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Effect of milling and acid washing on the pozzolanic activity of incinerator sewage sludge ash

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ABSTRACT

Incinerator sewage sludge ash (ISSA) is a problematic waste that contains significant levels of phosphates, primarily in the form of whitlockite ($Ca_3(PO_4)_2$). Phosphate is a valuable finite resource, and a number of studies have shown that it can be extracted from ISSA by acid washing. This produces an acid washed residue that has potential to be used in construction products. The effects of milling and acid washing on the pozzolanic activity of ISSA have been evaluated using the strength activity index (SAI) test and the Frattini test. Coal fly ash (FA), metakaolin (MK) and quartz sand were also tested for comparison. Milling improved the pozzolanic activity of FA and ISSA according to both the SAI and Frattini tests. If ISSA is acid washed to recover phosphate, the process is likely to produce an acid insoluble material with little or no pozzolanic activity. The Frattini test is considered a more suitable method for directly assessing pozzolanic activity as a range of factors can affect SAI test results.

1. Introduction

Concern over carbon dioxide emissions associated with the manufacture of Portland cement has led to increased interest in the use of pozzolans in construction products. Pozzolanic activity arises from the reaction of amorphous silica with $Ca(OH)_2$ to form calcium silicate hydrate gel. The American Society for the Testing of Materials (ASTM C125) defines a pozzolan as a siliceous or siliceous and aluminous material which, in itself possesses little or no cementitious value, but which will in finely divided form, in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

A number of test methods have been developed to measure pozzolanic activity. Direct test methods monitor the reduction in $Ca(OH)_2$ with time as the pozzolanic reaction proceeds, using analytical methods such as X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) or chemical titration. Examples of titrimetric methods include the Frattini test [1–3], the saturated lime test [4–7] and the Chapelle test [8]. Indirect tests involve the measurement of physical properties related to pozzolanic reactions such as compressive strength [3,9,10] electrical conductivity [5,11,12] or heat evolution by conduction calorimetry [13,14]. Results from indirect pozzolanic activity tests are often corroborated using direct tests to confirm that pozzolanic reactions are occurring.

Industrial by-products that could potentially be used as pozzolanic materials include paper sludge ash [4], sugar cane straw and bagasse ash [6,8,15], wheat straw ash [16], rice husk ash [17], calcined red mud [18], catalytic cracking residue [19,20], incinerator bottom ash [9], crushed brick [3], waste glass powder [10] and sewage sludge ash [21]. The use of these materials as partial replacements for cement confers the environmental benefits of waste re-use and carbon dioxide savings by reducing cement content. A key point in ASTM C125 is that the pozzolan should be finely divided to improve the rate of reaction and therefore pozzolanic materials are often milled to increase reactivity.

Legislative barriers for sewage sludge disposal to sea and a negative public perception regarding the application of sewage sludge to agricultural land have led to an increase in sludge incineration. This reduces the sludge volume by ~95%. A typical incineration plant will dewater sewage sludge to 25–30% dry solids before combustion in a fluidised bed furnace at 800–900 °C. The ash generated is separated from exhaust gases in filter bags or via electrostatic precipitators prior to gas scrubbing. The separated fly ash contains high levels of phosphate, typically 10–20% mass as P_2O_5. It is estimated that 1.2 million tonnes of incinerator sewage sludge ash (ISSA) are currently produced annually in the EU and North America [22] and a further 0.5 million tonnes/yr in Japan alone [23].

ISSA disposal to landfill represents a loss of phosphate and a possible cement replacement material. Acid washing of ISSA to recover phosphate has been reported, with average extraction efficiencies of 76% and 61% achieved using H_2SO_4 and HCl at pH 1.5,

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respectively, while 1.8 M H_2SO_4 resulted in a removal efficiency of 90% [24]. Other research has shown 90% phosphate extraction by leaching with sulfuric acid at pH 2 [25], 85% of total phosphate was recovered by leaching with 1 M HCl [26] and 66–99% phosphate was removed using 2.5 M H_2SO_4 [27]. After recovering phosphate from ISSA an acid insoluble residue remains.

The primary objective of this work was therefore to investigate the pozzolanic activity and crystalline phase chemistry of ISSA before and after acid washing to remove phosphate. For comparison, the effects of milling and acid washing on pozzolanic activity and crystalline phase chemistry on coal fly ash (FA), metakaolin (MK) and inert silica sand have also been assessed. Furthermore, the effect of pozzolanic activity method on results has also been evaluated by applying two different standardised tests for each test material, one direct method (EN 196-5) and one indirect method (ASTM C618).

2. Experimental

2.1. Materials and characterisation methods

The materials used were ISSA (United utilities, Widnes, UK), coal fly ash (FA, Drax Power Station, UK), metakaolin (MK, Metastar 501, Imerys Minerals Ltd.) and natural quartz sand. The pH was determined by preparing 5:1 liquid to solid ratio suspensions using deionised water. The mixture was shaken for 5 min and left for 3 h to equilibrate before measuring the pH (BS 7755-3.2). Particle size distribution over the range 0.4–900 μm was determined by laser diffraction (Beckman Coulter LS-100). The specific surface area of materials was determined by N_2 adsorption (Coulter Omnisorp 100) using the Brunauer–Emmett–Teller (BET) method. Specific gravity was determined using a pycnometer.

The particle morphology of milled and as-received materials were characterised on carbon-coated samples using scanning electron microscopy with 20 kV anode voltage (JEOL-JSM-840A). X-ray diffraction (XRD) of as-received and acid washed samples was used to determine changes in crystalline phases present (Philips PW 1700 using Cu Kα radiation at an acceleration voltage of 40 kV and a current of 40 mA).

