in a following sections. The variation in superplasticizer was dependent on the maximum allowable superplasticizer content for ordinary concrete as recommended by the product data sheets.

The additive quantities were kept constant at 10% of the mass of fly ash. This ratio is within the limits used for the production of geopolymer concrete.  

The initial process was based off an approximation of the method used by O. Kayali and K. Shaw to produce Flashag. This was deemed unsuccessful in producing a suitable hybrid aggregate from any of the mix designs. From this point, the process was altered in an iterative manner.

B. Materials

1. Fly Ash

Two different types of fly ash were used during the research. The first fly ash used was commercially procured from Boral. This fly ash has been screened, and can be classified as 'Class F' in accordance with ASTM C618. The second fly ash was sourced directly from the hoppers of the Bayswater power plant. It has not been screened or processed. The composition of each can be seen in Table 3.

2. Hydroxides and Silicates

12 Molar NaOH solution was prepared by hand mixing sodium hydroxide flakes with tap water. The NaOH was mixed a minimum of 24 hours prior to the intended time of use. The 24 hour waiting time was implemented to ensure that the solids were fully dissolver prior to use. The sodium hydroxide was stored in a sealed airtight plastic container when not in use.

D Grade liquid Sodium Silicates were used, with a 1:2 NaO2: SiO2 ratio.

3. Superplasticizers

Two different superplasticizers were used. The first was Centrox MWR, a mid range, carboxylic based water reducing agent, suitable for use in high performance concrete to increase workability. The second was Daracem 100, a formaldehyde based water reducing admixture.

C. Procedure

While aspects of the procedure were modified through the conduct of the research, the four general stages remained unchanged. These will each be explained.

---

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Mix 1 (NaOH)</th>
<th>Mix 2 (Na2SiO3)</th>
<th>Mix 3 (Combination)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly Ash (kg)</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NaOH (kg)</td>
<td>0.2</td>
<td>0</td>
<td>0.065</td>
</tr>
<tr>
<td>Na2SiO3 (kg)</td>
<td>0</td>
<td>0.2</td>
<td>0.135</td>
</tr>
<tr>
<td>Super Plasticizer</td>
<td>Max</td>
<td>Max</td>
<td>Max</td>
</tr>
<tr>
<td>Water Content</td>
<td>Variable</td>
<td>Variable</td>
<td>Variable</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Boral FA (%)</th>
<th>Bayswater FA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>65.9</td>
<td>55.4</td>
</tr>
<tr>
<td>Al2O3</td>
<td>24</td>
<td>25.2</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>2.87</td>
<td>7.8</td>
</tr>
<tr>
<td>K2O</td>
<td>1.44</td>
<td>1.1</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.91</td>
<td>1.7</td>
</tr>
<tr>
<td>CaO</td>
<td>1.6</td>
<td>4.1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.42</td>
<td>1</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.49</td>
<td>0.3</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.19</td>
<td>0.45</td>
</tr>
<tr>
<td>Mn3O4</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>LOI</td>
<td>1.53</td>
<td>1.25</td>
</tr>
</tbody>
</table>

% passing 45 μm | 94% | 65%
Specific gravity | 2.28 | 2

---

2 Correspondence with Muhammad Talha Junaid.
1. **Mixing of Materials**
   All mixes were machine mixed. The order of mixing remained unchanged, as the following: (1) fly ash (2) water (3) hydroxides and silicates and (4) superplasticizers. It was key that the superplasticizer is added last, to ensure that it was not absorbed by the dry fly ash. Variables within this stage were the time allowed for mixing, the water content, the type of fly ash used and the superplasticizer used.

2. **Compaction**
   The materials were then compacted. Methods varied between hand and vibro-compaction, at varying numbers of blows and time of vibration.

