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Municipal incinerated bottom ash use as a cement component in concrete

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1 T	TITLE: MUNICIPAL INCINERATED BOTTOM ASH USE AS A CEMEN	T COMPONENT IN CONCRETE
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26 ABSTRACT

27	The characteristics of municipal incinerated bottom ash (MIBA) and its potential use as a
28	cementitious component in concrete applications is examined through the analysis and evaluation of
29	global experimental data. As raw feed in cement clinker production, MIBA can be incorporated at
30	minor contents without compromising performance. Treatment of MIBA is required for use as
31	cement components in cement, mortar and concrete to avoid damaging hydrogen gas expansive
32	reactions arising due to the metallic aluminium in the ash. As such, thermal and chemical
33	treatments, as well as tailored slow and wet grinding treatments, have been effective in improving
34	performance. The hydrogen gas expansion associated with MIBA can beneficially contribute towards
35	the lightweight properties required for aerated concrete, with the ash serving as an alternative to
36	aerating agents and also contributing to strength development. Initial work on controlled low
37	strength materials highlighted MIBA as a potential cement replacement material that can meet the
38	low strength requirements.
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42	Key Words: Cement/cementitious materials, sustainability, mortar, aerated concrete.
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50 1. INTRODUCTION

51 Incineration of municipal solid waste (MSW) is being increasingly adopted as an alternative to 52 landfilling, with rising incineration rates of 20, 23 and 27% reported in the 28 European countries in 53 2006, 2010 and 2014, respectively (Eurostat, 2016). This management option results in a large 54 reduction in the quantity of waste to manage, leaving behind residues approximately 30% by mass 55 of the original waste, of which 80-90% is municipal incinerated bottom ash (MIBA). For every tonne 56 of MSW incinerated, approximately ¼ tonne of MIBA is generated. 57 58 With the 27% incineration rate and total of 64 MT of MSW incinerated in 2014 in the European 59 Union (Eurostat, 2016), it is estimated that approximately 16 MT of MIBA may be generated annually

in these 28 countries. On the global scale, based on data gathered for 97% of the world's population,
including records from around 700 waste-to-energy treatment plants, Waste Atlas (2013) calculated
that 1.84 billon tonnes of MSW is produced worldwide per annum.

63

64 The quantity of MIBA produced presents a significant management challenge for governing bodies. 65 Countries such as Belgium, Denmark, Germany and The Netherlands lead the way with extensive use of MIBA, primarily in as fill and in road pavement material (An et al., 2014; Qing and Yu, 2013; ISWA, 66 67 2006). The practical use of MIBA in concrete related applications is much less developed, particularly 68 on the focus of this paper, as a cementitious component in ground form. However, as the cement 69 production process carries a high carbon footprint and driven by increasing importance on 70 sustainability, there is significant incentive to develop this higher value use of MIBA. Indeed, there 71 have been a number of other additions, such as fly ash and ground granulated blastfurnace slag, that 72 have been successfully established as concrete constituents.

74 2. THE PROJECT

75 This paper presents a critical assessment of the characteristics of MIBA and its use as a cementitious 76 component in concrete related applications, through the analysis and evaluation of the globally 77 published experimental results on this subject. With substantial work undertaken, the coherent and 78 incisive dissemination of the combined resources aims to assist in progressing the sustainable use of 79 MIBA, covering its use as raw feed in cement clinker production and cement components in pastes, 80 mortar, concrete, controlled low strength materials, self-compacting concrete and aerated concrete. 81 82 Significant work has been undertaken on the use of MIBA as a cement component in concrete 83 applications and although only starting quite recently in 1998, the interest has been trending 84 upwards, with a particularly large number of publications produced over the last three years (2014-85 2016). Research in this area has been undertaken in twelve countries worldwide, with the largest 86 share of the work coming from Europe (59%), followed by Asia (38%) and North America (3%). The 87 largest individual contributions have come from Italy, China and Taiwan. On the characteristics of 88 MIBA, an overwhelming quantity of data was obtained, though to retain clarity in the text, the 89 references containing solely numerical data on the material properties were listed in Appendices as 90 supplementary data.

