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ACHIEVEMENTS AND INOVATIONS IN CIVIL ENGINEERING

INITIAL INVESTIGATION INTO THE EFFECT OF IRON-SILICATE FINES ADDITION TO METAKAOLIN-BASED GEOPOLYMERS

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Abstract. *Geopolymer cement is a sustainable, high performance alternative to ordinary Portland cement. An increasing interest in the development and use of geopolymer cement has led to new research into the use of available waste materials and by-products. Aside from the typical geopolymeric materials such as metakaolin, fly ash and GGBS, other materials such as red mud and mining wastes have been found to have potential. Produced and landfilled in Bulgaria, iron-silicate fines (ISF) have been identified as an alternative material which can enhance the properties of geopolymers, as reactive component in metakaolin-based geopolymer mortars. To date, ISF has not been considered for use as a geopolymeric material. This paper presents the results of an initial study into the potential use of ISF as a component of metakaolin-based geopolymers. The effect of ISF of geopolymer mortars is considered. Increasing the ratio of ISF was found to significantly increase the mortar flow, but also increase the setting time of the mortar. The replacement of metakaolin with ISF, up to 20 %, improved the 7 day compressive strength by more than 13 %. The potential use of a synthetic geopolymer aggregate, containing ISF, as a high polished stone value aggregate was also considered. Initial testing suggest a good resistance to coarse polishing, but a much lower resistance to fine polishing. However, the study has identified that ISF has good potential for use in geopolymer applications.*

1. Introduction

With focus on the use of sustainable and environmentally responsible construction materials increasing annually, research into ordinary Portland cement (OPC) alternatives has also increased. Latest figures [1] show that OPC production accounts for 8 % of global anthropogenic CO_2 emission. The decomposition reaction involved with the calcination of limestone accounts for 50 % from the burning of fossil fuels to heat the calcination kilns. One alternative to OPC is geopolymer cement, due to its preferable environmental properties and impressive performance properties. Geopolymer cement is a 2 part cementitious binder, consisting of an aluminosilicate powder and a liquid alkaline activator [2]. CO_2 emission reductions of up to 90 % compared with OPC have been claimed [3], in addition to high mechanical strengths [4] and resistance to acid and freeze-thaw attacks [5, 6]. Despite the benefits, the use of geopolymer cement is yet to become widespread. This can be attributed to a lack of harmonised standards to govern the use of geopolymers, and lack of durability testing. While full harmonised standards do not exist at present, a Publicly Available Specification (PAS) was published in 2016 [7]. This document has set performance based requirements for alkali-activated cementitious materials (AACM) where an aluminosilicate material and an alkali activator are used to form a cementitious binder. While some researchers argue that AACMs and geopolymer cements are different materials, this PAS will include cementitious binder systems which are marketed as geopolymer cements.

Geopolymers are typically produced using metakaolin, fly ash, or ground granulated blast furnace slag (GGBS) as reactive powder sources, with materials such as red mud, basalt and granite having been considered [8], with some success. Other more uncommon materials have been tested, often as a means of using waste materials. An Austroads report discussed the successful use of materials such as pulverised recycled concrete, mine wastes and oil shale ash as geopolymeric materials [9]. One material which has not been considered for use in geopolymers in ISF. ISF is a by-product produced during the processing of copper slags. The copper slag is processed to remove the copper content for use, leaving an iron-rich residual material [10]. At present, the use of ISF, or fayalite, is limited to use as an additive by cement manufacturers during the clinker production process, or in the production of bricks, tiles and concrete blocks [10]. Beyond the construction industry, ISF can also be used as an iron source for steel palletisation [10]. With large amounts of this material available globally, its incorporation into geopolymer cement use may identify a new application for the material.

This paper discusses the initial testing of a metakaolin-based geopolymer mortar, included increasing amounts of ISF as a reactive geopolymeric component. The effect of ISF on fresh geopolymer mortar properties, and 7-day and 28-day compressive strength is discussed. Finally, as ISF has known abrasion resistance properties, this paper presents an early attempt to produce an abrasion resistant, synthetic geopolymer aggregate for use as an anti-skid aggregate.