3. **Curing**
   The samples were then cured for a duration of three days. The temperature of curing was varied. The purpose of the curing was twofold. Curing forms part of the original Flashag procedure, allowing the evaporation of excess water from the fly ash briquettes. The curing phase also provided the opportunity for polymerisation to occur. To ensure that polymerisation was not complete, temperatures were consistently below the optimal 80°C.
   
   In accordance with the Flashag procedure, moisture content was not controlled during curing. This is contrary to best practice when producing geopolymer concretes, where drying can cause cracking and limit polymerisation. However, as the samples were produced with the intention of crushing to form aggregates and complete polymerisation was undesirable, the controlled moisture content was neglected.

4. **Sintering**
   Following the curing phase, samples were sintered. The sintering temperature, rate of heating and time at heat were all varied during the research. Regardless of how the samples were heated, samples were allowed to cool in the kiln until they had reached room temperature. During the conduct of the research it was necessary to validate the accuracy of the kiln's inbuilt thermocouple. This was conducted using an handheld thermocouple. The exterior readings were found to be within + 10 - 0°C of the kiln readings. Hence, the temperature in the kiln was at, if not slightly greater, than the temperature specified for each mix design.

   Typical time from mixing of materials to removing the samples from the oven was six days.

V. **Phase 1 Testing - Procedure Development**

A. **Outline**
   The first two iterations of the procedure failed to produce aggregates with any degree of sintering or polymerisation. This was largely due to fundamental errors in water content, method of compaction and rate of heating. The product of each iteration will be briefly recounted, followed by a discussion of the important changes made to the procedure.

B. **Methodology**
   The varying aspects of the procedure used can be seen in Table 4.

<table>
<thead>
<tr>
<th>Mix</th>
<th>FlyAsh</th>
<th>SP</th>
<th>Water (% FA)</th>
<th>Mixing Time (m)</th>
<th>Compaction</th>
<th>Curing Time (days)</th>
<th>Curing Temp (°C)</th>
<th>Rate of Heating (°C/m)</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Boral</td>
<td>Centrox</td>
<td>20</td>
<td>5</td>
<td>Hand</td>
<td>3</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Boral</td>
<td>Centrox</td>
<td>26</td>
<td>5</td>
<td>Vibro</td>
<td>3</td>
<td>40</td>
<td>4</td>
<td>3</td>
<td>1200</td>
</tr>
<tr>
<td>3</td>
<td>Boral</td>
<td>Centrox</td>
<td>Optimal</td>
<td>20</td>
<td>Vibro</td>
<td>3</td>
<td>40</td>
<td>1.67</td>
<td>1</td>
<td>1000</td>
</tr>
</tbody>
</table>

C. **Results**

1. **Mix 1**
   The first mix samples were stopped at the end of the curing phase. At this stage, all samples were still soft, and powdery to the touch. This was indicative that no polymerisation had occurred. These samples were deemed unsuitable for sintering, and the process was not continued. Upon consultation with O. Kayali, the water content in all samples was increased to 26%. This allowed for a change from hand compaction to vibro-compaction.
2. **Mix 2**

The second mix samples appeared to fix several of the issues from the first mix design. Post curing, the control sample appeared less soft and powdery. The additive samples appeared harder and no longer powdery. From this, it was inferred that polymerisation had occurred. Breaking apart on of each sample type, large numbers of voids, approximately .5 - 1.5 mm in diameter, were found concentrated towards the top of each sample. Post sintering, all additive samples had appearance similar to that of concrete after spalling. The degree of spalling appeared proportional to the quantity of NaOH in the mix design. It was assumed that the rate of heating had been too rapid, and was reduced in subsequent mixes.

3. **Mix 3**

Excessive void formation in the top of the samples was no longer apparent. Furthermore, none of the samples had spalled. All three additive samples appeared to have sintered, with a hard, pock marked outer surface. Fig 5, from left to right displays the NaOH, Na2SiO3 and combination samples. These samples when viewed from the bottom demonstrated that the apparent sintering was only 0.5 - 2 mm thick. The insides of the aggregates appeared weak and poorly sintered. Overall, the samples were unsuitable for crushing and aggregate production. Significantly, the control sample had failed to reproduce an aggregate resembling the original Flashag.