91

92 3. MATERIAL CHARACTERISTICS

93 3.1 Oxide Composition

The most abundant oxides found in MIBA are SiO₂, CaO, and Al₂O₃ whilst Fe₂O₃, Na₂O, SO₃, P₂O₅.
MgO and K₂O are also present in smaller quantities (references in Appendix A). These main oxides
are similar to what is customarily found in common cementitious materials and as such, a ternary
plot of their contents in worldwide bottom ash samples is presented in Figure 1 (based on data from
the references in Appendix A).

It is evident that the bulk of the samples fall close to latent hydraulic and pozzolanic regions, with
MIBA generally having a CaO content above the pozzolanic fly ash, but below the latent hydraulic
GGBS. Comparing with fly ash in concrete, ASTM C618 (2015) specifies that the SiO₂+Al₂O₃+Fe₂O₃
content should be a minimum of 70% and 50% for Class F and Class C, and it was found that 16% and
66% of MIBA samples satisfied these respective limits.

105

106 The bottom ash was found to have an average SO₃ content of 2.4%, which satisfies the maximum 3%107 and 5% limits specified in EN 450 (2012) and ASTM C618 (2015) for fly ash in concrete. However, 108 approximately 1/3 of MIBA exceeded the more stringent EN 450 (2012) limit and as such, could 109 require treatment if used in concrete. Phosphate and magnesium can affect the setting behaviour 110 and soundness of cementitious products, though the contents present in MIBA, average contents of 111 2.4% P₂O₅ and 1.9% MgO, are well below the 5% and 4% limits specified for fly ash in EN 450 (2012). 112 Minor amounts of alkalis (Na₂O) are also present in the ash, on average at contents of 2.9%. This is within the 5% limit outlined in EN 450 (2012) and similarly to fly ash, MIBA may have a net positive 113 114 effect on alkali-silica behaviour as a cement replacement, due to alkaline dilution.

115

116 3.2 Loss On Ignition (LOI)

117 Loss of ignition values for the tested MIBA samples are presented in Figure 2 in ascending order 118 (references in Appendix B). The material was determined to have an average LOI of 5.8%, though 119 this is slightly distorted by a number of very high values. LOI limits vary for additions, though 120 compared to fly ash requirements, 61% and 67% of the MIBA samples satisfied the respective 121 requirements of 6% in the American ASTM C618 (2015) and 7% in the UK National Annex to EN 197 122 (2011). As excessive organics can impair the strength and durability of the concrete, this parameter 123 is important to monitor after the incineration stage, in assessing the potential for use of MIBA as a 124 cementitious component.

126	3.3 Mineralogy
127	Amorphous contents from 15-70% have been reported for quenched MIBA (Bayuseno and Schmahl,
128	2010; Dhir et al., 2002; Inkaew et al., 2016; Paine et al, 2002; Rubner et al., 2008 and Wei et al.,
129	2011), suggesting that the material may have some degree of reactivity when ground to a cement
130	fraction. Quartz is the most abundant mineral found in the ash, followed by calcite, hematite,
131	magnetite and gehlenite which are frequently present and then a wide range of other silicates,
132	aluminates, aluminosilicates, sulfates, oxides and phosphates that appear infrequently (references in
133	Appendix C).
134	
135	3.4 Element Composition
136	Data on the element composition of the MIBA samples is presented in Table 1, sorted from highest
137	to lowest average contents. For use as a cementitious component, the chloride and metallic
138	aluminium contents are particularly important. Chloride limits of 0.1% are specified in EN 197 (2011)
139	for common cements and EN 450 (2012) for fly ash in concrete and as such, the average value of
140	0.9% in MIBA indicates that further treatment would be required to reduce this to the accepted
141	level.
142	
143	The issue of the metallic aluminium is a problem more specific to MIBA use in concrete and has been
144	highlighted as a key concern by Tyrer (2013), Pecqueur et al. (2001), Muller and Rubner (2006) and
145	Weng et al. (2015). Aluminium reacts in the alkaline environment in cement and is accompanied by
146	formation of hydrogen gas bubbles, leading to expansive behaviour and spalling damage that can
147	greatly compromise the concrete performance. In aerated concrete, the expansive reaction is
148	advantageous, though in the other applications, treatment is suggested to either remove the
149	metallic aluminium or dissipate the expansive reactions before its use in concrete.

The presence of soluble lead, zinc, phosphates and copper in MIBA may potentially affect the setting
behaviour of concrete, as these constituents are sometime used in admixtures as set retarders.