2.2. Milling, acid washing and pozzolanic activity assessment

2.2.1. Milling

Dry milling used a tungsten carbide Tema mill (Gy-Ro, Glen Cresten Ltd.). Test materials were milled for 1, 2 and 3 min. Milling of MK was found to cause agglomeration and therefore milled MK was not tested for pozzolanic activity.

2.2.2. Acid washing

Sulfuric acid was used as it has been extensively used in other research [24–27]. It is the main acid used for industrial scale phosphoric acid production and is comparatively cheap and widely available. Three hundred grams of ISSA, FA, MK or sand were weighed into 2 L conical flasks and 900 mL of 4 M H_2SO_4 added to each flask. The flask tops were sealed and shaken for 20 min. The slurry was then passed through hardened ashless filter paper under vacuum. The retained solids were oven dried at 105 °C before being dry-milled for 2 min. In the case of FA and MK, the oven dried material had to be manually broken into smaller lumps before milling.

2.2.3. Pozzolanic activity tests

Standardised tests were used to measure pozzolanic activity, the strength activity index (SAI) test, an indirect method, and the Frattini test, a direct method.

2.2.3.1. Strength activity index (SAI) test (adapted from ASTM C618-05). The SAI test requires that a mortar with 20% of the cement replaced by the test pozzolan develops a minimum of 75% of the compressive strength of a reference mortar containing only cement and sand after 7 and 28 days.

Four hundred and fifty grams of CEM-I and 225 mL water were mixed at low speed for 30 s. 1350 g of sand (coarse sand sieved <2 mm) was then added and mixed for a further 30 s at low speed followed by high speed mixing for 30 s. The paste from the sides and bottom were manually scraped and homogenised before being re-mixed at high speed for 60 s. The resulting mortar paste was subjected to a flow test (BS EN 1015-3) to determine the mortar spread on a flow table. After the flow test the paste was returned to the bowl and mixed at a low speed for 30 s before casting into six 50 mm cube moulds on a vibrating table.

Mixtures containing pozzolans were prepared using the same procedure as control mortar above except that 20% of the cement was replaced by unmilled, milled or acid washed and milled pozzolan. Where the replacement of cement by a pozzolan altered the mortar flow, the water content was adjusted so the flow was within 5 mm of the control mortar. The amount of water required for each mixture was previously determined and is given in Table 1. The consistency of acid washed and milled pozzolan mortars was not investigated and the water/cement ratio used the same as for the dry-milled samples to prevent results being influenced by changes in water content.

Blocks were de-moulded after 24 h and cured in a water bath at 23 °C. After 7 and 28 days the blocks were removed, surface dried and tested for compressive strength (Contest Instruments Ltd model GD10-A compression machine, loading rate 300 kPa/s).

2.2.3.2. Frattini test (BS EN 196-5). The Frattini test requires that a mixture of cement and test pozzolan containing between 6 and 55% by mass of pozzolan removes $Ca(OH)_2$ produced by cement hydration from solution so that after 8 or 15 days, the solution is not saturated with $Ca(OH)_2$. Test samples consisted of 20% test pozzolan and 80% CEM-I by weight, with 100 mL of distilled water as described in Table 2. Samples were left for 8 days in a sealed plastic bottle in an oven at 40 °C. They were then vacuum filtered (Whatman No. 542 filter paper, nominal pore size diameter ~3 μm) and the filtrate cooled to ambient temperature in a sealed bottle. The filtrate was analysed for $[OH^-]$ by titration against dilute HCl with methyl orange indicator and for $[Ca^{2+}]$ by pH adjustment of the HCl titrated solution to 12.5 followed by titration with 0.03 M EDTA solution in the presence of Patton and Reeders reagent.

According to BS EN 196-5, results are plotted with [OH] in mmol/L on the *x*-axis and [CaO] in mmol/L on the *y*-axis. The standard solubility curve of $Ca(OH)_2$ is plotted and a control sample of 100% CEM-I is tested to ensure that the result lies on the saturation curve. Test results below this line indicate a positive removal of Ca^{2+} from solution which is attributed to pozzolanic activity.

3. Results and discussion

3.1. Effect of milling on test materials

Fig. 1 shows the effect of milling time on the average particle size of FA, ISSA and sand. After two minutes of dry milling the materials all had similar average particle size ~10 μm. As there was little further particle size decrease after 3 min, it was decided to carry out pozzolanic activity tests on samples milled for 2 min.

Table 1 shows the physical properties of the materials before and after milling. The surface area of unmilled sand was too low to measure accurately by the BET method, but after milling the surface area was 5.6 m^2/g. Milling reduced the mean particle size of

Table 1
Effect of milling on physical properties of FA, ISSA and Sand.