![Figure 5](image_url)

**D. Discussion**

This section will discuss the importance of the variable changes made during Phase 1.

1. **Compaction Methods**

   It was determined that hand compaction is not suitable for the production of Flashag. Instead, the sample must be vibrated until appears to 'melt' transitioning from a wetted powder to a sheer thickening liquid. This effect could not be replicated using hand compaction. It was evident that the samples compact during this stage, as the was an observed volume reduction before and after vibrating. This degree of compaction was greater than that observed using hand compaction. It is likely that the improved compaction contributed to achieving a greater degree of sintering; the greater the number of physical contact points between fly ash molecules, the greater the degree of sintering [4].

   The time of compaction was also found to be important. Excessive compaction is likely to cause aeration of the top of the sample, causing excessive void formation. This is likely what occurred with the second mix design.

2. **Water Content**

   The Phase 1 demonstrated the importance of the water content. The water content is important if vibro-compaction is to be successful. If the water content is too low, the sample crack excessively until it resembles a powder, and will fail to transition to a sheer thickening liquid. Alternatively if the water content is too high excessive bleeding will occur during vibration. Similar to concrete, bleeding will weaken the resulting aggregate.

   The term 'Optimal' moisture content is used in this report. Optimal moisture content is deemed to be the water content, as a percentage of fly ash weight, at which the transition between powder and liquid will occur. The optimum moisture content varies with the type of fly ash, the type of superplasticizer and the quantity of aggregate. The optimal moisture contents were calculated to the nearest .5% for all mix designs used in this presentation.

3. **Rate of Heating**

   The second mix demonstrated the importance of the rate of heating. The rate of heating was assumed to be responsible for the 'spalling effect' observed on the post sintering samples. This was validated in the third mix,
where no spalling was observed. It is not yet known why the rate of heating had a greater effect on the samples containing sodium hydroxide.

E. Progression to the Second Iterations

At the conclusion of Phase One, hybrid aggregate briquettes were successfully produced. However, the variation in sintering quality between the inside and outside of the briquettes meant they were unsuitable for crushing and use as aggregates. Further iterations of the procedure were attempted in Phase 2 to attempt to overcome this issue and produce isotropic briquettes.

VI. Phase 2 Testing - Procedure Optimization

A. Outline

Work was conducted in phase 2 to attempt to overcome the apparent differential sintering in the aggregate briquettes. It was initially assumed that the cause was differential heating in the samples. The first attempt to mitigate this involved increasing the time at maximum heat to five hours. Further iterations were conducted, changing other variables as a greater understanding of fly ash sintering was developed.

B. Methodology

As summary of the procedures used in phase two can be seen in the table below.

<table>
<thead>
<tr>
<th>Mix</th>
<th>FlyAsh</th>
<th>SP</th>
<th>Water (% FA)</th>
<th>Mixing Time (m)</th>
<th>Compaction</th>
<th>Curing Time (days)</th>
<th>Curing Temp (oC)</th>
<th>Rate of Heating (oCm-1)</th>
<th>Time (h)</th>
<th>Temp (oC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Boral FA</td>
<td>Centrox</td>
<td>Optimal</td>
<td>20</td>
<td>Vibro</td>
<td>3</td>
<td>40</td>
<td>1.67</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>5</td>
<td>Bayswater</td>
<td>Centrox</td>
<td>Optimal</td>
<td>20</td>
<td>Vibro</td>
<td>3</td>
<td>60</td>
<td>1.67</td>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>6</td>
<td>Bayswater</td>
<td></td>
<td>Optimal</td>
<td>20</td>
<td>Vibro</td>
<td>3</td>
<td>60</td>
<td>1.67</td>
<td>5</td>
<td>1200</td>
</tr>
<tr>
<td>7</td>
<td>Bayswater</td>
<td>Daracem</td>
<td>Optimal</td>
<td>20</td>
<td>Vibro</td>
<td>3</td>
<td>60</td>
<td>1.67</td>
<td>5</td>
<td>1250</td>
</tr>
</tbody>
</table>

C. Results

1. Mix 4

Increasing the time at heat had no apparent effect on the apparent sintering depth, or the quality of the sintering on the inside of the briquettes.