2. Experimental Programme

2.1. Geopolymeric Materials

This study focuses on the development of a metakaolin-based geopolymer mortar, with increased amounts of ISF replacing the metakaolin. The metakaolin was sourced from Imerys UK, sold commercially as Metastar 501. The main chemical composition of the material is given in table 1. The particle size was recorded, with 80 % of the particles measuring between 0.9 and 8.2 μm. The ISF for this project was provided by Aurubis Bulgaria. The main chemical composition is given in table 1. Particle size distribution showed that 90 % of the particles measured between 0 and 70 μm.

Table 1. Typical chemical composition of Metastar 501 and Aurubis ISF.

Element	Metakaolin (%)	ISF (%)
SiO_2	55	27
Al_2O_3	40	3.2
Fe	1.4	46
CaO + MgO	0.3	2.5
TiO_2	1.5	>0.01
Zn	>0.01	1.5
Cu	>0.01	0.4

The geopolymer liquid activator was supplied by Woellner, and sold commercially as Geosil. The activator had a solid potassium silicate content of approximately 45 %, and a water content of approximately 55 %.

2.2. Mortar Mix Designs

The mortar mix designs were based on one metakaolin mix. Subsequent mixes had an increased ISF content. The first mix replaced 10 % (by mass) of the metakaolin with ISF, with the next mixes replacing up to 60 % of the metakaolin. Activator, added water, and sand contents were maintained at a constant level throughout the study. The mix designs are shown in table 2.

Table 2. Geopolymer mortar mix designs containing ISF.

	Mix Proportions (kg/m^3)					
	10 %	**20 %**	**30 %**	**40 %**	**50 %**	**60 %**
MK	488.0	433.8	379.5	325.3	271.1	216.9
ISF	54.2	108.4	162.7	216.9	271.1	325.3
Silicate	452.8	452.8	452.8	452.8	452.8	452.8
Water	134.2	134.2	134.2	134.2	134.2	134.2
Sand	1339.9	1339.9	1339.9	1339.9	1339.9	1339.9

2.3. Mortar Testing

Workability Testing

Two workability tests were carried out on each mix, to determine the effect of increased amounts of ISF on geopolymer mortar fresh properties. Mortar flow was measured using a table top flow table, in accordance with BS EN 1015 – 3: 1999 [11]. Mortar setting time was measured, according to BS EN 196 – 3: 2005 [12], using manual Vicat apparatus.

Compressive Strength

Geopolymer mortar cubes, measuring 50 x 50 x 50 mm were cast in steel moulds, wrapped in a polythene sheet for moisture retention. After 24 hours at an ambient temperature of 20 ± 2 °C, the cubes were demoulded and transferred to a sealed plastic container, stored at the same ambient temperature. Specimens were stored in the sealed container until testing. Compressive strength was measured at 7 days and 28 days, according to BS EN 1015 – 11: 1999 [13].

2.4. Synthetic Aggregate Testing

Aggregate Production

After testing the compressive strength, the highest strength mix was selected to produce the synthetic geopolymer anti-skid aggregate. The aggregate was produced by mixing the selected geopolymer paste with a percentage of fine aggregate particles (< 300 μm). The mixture was spread across a large polythene sheet to a thickness of between 5 and 10 mm to form a slab. The slab was covered, and left to cure overnight. The slab was then crushed to form aggregates sized between 1 and 3 mm. The aggregates were then transferred to a sealed container and left to cure for 28 days.

Modified Polished Stone Value (PSV) Test

The aggregates were then subjected to a modified version of the PSV test described by BS EN 1097 – 8: 2009 [14]. As the typical PSV test is used on larger aggregate particles, specimens for the modified test were formed by producing blank epoxy resin moulds. The moulds were then coated in a 3 mm thick layer of Araldite 2-part epoxy glue, which was then rolled in the geopolymer aggregate. This formed a PSV test-sized anti-skid specimen. The rest of the test was then carried out in accordance with the standard method. The samples are subjected to two, 3 hour polishing cycles. The first cycle involved resistance to polishing using coarse emery grit, and the second cycle using a fine emery corn. The friction test value was measured prior to testing, and at one hour intervals during the test. This was followed by measurement of the modified polished stone value after testing. Two calcined bauxite samples were tested as control samples.