153

154 **3.5 Density**

155 Specific gravity results for MIBA are presented in Figure 3, with the samples divided into (a) 156 unspecified or screened to remove oversized fraction or sieved as aggregate, (b) subjected to metal 157 recovery treatment and (c) ground as cementitious components. Based on the total samples, the 158 material had an average specific gravity of 2.36 (references in Appendix E), however the process of 159 recovering the denser metal fractions led to a decrease, and the process of grinding, which is a 160 prerequisite for its use a cementitious component, led to an increase due to the smaller, more 161 compact particles and lower porosity. In ground form (average specific gravity of 2.63), the density 162 of the material is significantly lower than the typical value of 3.15 for Portland cement, though 163 above to the 2.3 value of fly ash (Jackson and Dhir, 1996).

164

165 **3.6 Grading**

After incineration, the residual MIBA contains a mix of metallics, ceramics, stones, glass fragments and unburnt organic matter and despite the term "ash", can contain large particles up to 100mm in size. The material typically then goes through a screening process to remove the oversized fraction. For use as a cementitious component, the material is subsequently ground into powder size. Particle size distribution curves for screening MIBA and samples ground for use in concrete are presented in Figure 4 (references in Appendix F) and show that the ground ash achieved well graded distributions comparable to Portland cement and fly ash.

173

The grindability of MIBA has not been a point of focus in the reported data on the characterisation
of MIBA. Metals tend to have a high degree of hardness and it is expected that these constituents in
MIBA would be more difficult to grind. However, with common ferrous and non-ferrous metal

177 recovery treatments of the ash after incineration, combined with the previously highlighted metallic 178 aluminium expansion concerns that may necessitate further treatment, the quantity of the metal 179 constituents may be notably reduced. It is interesting to note that in a study on alternative energy 180 sources in cement manufacturing, Albino et al. (2011) reported that the use of MSW would lead to 181 savings in coal grinding energy costs. 182 3.7 Morphology 183 184 The ash contains irregular, angular shaped particles with a porous microstructure, arising from the 185 heating and cooling process during combustion (references in Appendix G). In this as-produced form, the higher specific surface area, porosity and associated water absorption properties suggest that 186 187 the material would lead to an increase in the water demand of the concrete. 188 189 4. USE AS A CEMENT COMPONENT IN CONCRETE RELATED APPLICATIONS 190 4.1 Raw Feed in Cement Clinker Production 191 The use of MIBA in cement clinker manufacture can reduce CO₂ emissions and contribute to the 192 clinker compounds formation with its calcium, silicon, alumina and iron oxide contents. A description 193 of the work undertaken with MIBA in this area is presented in Table 2, outlining its use as a minor 194 component, at contents from 2-10% of the cement clinker feed. 195

196 To ensure the same main clinker phases are produced with MIBA, the SiO₂, CaO, Al₂O₃ and Fe₂O₃

197 contents and source materials were precisely regulated. As such, MIBA clinkers had chemical

198 compositions comparable to the control (Table 2), however, at the upper end of the tested MIBA

199 contents, the concurrent build-up of minor constituents such as P₂O₅, SO₃ led to the suppression of

200 C₃S formation, which consequently affected strength and setting behaviour, though improved

sulfate susceptibility. Chlorides in the ash can also lead to corrosion of the kiln equipment in the long

term and as a result, MIBA samples used by Pan et al. (2008) were washed prior to their inclusion in
the cement clinker feed.

204

205 Based on the above data, it is expected that MIBA could be viably incorporated in the cement clinker 206 feed at low contents, suggested up to about 5%, without compromising performance. There may 207 also be scope for higher MIBA contents to be incorporated, if the P_2O_5 , SO_3 and Cl^- contents of the 208 material are particularly low. With the vast size of the cement manufacturing industry, reported to 209 produce 250 million tonnes in the European Union countries in 2015 (Cembureau, 2016), it is 210 projected that around 80% of the ash generated in these countries would be consumed though this 211 use alone, if this 5% MIBA content was adopted throughout. 212 213 Of further interest, there was also a number of additional studies that utilized combined ash 214 (municipal incinerator bottom ash and fly ash) as part of the raw feed for cement clinker production, 215 which are listed as follows: Kikuchi (2001); Shih et al. (2003); Torii et al. (2003); Wiles and Shephard 216 (1999). 217 218 4.2 Cement Component 219 This section examines the use of MIBA in ground form as a binder component in cement pastes. 220 Despite serious concerns regarding potentially damaging expansive reactions arising from the 221 presence of metallic aluminium (covered in section 3), much of the work undertaken did not include 222 additional treatment of MIBA beyond the standard grinding (Fernandez et al. 1998; Filipponi et al., 223 2003; Giampaolo et al., 2002; Kim et al. 2016; Kokalj et al., 2005; Polettini et al., 2000; Whittaker et 224 al., 2009). Others adopted chemical activation or thermal treatments for general improvement of 225 the mechanical properties (Lin and Lin, 2006; Lin et al., 2008, Onori et al, 2011; Polettini et al., 2005; 226 Polettini et al., 2009), whilst Tang et al. (2014b/2016) carried out a series of grinding + thermal 227 treatments on MIBA specifically aiming to reduce the damaging expansive behaviour.