	FA		ISSA		MK	Sand	
	Unmilled	Milled[d]	Unmilled	Milled[d]	Unmilled	Unmilled[a]	Milled[b,d]
pH	10.4		7.2		4.8	8.3	
Mean particle size (μm)	31.3	11.6	140.8	7.5	6.6	113.3	9.8
d_{10}[c]	2.3	1.2	13.5	0.8	1.1	25.4	0.9
d_{50}[c]	19.4	6.8	106.8	4.8	4.2	118.3	5.4
d_{90}[c]	81.0	30.6	314.4	18.6	15.6	180.8	26.4
BET surface area (m^2/g)	7.2	10.0	6.4	19.9	17.3	[a]	5.6
Dry loose bulk density (ton/m^3)	0.93	0.89	0.68	0.76	0.29	1.45	0.89
Specific gravity	1.97	2.11	2.43	2.16	2.23	2.20	1.92
Water requirement[e]	1.04	0.98	1.16	1.00	1.23	1.01	0.96

[a] Unmilled sand was passed through a 150 μm sieve and the surface area would be too low for BET surface area analysis.
[b] Only the sand fraction passing a 2 mm sieve was used for milling experiments.
[c] $d_{10}/d_{50}/d_{90}$ – 10%/50%/90% of particles have diameters smaller than this size (μm).
[d] The data are from 2 min milling trials.
[e] Water requirement is the relative quantity of water added to test mortars in the SAI test to achieve the same flow as the control mortar (3 parts 2 mm sieved sand to 1 part PC), with a w/b ratio of 0.5.

Table 2
Mix proportions used in SAI and Frattini tests.

Test	Pozzolan (g)	H_2O (g)	Pozzolan (g)/cement (g)	Mortar sand (g)[a]	w/b Ratio[b]
SAI	n/a (control)	225	0/450	1350	0.50
SAI	FA	234	90/360	1350	0.52
SAI	Milled FA	220.5	90/360	1350	0.49
SAI	Acid FA	220.5	90/360	1350	0.49
SAI	ISSA	261	90/360	1350	0.58
SAI	Milled ISSA	225	90/360	1350	0.5
SAI	Acid ISSA	225	90/360	1350	0.5
SAI	MK	272	90/360	1350	0.605
SAI	Acid MK	272	90/360	1350	0.605
SAI	Sand[c]	227.5	90/360	1350	0.51
SAI	Milled sand[d]	216	90/360	1350	0.48
SAI	Acid sand	216	90/360	1350	0.48
Frattini	n/a (control)	100	0/20	n/a	5.0
Frattini	All test samples	100	4/16	n/a	5.0

Note that for all Frattini tests, the water to binder ratio was constant at 100 g:20 g and for all samples except the control, the pozzolan to cement ratio constant at 4 g:16 g for all test samples.
[a] Sand fraction passing a 2 mm sieve.
[b] w/b stands for water/binder ratio and binder is sum of cement and test pozzolan.
[c] Sand fraction passing a 150 μm sieve.
[d] Milling of <2 mm fraction as there was not much material <150 μm.

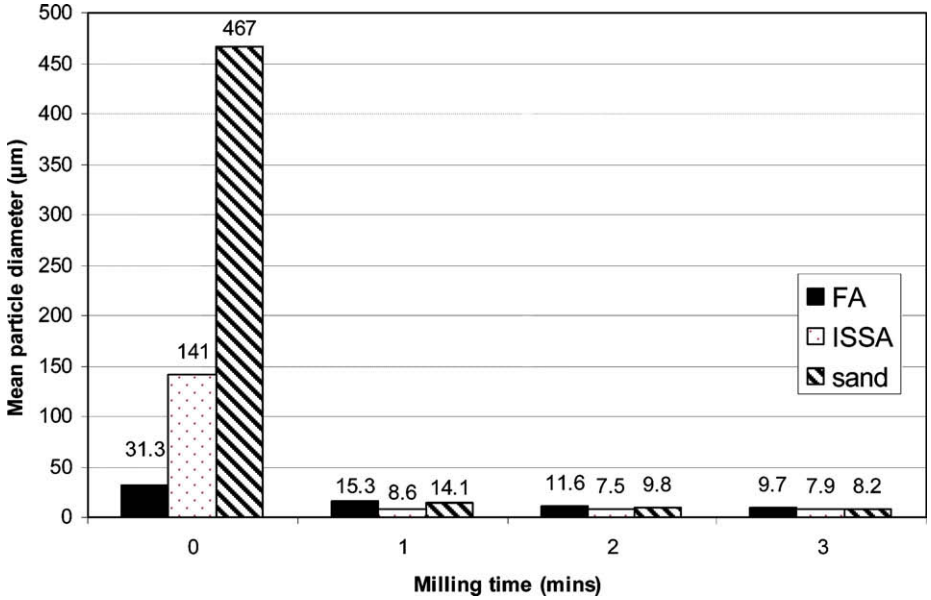

Fig. 1. Effect of Tema milling time on average particle size of FA, ISSA and sand.

ISSA by a factor of 18, although the surface area only increased by a factor of 3. A significant fraction of the original ISSA surface area must therefore be derived from open and interconnected internal pores in larger particles. The higher water requirement of unmilled ISSA is due to trapping water in pores of larger particles during mixing and casting.

Fig. 2 shows the physical morphology of FA, ISSA and sand particles before and after dry milling for two minutes. Irregular particles larger than 100 μm in as-received samples are completely broken down by milling. Some of the smaller cenospheres in FA have also been destroyed.

3.2. Effect of milling on pozzolanic activity results

3.2.1. The effect of milling on the SAI test

Milled FA and ISSA both show improved strength development compared to unmilled material. After 7 days the improvements in SAI show some correlation with the relative increase in surface area caused by milling. However, after 28 days such a correlation was not evident. Unmilled ISSA and unmilled sand failed to meet the ASTM requirement of SAI greater than 0.75 after 7 and 28 days, although the respective milled materials did meet the requirement. Milled sand passed the test for pozzolanic activity and this is a concern as this material consists of crystalline, non-reactive silica. Milled sand mortar had a lower water requirement and this fine sand may be a more effective filler. Possible changes to the ASTM requirement to prevent this type of misleading result could involve increasing the required SAI value, although the curing time would also need to increase to allow for slower reacting pozzolans. Another possibility would be to increase the cement replacement level to 25% or 30%.