Further research was conducted into the apparent sintering on the outside of the aggregates. J.M. Bijen stated that 'In case too much coal is present, the sintering temperature can be too high.' [4]. Furthermore, Bijen suggests that the unburnt coal produces a reducing environment within the mix. In this reducing environment, silicates react with ferrous oxides to produce ferro-silicates. These ferrous silicates have a relatively low melting point. As a result, ferrous silicates tend to form and melt around the outside of samples. The ferro-silicates form an impermeable layer, preventing the ingress and egress of gases necessary for the sintering of the inside of the sample. The readings seemed to accurately describe the observations made of the aggregate briquettes.

It was inferred that the hydroxide and silicate additives were greatly contributing to the formation of ferrous silicates. Two avenues were explored to attempt to mitigate the ferro-silicate formation. The first of these was to move to a lower carbon content fly ash. The curing temperature was increased on recommendation from O. Kayali.

2. Mix 5

Post curing, the samples appeared firmer, indicative of a greater degree of polymerisation. Otherwise, changing to an alternate fly ash had no observable effect on the aggregate briquettes produced. Curiously, the control sample still failed to resemble the original Flashag, despite being produced at the same temperature, heating rate and exactly the same fly ash.

At this stage, it was realized that the superplasticizer was also carbon based. Hence, the superplasticizer was omitted from the next mix. Furthermore, it was believed it was possible that the temperature was insufficiently
high at the given carbon content to allow for sintering. Hence, the temperature in the next mix was raised to 1250°C.

3. Mix 6
   The alterations made for this mix appeared to increase the quantity of ferro-silicates produced. This is clearly seen in Fig 6. Depth of ferro-silicate formation increased to 2 - 8 mm. The briquettes produced were completely unsuitable for crushing into aggregates. The control sample still failed to resemble Flashag, despite raising the temperature by a further 50 degrees.

   It was deduced that the small changes in carbon content appeared to have little to no effect on the ferro-silicate formation. Further research was conducted, and the previously quoted statement 'In case too much coal is present the sintering temperature can be too high.'[4] was re-evaluated. As opposed to increasing the temperature required for sintering, the un-burnt carbon in the fly ash burns during sintering, further raising the temperature of the sample. Given that the increasing temperature had led to increased ferro-silicate formation with no improvement to the interior sintering, it was decided to lower the temperature for mix 7 to 1150°C. Furthermore, a formaldehyde based superplasticizer was added to the mix.

4. Mix 7
   Due to experimental time restraints, Mix 7 was a limited mix, of only a control and hydroxide – silicate combination samples. It can be seen in Fig 7. While a slight discoloration can be seen at the edge of the briquette, the sample is largely isotropic. Breaking open the sample, it was noted that the layered discoloration had no longer occurred.

D. Discussion – Ferro-Silicate Formation
   Retrospectively, Phase 2 was spent attempting to maximize fly ash sintering, while preventing the formation of ferro-silicates. This section of the report will discuss the effect of variable changes on these two reactions.

1. Time at heat
   Several studies have demonstrated that the strength of sintered fly ash aggregates is affected by the time at maximum heat [22]. However, as this study did not progress to aggregate property testing, the effect on aggregate strength cannot be further commented on.

   However, based on the Mix 4, it can be stated that the time at maximum heat had little to no effect on the degree of ferro-silicate formation. If a hybrid aggregate could be achieved, further research would be needed to establish the optimum time at maximum heat for aggregate strength.