229	Compressive strength results are presented in Figure 5 for cement pastes using MIBA after (a)
230	standard processing (typically grinding) and (b) chemical activation with $CaCl_2$, $CaSO_4$ or high
231	temperature treatment. The large strength losses evident with only standard grinding treatment can
232	likely be attributed, for the most part, to the detrimental expansion behaviour arising due to the
233	reactive metallic aluminium in MIBA. As such, it is expected that additional treatment of the material
234	would be essential for its use in this application. One exception in Figure 5 (a) (Kokalj et al., 2005) did
235	manage to achieve good strength performance, though this was because this ash sample originated
236	from a light fraction of MSW that contained minimal metals.
237	
238	Specific testing of the hydrogen gas development confirmed the increase in expansive gases with
239	increasing MIBA, reaching 4% of the volume of the tested cylinder at the highest tested 30% MIBA
240	content (Kim et al., 2016). Thermal treatment of MIBA to reduce the metallic aluminium was
241	effective when combined with a subsequent lower speed grinding technique that allows the ductile
242	metallic aluminium to form into plate shapes and be subsequently removed during sieving, thus
243	greatly reducing the metallic AI (Tang et al., 2016).
244	
245	The additional chemical or thermal treatments have been effective in improving the MIBA strength
246	performance, Figure 5 (b), though were not specifically focused on metallic aluminium reduction.
247	The chemical activators alter the mineralogical composition to promote greater formation of
248	hydration products, whilst the thermal treatment converts the ash into a highly glassy material with
249	enhanced reactivity. Part of the chemical activation process involved a low heat treatment at 90°C
250	for 3 hours of the slurry of ground MIBA + activator. The best results were achieved with $CaCl_2$ as the
251	activator, exceeding the control strength at times, followed by CaSO ₄ , whilst Na ₂ SiO ₃ ·9H ₂ O, NaOH,
252	Na_2SO_4 , KOH and K_2SO_4 (results not shown) were not effective. Pastes using melted MIBA slag
253	achieved compressive strengths close to the control at cement replacement levels up to 20%.

255	The large strength losses with the standard processed MIBA were symptomatic of poor overall
256	performance, as corresponding reductions in density, along with increases in porosity, absorption
257	and additional cracking problems have also been evident in these pastes (Fernandez et al., 1998; Kim
258	et al., 2016; Polettini et al., 2000; Tang et al., 2014b; Tang et al., 2016).
259	
260	Heat flow analysis showed that MIBA, at contents up to 40%, led to a retardation of the hydration of
261	the pastes and lower maximum heat releases (Onori et al., 2011; Tang et al., 2014b; Tang et al.,
262	2016; Whittaker et al., 2009), attributed to the organic fraction and presence of zinc and phosphate.
263	This was also resulted in increases of 7-57% in initial and final setting times (Kim et al., 2016;
264	Whittaker et al., 2009), including with the melted MIBA slag (Lin and Lin, 2006; Lin et al., 2008).
265	
266	The material did make a tangible contribution to the hydration reactions, which was quantified from
267	pozzolanic activity tests. Frattini and lime saturation tests, which directly measured the quantity of
268	Ca(OH) $_2$ in the presence of MIBA, revealed that the material generally satisfied the pozzolanic
269	activity requirements and when compared to established materials, performed similar tol fly ash and
270	natural pozzolan (Fernandez et al., 1998; Filipponi et al, 2003; Giampaolo et al, 2002; Polettini et al.,
271	2005; Polettini et al. 2009). The melting treatment was effective in increasing the amorphous phases
272	in MIBA (Lin and Lin, 2006; Lin et al., 2008), whilst chemical activation was also found to further
273	support the development of pozzolanic reaction in the pastes (Onori et al., 2011).
274	
275	4.3 Mortar
276	As a cementitious component in mortar mixes, MIBA has been subjected to the perquisite grinding
277	processing, whilst at times, additional thermal treatment has been applied to the material. Using
278	MIBA as cement replacement at contents up to 50%, the effects on the mortar fresh properties are