3. Results and Discussion

3.1. ISF Geopolymer Mortars

Table 3 shows the effect of increasing amounts of ISF on the workability and compressive strength properties of metakaolin-based geopolymer mortars.

Initially, it can be seen that the inclusion of ISF, even in small quantities has a major effect on the flow properties of geopolymer mortar.

Table 3. Geopolymer mortar properties with fines

	0 %	10 %	20 %	30 %	40 %	**50 %**	**60 %**
Flow (mm)	197	>255	>255	>255	>255	>255	>255
Initial Setting Time (mins)	325	460	555	>12 hours	>24 hours	>24 hours	N/A
Final Setting Time (mins)	435	530	660	>12 hour	>24 hours	>24 hours	N/A
7 day strength	41.6	47.6	47.1	37.6	36.3	32.2	0.0
28 day strength	45.9	47.7	47.2	37.6	36.5	33.0	0.0

The mortar flow of the mix with no ISF was 197 mm. However, the replacement of 10 % of the metakaolin mass with ISF caused a significant increase in flow. The increased workability meant that flow could not be accurately measured, as the mortar flow table had a diameter of 255 mm. Therefore, all flow measurements were recorded as > 255 mm.

While the addition of ISF improved the mortar flow characteristics of the geopolymer mortar, increasing amount of ISF greatly increased the initial and final setting times of the mortars. Mixes with ISF contents greater than 20 % showed very slow setting times, with the 60 % ISF mix not setting at all. As the mortar flow continued to increase with the addition of ISF, this would suggest that the dissolution and gelation phases of the geopolymerisation had occurred. However, the longer setting times suggest that ISF was having a negative effect on the polymerisation and hardening phases of geopolymerisation. As heat curing on geopolymers is a more common mechanism than ambient curing, it may be the case that geopolymers with higher amounts of ISF are not suitable for ambient curing, instead requiring some additional heat source to promote the hardening phase of geopolymerisation in the early stages of curing.

The addition of ISF was also found to have an effect on the compressive strength of geopolymer mortar. The replacement of 10 % metakaolin with ISF increased the 7 day compressive strength by 13 %, from 41.6 N/mm^2 to 47.6 N/mm^2. The addition of 20 % ISF showed a slight decreased in strength after 7 days, compared with the 10 % mix but still an improvement on the 7 day strength without ISF. As the ISF increased further, the 7 day compressive strength started to decrease dramatically. The mix with 30 % yielded a 7 day compressive strength of 37.6 N/mm^2, the 40 % mix had a strength of 36.3 N/mm^2, and the 50 % mix, a strength of 28.9 N/mm^2. No compressive strength was recorded for the 60 % ISF mix, as this mix did not set.

Similar trends were noted for the 28 day compressive strengths. The 7 day and 28 day compressive strengths are illustrated in figure 1.

It can be noted that the geopolymer mortars showed minimal strength development between 7 and 28 days, with more than 95 % of the 28 day strength achieved after 7 days for all mixes.

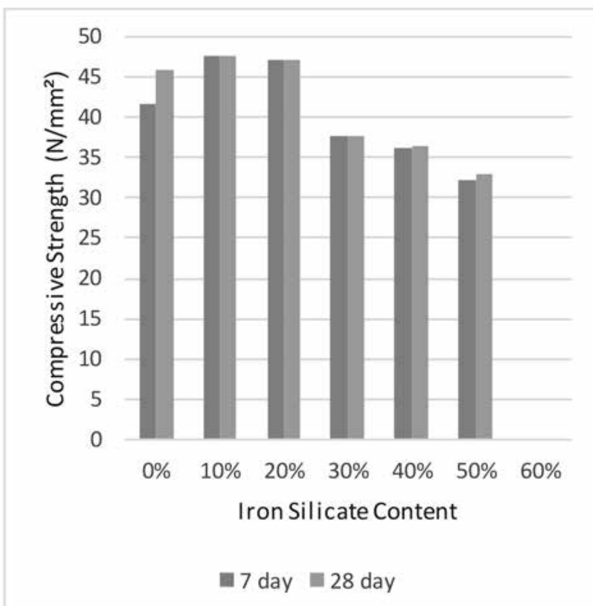

Figure 1. Effect of ISF on compressive strength.