2. Temperature
   Prior research has been conducted into the effects of temperature on the sintering of fly ash. J.M. Bijen found that sintering can begin to occur from 900°C [4]. J.J. Biernacki et al. found the optimal temperature for the sintering of mill pressed aggregates was 1200°C [22]. O. Kayali found the optimal temperature for the production of Flashag was also 1200°C.

   No prior research has been conducted regarding the effect of temperature of ferro-silicate formation. Due to the limited number of mixes conducted, it is difficult to deduce specific rules regarding temperature and ferro-silicate formation. However, a number of generalizations can be made. First of all, ferro-silicate formation is a product of both chemistry and temperature. The effect of chemistry will be discussed later in the report. For all cases, the degree of ferro-silicate formation was proportional to temperature. From Mix 7 it can be inferred that for each mix a temperature exists at which no ferro-silicates will be produced. For the additive quantities used, there is potential that the optimal temperature for ferro-silicate formation is below the optimal temperature for sintering.

3. Additives
   The degree of ferro-silicate formation is directly affected by the chemicals added to achieve polymerization. Of these, NaOH seems to have a greater effect than the Na2SiO3. This is clearly seen in all mixes, as the hydroxide sample (10% NaOH) presented greater ferro-silicate formation than the combination samples (3.5% NaOH), which again had a greater degree of formation than the silicate samples (0% NaOH). The reason for this is currently unknown.
4. **Carbon Content**

Other research has stipulated that the reducing environment produced by the combustion of carbon during sintering is responsible for initiating the formation of ferro-silicates. During the research, the minor changes were made to the carbon content of the samples. These changes had no observable effects on the aggregates produced. There are several possible explanations for this. The carbon content (indicated by the LOI) of both fly ashes was very low (< 2%). The reductions in carbon content achieved were also small.

Most significantly, Mix 6 was likely the lowest possible carbon content achievable while producing fly ash aggregates, and still had no discernible difference in ferro-silicate formation. This shows that reducing the carbon content is not a viable avenue for further experimentation in reducing ferro-silicate formation.

E. **Discussion – General**

1. **Inability to reproduce Flashag**

The control sample in every mix was an attempt to reproduce the original Flashag aggregate. Despite using similar if not identical processes, this was not achieved. The reason for this is currently unknown. This should be of interest to the owners of the Flashag patent, as it demonstrates potential difficulties in the commercial reproduction of Flashag.

VII. **Conclusions**

This research has several achievements. It has demonstrated that the production of hybrid sintered geopolymer aggregates is difficult, but possible. The key difficulties are achieving an adequate degree of sintering, while preventing the formation of ferro-silicates. The degree of ferro-silicate formation is governed by two key factors: the temperature during sintering, and type and quantity of chemical additives. The future production of hybrid aggregates with superior properties to Flashag would involve the balancing of extra strength gained though polymerization, and the strength loss due to the lowered maximum allowable sintering temperature.

VIII. **Recommendations**

There are several key research steps that should be taken to better understand the potential for hybrid aggregates. The first step would be to determine a relationship between the key variables, and ferro-silicate formation. This could be conducted using an experimental program as pictured below.

The second key step would be to determine the key properties the aggregates produced. Key properties include specific gravity (SSDS and oven dry), crushing strength and absorption. In order to conduct these tests, it is required to produce relatively large quantities of the aggregates. In order to minimize the lab workload, this could be conducted by testing the aggregates produced at the highest allowable temperature, as these are likely to have the highest degree of sintering, and hence be the strongest.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Additive (% FA)</th>
<th>Sintering Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
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</tr>
</tbody>
</table>

Table 6
Acknowledgements

The author would like to thank O. Kayali and M.J. Junaid for their continual support during this research. In particular, this research would not have been possible without O. Kayali’s intimate knowledge of the Flashag production process. The author would also like to thank J. Baxter, D. Sharpe and M. Barrett. Their technical knowledge and expertise was paramount in enabling the experimentation conducted during this research.

Works Cited