presented in Table 3. The ash generally led to minor decreases in the mix flow values, which can be

attributed to the irregular particle shape and high porosity of the material. The additional thermal
treatment did not significantly alter the effect of MIBA on the workability. Moderate increases in
setting times were evident with MIBA, which is expected when using pozzolanic materials as a
replacement of Portland cement. The lower specific gravity of MIBA led to a slight reduction in its
fresh unit weight, whilst its higher water retention resulted in lower bleeding.

285

On the hardened properties, the effect of MIBA as a binder on the mortar compressive strength development with age is shown in Figure 6 (a) using ash samples subjected to the standard grinding treatment and Figure 6 (b) for samples with an additional thermal treatment. The results are presented as a percentage of the control at the same age and as such positively sloped lines imply that the pozzolanic activity of the material is contributing to greater later age strength development.

291

292 This greater rate of later strength development has been evident in most MIBA mixes. As is generally 293 the case with pozzolanic materials, due to the delayed pozzolanic reaction, lower early age strengths 294 were evident, however, the thermal treatment (Figure 6(b)) improved the material reactivity, 295 leading to both higher early age strengths and long term strengths that exceeded the control mix. 296 Additional work by Carsana et al. (2016) and Tang et al. (2016), with treatments specifically aiming to 297 reduce the metallic aluminium, showed that the associated expansive reaction can have a drastic 298 impact on the strength performance. Reductions in the metallic aluminium and much improved 299 mechanical performance has been achieved using a combined metal separation + wet grinding 300 treatment (Carsana et al., 2016) and a combined thermal + lower speed grinding treatment (Tang et 301 al., 2016).

302

The wet grinding step is particularly effective, for the reason that the aluminium fractions become more exposed as the particles fragment during grinding (Carsana et al., 2016) and in the alkaline environment, the expansive reactions develop from the formation of aluminium hydroxide and

306	hydrogen gas and eventually are depleted before the material is introduced into the cement
307	mixture. A slower grinding speed can also be beneficial as it allows better removal of the dust-like
308	particulates that reside on the MIBA particle surface (which are believed to be the most reactive
309	fractions) by means of inter-particle friction, and as a result, the subsequent expansive reactions in
310	the cement environment are reduced (Tang et al., 2016).
311	
312	In addition to hydrogen gas expansion, the effect of MIBA on a number of other aspects of the
313	mortar durability has been tested:
314	
315	Drying shrinkage: Using ground MIBA, the drying shrinkage of mortar mixes increased with
316	increasing MIBA content, accompanied by increases in porosity. However, after thermal treatment
317	(max temperature of 1450°C for 12 hours), the opposite behaviour was evident, as MIBA mixes had
318	lower drying shrinkage compared to the control, due to the lower porosity and denser
319	microstructure associated with the greater pozzolanic reactions and filling effects (Cheng, 2012;
320	Cheng et al., 2011).
321	
322	Chlorides and sulfates ingress: The use of thermally treated (1500°C for 4 hours) MIBA as a cement
323	replacement in mortar reduced the depth of penetration of chlorides and sulfates (Saccani et al.
324	2005). This again, can be linked to the lower porosity of the MIBA mixes.
325	
326	Alkali aggregate reaction: Accelerated tests on alkali silica reactivity showed that thermally treated
327	MIBA, as a replacement of 20 and 30% of the cement, led to a significant reduction in the mortar
328	expansion (Saccani et al., 2005), as is typically expected with the use of pozzolanic materials due to
329	the dilution in the alkalinity.
330	

331 **4.4 Concrete**

The use of MIBA as a cement component in concrete mixes is expected to show similar behaviour to its use in mortar, with the potential hydrogen gas expansion likely to dictate that additional treatment of the ash, after grinding, should be undertaken. Concrete compressive strength results are presented in Figure 7, in the same manner as the mortar results in Figure 6, using MIBA (as binder) subjected to (a) standard processing and (b) an additional thermal treatment.