It is uncertain whether the increase in strength with milling is due to: (a) the reduced water in the mortar; (b) the milled material having greater available amorphous silica surface area and thus greater pozzolanic reactivity; (c) the finer materials acting as improved fillers or (d) a combination of these factors. Dry milling of FA, ISSA and sand reduced the water requirements from 1.04 to 0.98, 1.16 to 1.00 and 1.01 to 0.96, respectively. The reduced water requirement after milling was the opposite of the expected effect. MK and silica fume contain many sub-micron particles and have characteristically high water requirements due to their fineness. It is possible that by milling until the mean particle diameter is ~10 μm, the ISSA, FA and sand particles are at an optimum size distribution where they are small enough to avoid absorption of water inside large, porous particles but also not so small that adsorption of water to external surfaces increases the water requirement.

The significance of the change in water requirement is the subject of further research. If the SAI test procedure specified a fixed w/b ratio and consistency with the use of a requisite quantity of super-plasticiser, the doubts over the influence of different water requirements could be avoided. However, it should be noted that the MK mortar paste had the highest water requirement to achieve standard flow, but still showed the greatest compressive strength development.

3.2.2. The effect of milling on the Frattini test

Fig. 8 shows qualitative results for the pozzolanic activity of milled, unmilled and acid washed test materials. Data points on or above the lime solubility curve indicate zero pozzolanic activity. The further below the solubility curve a point is at any given [OH] the greater the pozzolanic activity. Control samples were previously tested and produced points directly on the lime solubility curve, illustrating that 8 days at 40 °C was sufficient time for cement hydration to create a saturated $Ca(OH)_2$ solution. Milling clearly improves the pozzolanic activity of FA and ISSA, yet makes no improvement for sand, which remained inert. MK was by far the most reactive material.

The water requirement is not a factor in this test as the w/b ratio is extremely high and constant. Improved Frattini test results must therefore be a consequence of a suitable reactive surface available, with the surface area being increased by milling.

3.3. Effect of acid washing on test materials

Washing with 4 M H_2SO_4 had a noticeable effect on the test materials. ISSA and sand had a grittier texture, possibly due to the formation of crystalline sulfates. FA hardened into a solid but

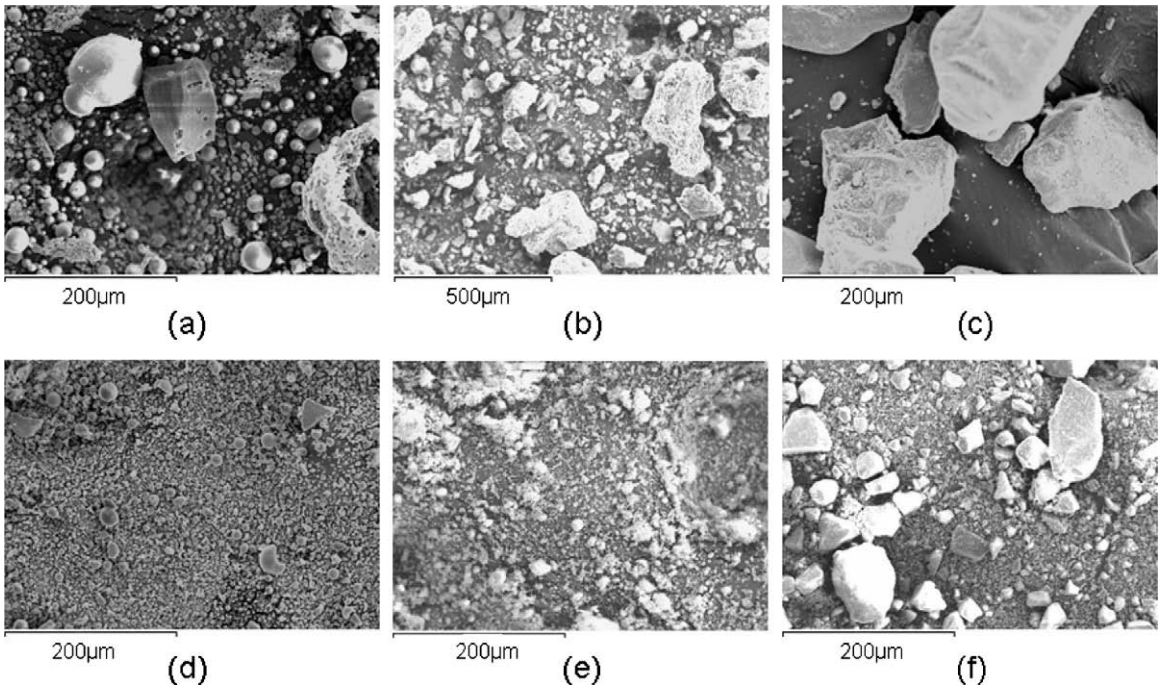

Fig. 2. SEM images of (a) FA, (b) ISSA and (c) sand as-received, compared with (d) milled FA, (e) milled ISSA and (f) milled sand after 2 min in a Tema mill. Secondary electron images, carbon coated, 20 kV anode voltage.

friable mass and MK hardened into a solid mass that was difficult to break.