3.2. Synthetic Geopolymer Aggregate

Synthetic geopolymer aggregates were produced containing 10 % ISF, selected based on its high compressive strength. Table 4 and figure 2 show the development of the polished stone value at hourly intervals during the test. From these results, the resistance of the ISF geopolymer to polishing from the coarse abrasive is similar to the grey bauxite specimen. However, fine abrasive polishing has a significant effect on the friction test value, with 1 hour of fine abrasion causing thee FTV to drop from 74.3 to 63.7.

Table 4. Modified PSV friction tester values at hourly intervals during testing

	T_0	T_1	T_2	T_3	T_4	T_5	T_6
Geopolymer Aggregate	77	77	74	74	64	66	63
Buff Bauxite	96	86	85	85	83	82	78
Grey Bauxite	92	80	82	76	74	72	74

Overall, the modified polished stone value of the ISF was significantly lower than the measured values for the calcined bauxite samples. However, the performance of the geopolymer aggregate during the first 3 hour testing using the coarse abrasive is promising.

4. Conclusions

This study considered the potential use of ISF, an industry by-product, as a reactive component in novel geopolymer cement systems. The effect of increasing amounts of ISF on the workability of fresh geopolymer mortar was considered. It was found that even a small addition of ISF had a major effect on both the flow and setting time. The flow values increased beyond the capability of the measuring apparatus, suggesting the need for an alternative method for determining the accurate flow value for these mortars. However, the increase in flow also resulted in an increase in initial and final setting times. The addition of 10 % ISF increased the final setting time by more than 15 %, with the setting times continuing to increase until the mortar containing 60 % ISF did not set.

The addition of ISF was also found to have an effect on the compressive strength of geopolymer mortar. Mixes containing 10 % and 20 % ISF exceeded the 7 day and 28 day compressive strengths measured for the control mix with no ISF. Beyond 20 %, however, the 7 day and 28 day compressive strengths fell below the control sample strengths. It was also noted that all the ISF mixes achieved at least 95 % of their 28 day strength after 7 days. This is compared with 91 % for the control mix.

Finally, the potential use of ISF as a component in a synthetic geopolymer aggregate was considered. During a modified polished stone value test, it was discovered that while the aggregate provided a modified PSV much less than the industry standard calcined bauxite, the aggregate containing ISF performed well during exposure to coarse abrasion, exhibiting minimal friction loss. However, the ISF-containing geopolymer was more susceptible to fine polishing, causing the friction tester value to decrease significantly during the second phase of the PSV test.

Overall, this study has indicated that ISF has some potential for use as an additional component in geopolymer cements. Based on these initial results, further testing is ongoing to improve the abrasion resistance of synthetic geopolymer aggregates.

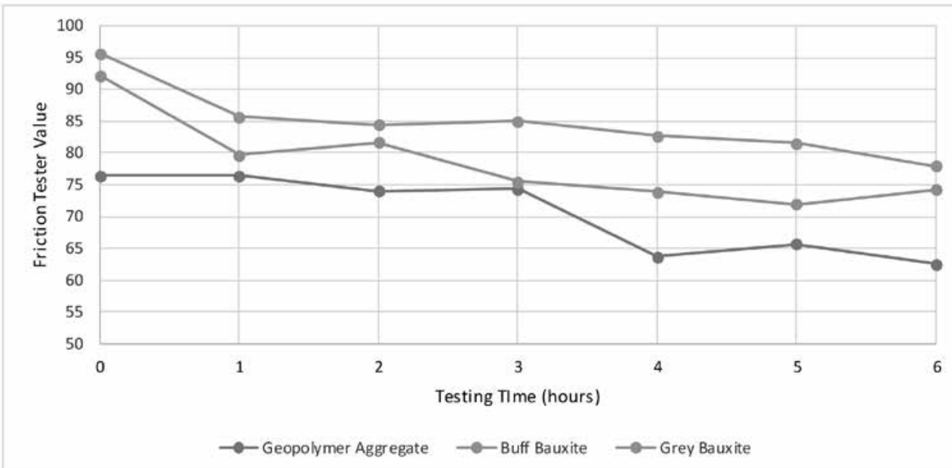

Figure 2. Friction tester values at hourly intervals during the modified PSV test

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