337

338 The concrete results with MIBA appear more positive that the mortar counterparts, achieving later 339 age strengths comparable to the control in some cases (Bertolini et al., 2004/2005 (wet ground); 340 Juric et al., 2006; Jaturapitakkul and Cheerarot, 2003). Hydrogen gas expansive reactions were 341 surprisingly only reported by Bertolini et al. (2004), with the dry-ground MIBA. The wet grinding 342 process (a slurry with a 1:1 solid/liquid ratio) led to the dissipation of the expansive reactions 343 (formation of visible gas bubbles). With a subsequent rest period before the use of MIBA (two days 344 was sufficient for Bertolini et al., 2004/2005, though this may vary), the metallic aluminium reactions 345 can be depleted, thus leading to drastic strength and density improvements. The additional thermal 346 treatment, though a more energy intensive option (1450°C for 1 hour, Cheng et al., 2011), produced 347 a more reactive MIBA slag due to its higher amorphous fraction, which also led to improvements in 348 the compressive strength (Figure 7(b)).

349

Mixed findings emerged regarding the effect of MIBA on the concrete mix consistence. With 30% of the cement replaced, the slump decreased from 60mm to 0mm with the finer wet ground MIBA (d₅₀ 3µm), compared to an increase to 110mm with the dry ground MIBA (d₅₀ 15µm) (Bertolini et al., 2004/2005). Additional slump increases from 162mm (control) to between 167-187mm for ground and thermally treated MIBA (passing 74µm) were evident (Cheng et al., 2011), though a contrasting drop from 105mm (control) to 44mm with 15% MIBA (unspecified fineness) was also reported (Juric et al., 2006). Differences in the ash fineness after grinding contributed somewhat to variability in the workability, with increased fineness found to lead to lower slumps, whilst the moisture content of
MIBA prior to its use is another important variable to consider. The irregular shape of the ash
particles and porous microstructure of the material, also point towards an expected reduction in the
mix consistence with MIBA, for a given water content.

361

On the concrete permeation properties, the inclusion of 20% ground MIBA reduced the initial
 surface absorption test (ISAT) value from 0.6 to 0.3 ml/m²s. Additional thermal treatment was also
 beneficial in achieving a denser concrete microstructure due to the increased pozzolanic activity
 (Cheng et al., 2011).

366

367 As a measure of the concrete corrosion resistance, open circuit potential (OCP) results matched up 368 consistently with the compressive strength performance (see Figure 7), with ground + melted MIBA 369 mixes performing similar to the control and just ground MIBA mixes showing greater susceptibility 370 (Cheng et al., 2011). This same behaviour with MIBA mixes was also evident in rapid chloride 371 penetration tests measuring the electric current passing through (Cheng et al., 2011). Indirect 372 electrical resistivity and direct chloride apparent diffusion coefficient results revealed that the higher 373 strength wet ground MIBA mixes had greater resistance than the control, whilst the lower strength 374 dry ground MIBA was less resistant (Bertolini et al, 2004/2005). Overall, the initial testing suggests 375 that for equivalent compressive strength, mixes with MIBA as binder will deliver resistance to 376 chloride ingress on par or greater than the control PC mix.

377

378 4.5 Controlled Low Strength Material (CLSM)

Controlled low strength materials are used as an alternative to soils as backfill material, with their
 main characteristics including high flowability, self-compacting, self-curing properties and strengths
 controlled to low levels to allow future excavation. As outlined in the American Concrete Institute

guidance report on CLSM (ACI, 2005), these products typically contain fly ash as filler, low contentsof cement and coarse and fine aggregate, with water.

384

385 The initial work undertaken with MIBA adopted a more unconventional approach using a mix of 386 dewatered sludge (DS) + calcium sulfoaluminate cement (CSA) + water as the control, with MIBA 387 (ground to less than 4mm) replacing up to 80% of the cement (Zhen et al., 2012/2013). The focus of 388 the testing was on the compressive strength development and the results are presented in Figure 8. 389 CLSMs with mix proportions of 1 or 4 units of CSA (or CSA+MIBA) per 1 unit of dewater sludge have 390 been produced. A few of the MIBA samples used were subjected to an additional thermal treatment 391 at 900°C for 1 hour. Other important properties such as flowabiility and compactability have not 392 been covered.