XRD data of materials before and after acid washing is shown in Figs. 3–6. Mullite and quartz in FA and were not affected by acid washing. However, low levels of Ca must be present in amorphous form, because after acid washing detectable levels of calcium sulfate hydrate were found. Acid washing of ISSA caused complete dissolution of Ca and P from whitlockite and precipitation of $CaSO_4$. After filtration of ISSA-acid slurries in a preliminary study, >95% of the total phosphate was in the filtrate. No increase in amorphous

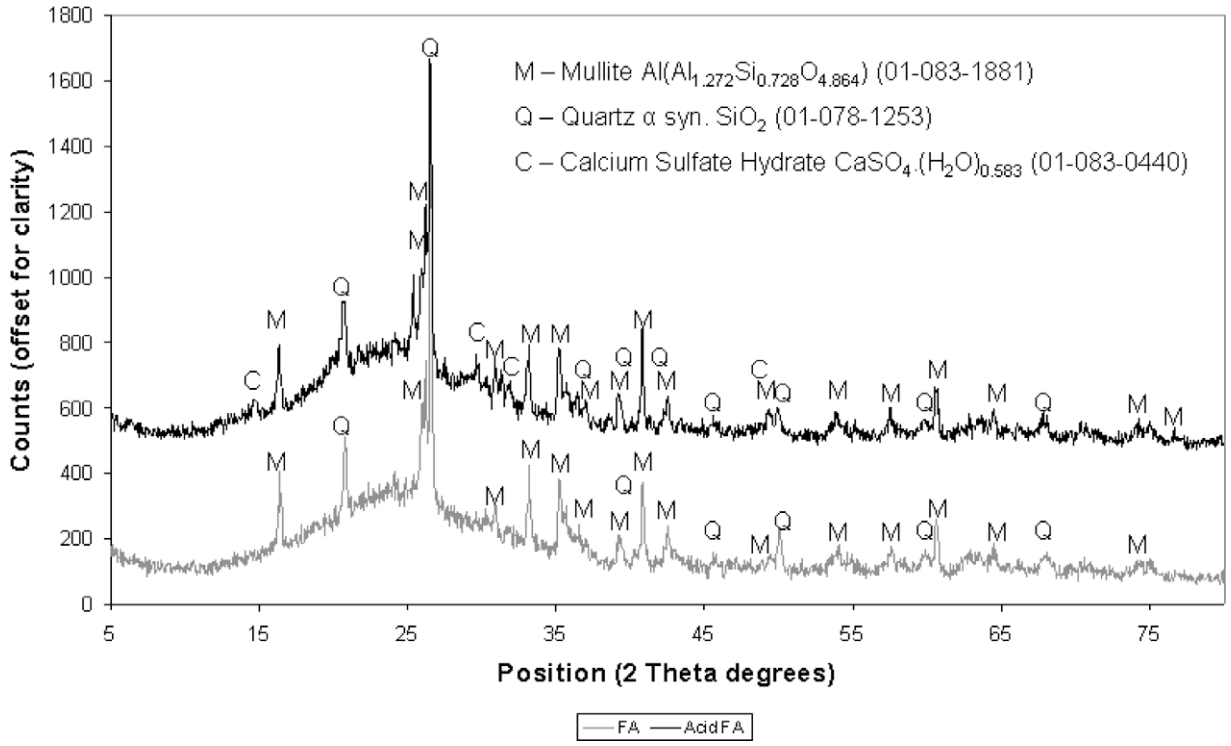

Fig. 3. XRD of FA before (bottom) and after (top) acid washing with 4 M H_2SO_4 for 20 min at ambient temperature.