393

394 The above CLSMs produced using MIBA appear more suited towards structural applications as all 395 mixes greatly exceeded the 0.3 MPa (50 psi) manual excavation guidance limit and indeed all but 396 two (CLSMs with 80% MIBA and the lower total CSA+MIBA proportion) exceeded the machine 397 excavation limit of 2.1 MPa (ACI, 2005). Accompanying XRD, TG-DSC and SEM-EDX analysis of the 398 microstructure and mineralogy by Zhen et al. (2012/2013) suggested that MIBA did contribute to the 399 strength performance, despite the consistent strength decreases with increasing MIBA contents in 400 the 1 DS: 4 CSA+MIBA: 1.6 water mixes. However, the use of MIBA or other pozzolanic material with 401 CSA may not be an effective combination as this cement type is less alkaline and does not produce 402 the calcium hydroxide needed for pozzolanic reactions (Pera and Ambroise, 2006). The increase in 403 strength with low MIBA contents in the lower CSA+MIBA mixes may be contributed by improved 404 mechanical filling. Thermal treatment of MIBA for use in CLSMs did not have a favourable effect on 405 the mechanical performance.

407 4.6 Aerated Concrete

Aerated concrete appears to be an ideal application for MIBA as the hydrogen gas expansive
reactions arising from its metallic aluminium can make a positive contribution towards the desired
low density properties. In the work undertaken, MIBA has served as a valuable aerating agent, whilst
also making a useful contribution to the silica required for strength development.

412

Prior to the implementation of MIBA in aerated mixes, the response of the material with varying
levels of alkaline solution (0.0016 - 1 mol/L of NaOH or Ca(OH)₂) has been examined by measuring
the hydrogen gas production at temperatures from 40-70°C (Chen et al., 2014; Song et al., 2015;
Song et al., 2016; Wang et al., 2016, Yang et al., 2015). The results were converted to a standard
measure of volume of hydrogen gas per gram of powder at 1 atm (pressure), 23°C and the following
findings emerged:

The hydrogen gas volume increased with MIBA fineness. This can be attributed to the increased specific surface area and greater exposure of the reactive components associated with higher particle fineness. The finest MIBA fraction (average particle size of 23.2 μm) produced approximately 1% of the gas produced by aluminium powder per gram in equivalent conditions.
 Hydrogen gas production increased both as the temperature rose and conditions became more alkaline (higher alkaline solution molarity), though comparable results were achieved with either

425 NaOH and Ca(OH)₂ as alkaline solution.

426

The mix designs for aerated concrete containing MIBA are presented in Table 4, along with the density and compressive strength results. Differing approaches have been adopted, using MIBA as a replacement of cement, coal fly ash or circulating fluidized bed combustion (CFBC) fly ash, along with variations in the other constituents, alkaline solutions and molarity and the water content.

432 As a cement replacement, increasing MIBA and NaOH molarity led to increasing porosity and 433 associated reductions in density and compressive strength (Chen et al., 2014; Song et al., 2016; Yang 434 et al., 2015), though the density was affected more by the MIBA content, whilst the alkaline solution 435 molarity had a greater influence on strength. The substitution of MIBA for coal and CFBC fly ashes 436 also resulted in reductions in density and strength due to the increased expansive reactions and 437 porosity (Song et al., 2015; Yang et al., 2015). The strength to density ratio for the mixes containing 438 MIBA is lower than those with coal and CFBC fly ashes, though is higher than those using aluminium 439 powder (1g of MIBA for 0.01g of Al powder based on the previous hydrogen gas experiments). As 440 such, the use of MIBA and these fly ashes appears to be an ideal combination that can produce the 441 desired low density, with better strength than the AI powder mixes, and at the same time, save the 442 costs of the expensive aluminium aerating agent.

443

The drying shrinkage of MIBA aerated concrete was found to stabilise at around 15 and 20 days respectively, with the CFBC fly ash and coal fly ash mixes. Consistent increases in shrinkage were evident with increasing MIBA content, due to the higher porosity and associated increased ease of moisture loss and the lower resistance to movement due to the lower strength. Despite this increased susceptibility, the drying shrinkage values of all MIBA aerated concrete mixes were within the targeted 0.50 mm/m Chinese National Standard limit (Song et al., 2015; Wang et al., 2016).