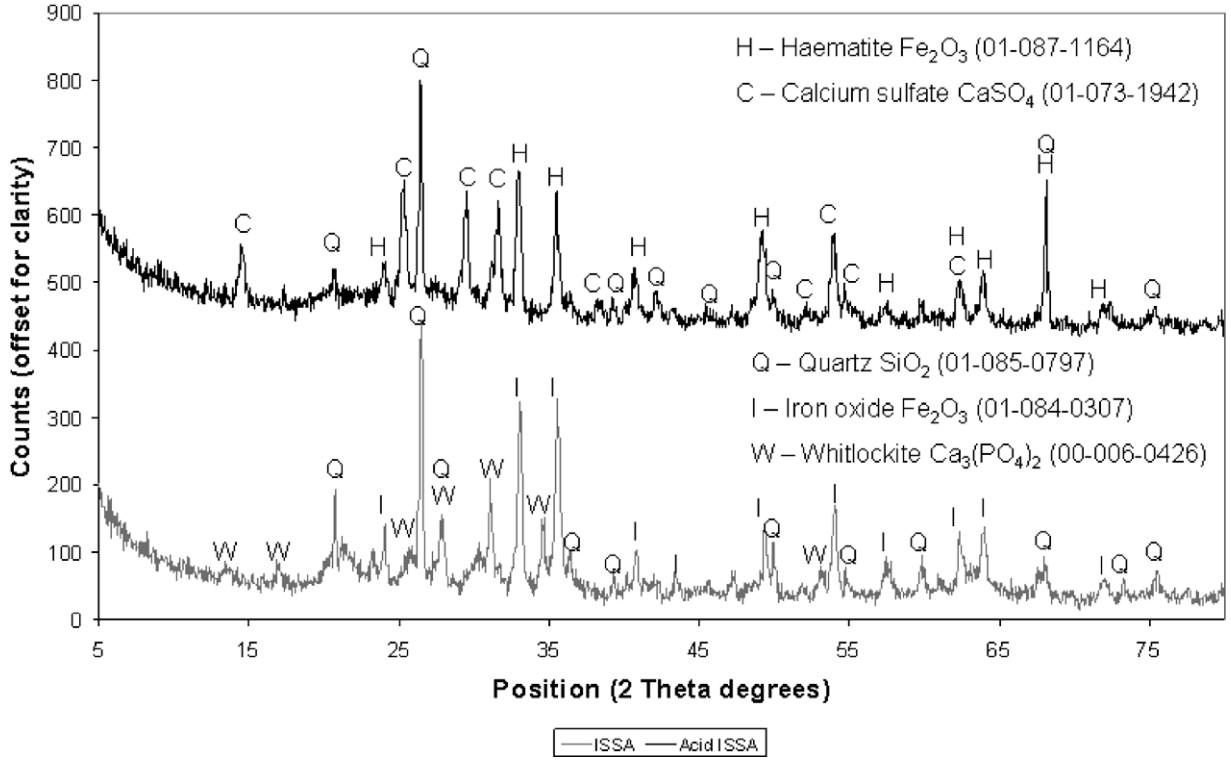

Fig. 4. XRD of ISSA before (bottom) and after (top) acid washing with 4 M H_2SO_4 for 20 min at ambient temperature.

silica occurred, and haematite and quartz present in ISSA were not affected by acid washing.

Acid washing had a dramatic effect on the mineralogy of MK. After drying the insoluble residue, the particles set into a hardened paste. XRD revealed high levels of amorphous silica both before and after acid washing. Quartz, calcium mica and orthoclase were detected in the original MK. After acid washing orthoclase and calcium mica were not detected, with the dominant crystalline phases being; potassium aluminium sulfate hydroxide, potassium hydrogen sulfate, sodium aluminium silicate and polyhalite. There was no observable change to the level of quartz or amorphous silica in sand after acid washing.

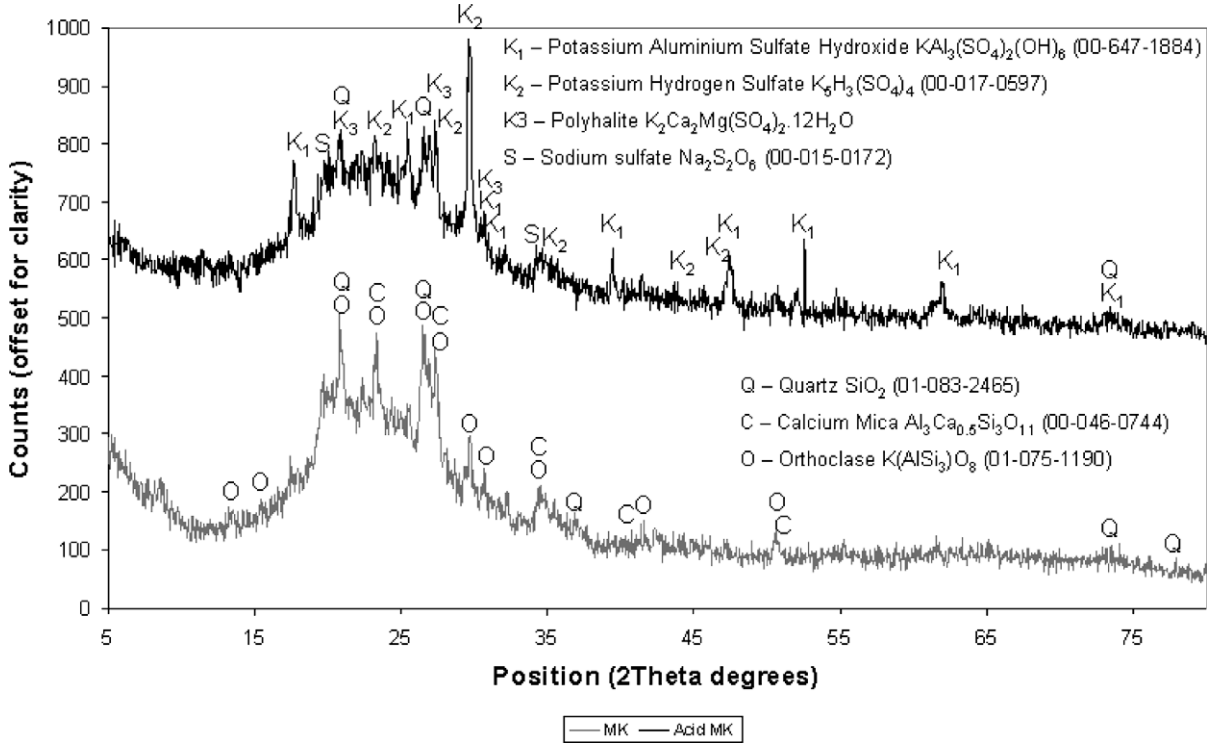

Fig. 5. XRD of MK before (bottom) and after (top) acid washing with 4 M H_2SO_4 for 20 min at ambient temperature.

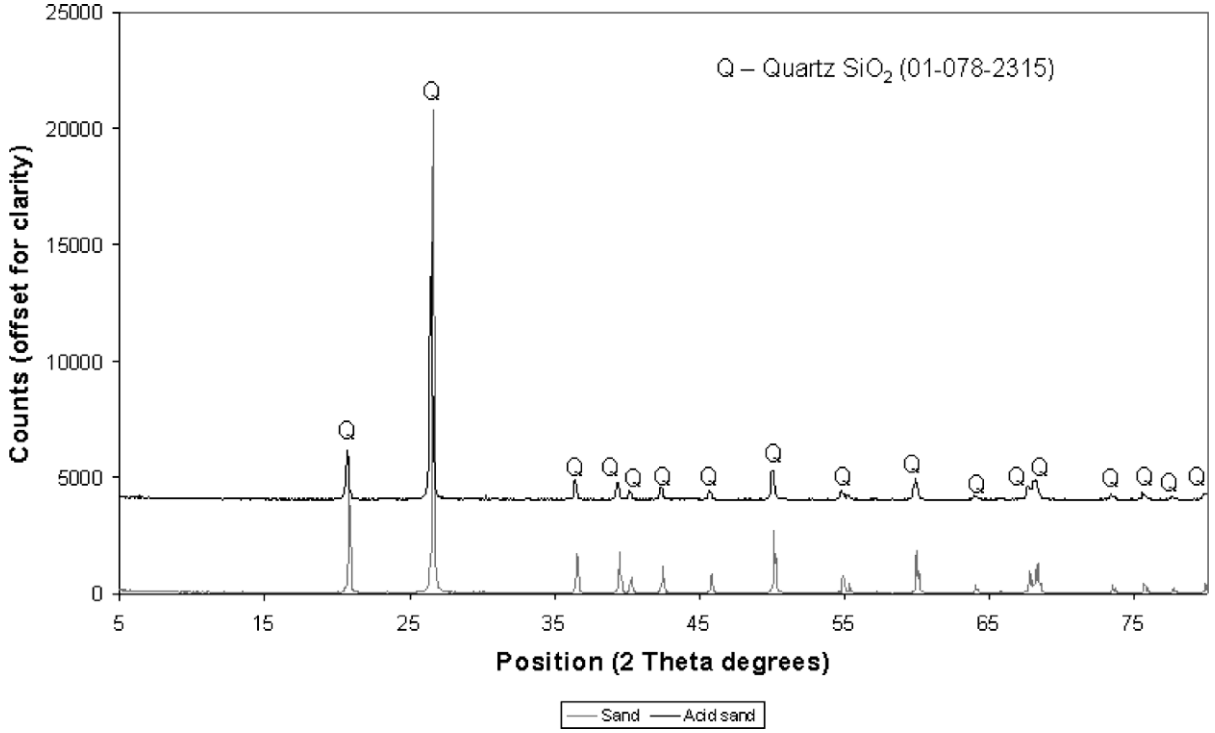

Fig. 6. XRD of sand before (bottom) and after (top) acid washing with 4 M H_2SO_4 for 20 min at ambient temperature.

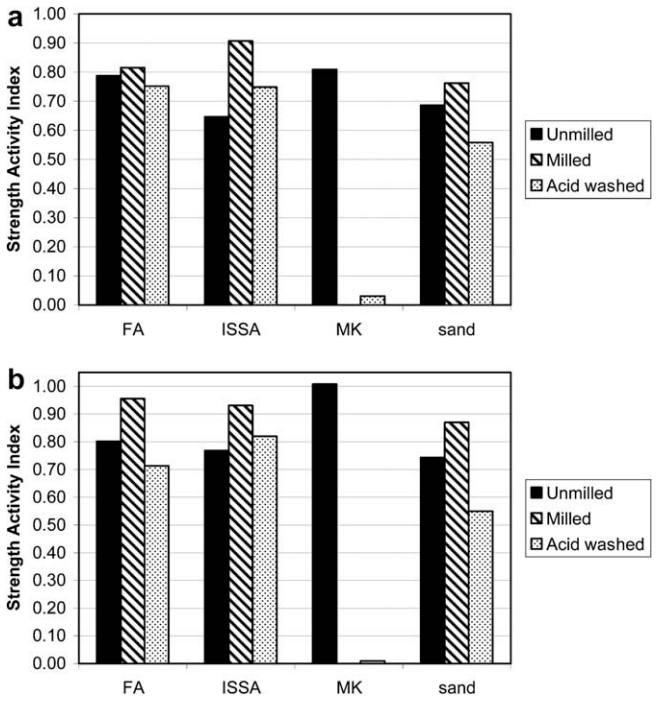

Fig. 7. SAI of milled, unmilled and acid washed test pozzolan mortars after (a) 7 days and (b) 28 days. 3:1 Sand:cement mortar blocks were cast from mixtures described in Table 2, results are averages of three replicates. Note that no milled MK mortar was prepared due to agglomeration of particles during the milling process. Reference mortar compressive strength (SAI = 1.00) after 7 days was 39.87 MPa and after 28 days was 49.84 MPa.

3.4. Effect of acid washing on pozzolanic activity results

Due to agglomeration of particles during drying and to isolate the effect of acid washing, acid washed samples were milled for 2 min and mortars prepared with an identical w/b ratio to the milled samples.

3.4.1. Effect of acid washing on SAI results

Fig. 7 shows that for FA and sand, the positive effect of milling is reversed by acid washing prior to milling. Acid washing ISSA had a negative effect on strength development compared to milled ISSA but develops slightly more strength than untreated ISSA. The most significant effect of acid washing was on MK, which, despite mortar blocks setting satisfactorily, caused a complete failure of strength development in test mortars cured under water.

The presence of $CaSO_4$ phases in acid washed FA and ISSA confirms that ettringite formation is a factor in lowering the rate of strength development and adversely affecting SAI results. Since no change occurred in the mineral phase composition of sand during the acid washing process, the negative effect of acid washing on sand SAI must be due to residual sulfate ions present in the sand particles causing subsequent ettringite formation in test mortars. With MK, crystalline sodium and potassium sulfates were detected by XRD. Whereas gypsum would simply decrease the rate of strength development, the presence of sodium and potassium sulfates in acid washed MK mortars has completely inhibited strength development.

3.4.2. Effect of acid washing on Frattini test results

Fig. 8 shows that acid washing of FA produced a slight pozzolanic activity, but to a lesser extent than the milled or as-received FA. Acid washed ISSA, MK and sand all showed no pozzolanic activity according to the Frattini test.

Strength development is not a factor in the Frattini test, which relies on the behaviour of dissolved and solid calcium species to distinguish between active and inactive materials. Portland cement hydration results in a saturated solution of $Ca(OH)_2$ and the presence of reactive silicate and aluminate surfaces in test pozzolans ensures removal of dissolved Ca from solution. While the reduction in pozzolanic activity with acid washing corresponds to the SAI results it is still surprising to see zero activity results for FA and ISSA because sulfuric acid washing could introduce a positive bias to results with the Frattini test. The effect would be caused by the presence of extra SO_4^{2-} ions in acid washed samples that could precipitate Ca^{2+} as $CaSO_4$, providing a means to remove Ca^{2+} from solution. The negative or reduced Frattini test results for acid washed materials confirm that this is not occurring.

The reduction in MK pozzolanic activity according to the Frattini test is difficult to explain because the presence of high levels of crystalline sulfates and the fact that a high level of amorphous silica is still present in acid washed MK should cause high removal of dissolved Ca^{2+} by pozzolanic reaction or gypsum precipitation. The most likely reason for this is that formation of new sulfate phases during acid washing coat MK particles and inhibits Ca ions from reacting with amorphous Si surfaces. With ISSA and FA, the same phenomenon could involve forming $CaSO_4$ coatings.

3.5. Suitability of pozzolanic activity methods

The SAI test represents an indirect pozzolanic activity test that is important when considering pozzolans as cement replacement

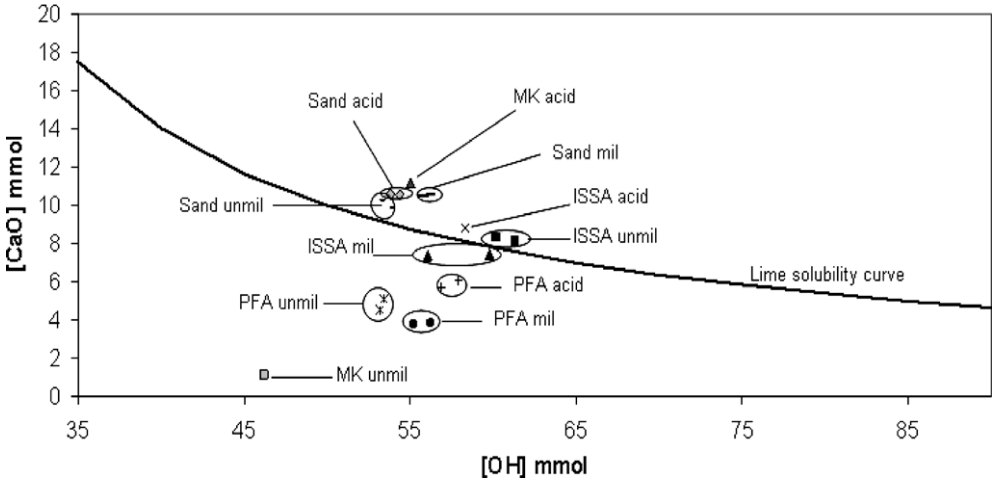

Fig. 8. 8 day Frattini test results for milled, unmilled and acid washed test pozzolans compared to MK. All test samples with 20% cement replaced by test pozzolans.

materials. However there are many factors other than pozzolanic activity that affect strength development in mortars such as particle morphology and water content. For slow acting pozzolans such as FA and ISSA, the 28 day curing period may not be sufficient to allow clear distinction from non-reactive materials. The Frattini test is a direct method of measuring pozzolanic activity where the only major variable influencing the concentration of $Ca(OH)_2$ in solution should be the presence of the test pozzolan. Therefore when considering the pozzolanic activity of a material according to the terms of the true definition of a pozzolan as per ASTM C125, greater consideration should be given to Frattini test results.

4. Conclusions

- Milling improved the pozzolanic activity of FA and ISSA according to both the SAI and Frattini tests. However there was also a false positive result for milled sand using the SAI test.
- The ASTM requirement for a 28 day SAI of 0.75 is too low for mortars with 20% cement replaced by test pozzolan. The SAI test could be modified to prevent anomalous results with inert materials if the 28 day threshold and required SAI value were raised or the percentage of cement replacement increased.
- If ISSA is acid washed to recover phosphate, the process is likely to produce an acid insoluble material with little or no pozzolanic activity. However as-received ISSA can be milled to produce a useful cement replacement material.
- Sulfuric acid washing decreased the pozzolanic activity of all materials according to the SAI and Frattini tests. The formation of ettringite phases due to the presence of sulfates is likely to be responsible for low SAI results of acid washed materials. The severe reduction in the SAI result for acid washed MK is caused by the formation of potassium and sodium sulfates which coat the reactive silica surfaces of MK particles and disrupt cement hydration reactions during water curing.
- The presence of sulfates may produce a false positive result by removing Ca from solution by gypsum precipitation. However this was not the case as all acid washed samples gave a negative Frattini test result.
- The Frattini test is considered a more suitable method for directly assessing pozzolanic activity as a range of factors can affect SAI test results.

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