450

451 5. CONCLUSIONS

The chemical composition of MIBA, with main oxides of SiO₂, CaO and Al₂O₃, combined with its amorphous fraction, indicates that it may have pozzolanic properties in ground form. The ash contains notable contents of SO₃, Cl and organic matter that should be monitored and treatment may be required at times to limit negative impacts on concrete performance. Metallic aluminium in MIBA is also a key concern that may demand treatment to avoid damaging expansive reactions. In ground form, MIBA was found to have an average specific gravity of 2.6, placing it above fly ash and 458 below Portland cement. Its irregular shaped particles, porous microstructure and higher absorption
459 properties indicate that MIBA may lead to a rise in the concrete water demand.

460

As raw feed in cement clinker production, MIBA can be viably used at low contents, recommended up to 5%, to produce cement clinker comparable to the control. At higher MIBA contents, the buildup of P_2O_5 and SO_3 affects the setting and strength development. Washing treatment may also be implemented to reduce long term corrosion of the kiln equipment due to the chlorides in MIBA.

466 As a cementitious component in paste, mortar and concrete mixes, treatment of MIBA beyond 467 standard grinding is needed to avoid expansive reactions and associated negative effects on 468 strength, density, absorption and cracking, arising from the metallic aluminium in the ash. Thermal 469 and chemical activation treatments have been effective in improving strength performance, whilst 470 tailored slow and wet grinding techniques targeting the removal of metallic aluminium also resulted 471 in drastic increases in performance. MIBA contributed to strength development as a partial cement 472 replacement, achieving long terms strengths greater than the control mortar and concrete mixes, 473 after suitable treatment. Increases in the water demand and setting times were evident when MIBA 474 was used as a binder in mortar and concrete. Products containing the appropriately treated ash 475 performed comparable or better than the control mixes at equivalent strengths, with regards to 476 permeability, drying shrinkage, chloride and sulfate ingress and alkali aggregate reaction.

477

MIBA appears suited for use in aerated concrete as the hydrogen gas expansive reactions can
contribute towards the desired low density properties, serving as an alternative to costly aerating
agents such as aluminium powder and also as a source of silica for strength development. The
material has been incorporated in varying mix designs as a replacement of cement, coal fly ash or
circulating fluidized bed combustion (CFBC) fly ash, achieving large reductions in density. The use of
MIBA in combination with coal fly ash also achieved a superior strength-to-density ratio compared to

- 484 mixes with aluminium powder, in addition to saving the costs of the aerating agent. Initial work on
- 485 controlled low strength materials also presented MIBA as a potential cement replacement that can
- 486 meet the low strength requirements of this application.
- 487

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- 651 TABLES
- 652 Table 1: Element composition of MIBA (references in Appendix D)
- Table 2: Description of the work undertaken and emerging findings on the use of MIBA as part of the
- 654 raw feed for cement clinker production
- Table 3: Fresh properties of mortars using MIBA as a cementitious component
- Table 4: Mix designs and density and compressive strength results for aerated concrete

- **.** -

ELEMENT	SAMPLE NO.	AVERAGE, mg/kg	ST DEV, mg/kg	CV, %
c:				
Si	13	210893	64046	30
Ca	31	117750	59238	50
Fe	36	53455	36393	68
Al	35	44047	15634	35
Na	24	22812	16526	72
Mg	29	14967	8664	58
Cl	37	8944	9443	106
К	29	8256	4716	57
Ti	12	6632	5553	84
S	27	5184	2208	43
Р	10	4866	3987	82
Zn	78	4044	2974	74
Cu	76	3071	2796	91
Pb	73	1641	1205	73
Ва	31	1312	910	69
Mn	41	921	599	65
Cr	77	398	325	82
Sr	17	379	179	47
Sb	18	253	714	282
Ni	58	182	132	73
V	22	167	286	172
Со	24	50	104	207
As	46	50	61	123
Мо	19	28	27	99
Cd	50	14	23	159
Hg	17	1.4	4.0	290

Table 1: Element composition of MIBA (references in Appendix D)

Table 2: Description of the work undertaken and emerging findings on the use

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of MIBA as part of the raw feed for cement clinker production

PUBLICATION	WORK UNDERTAKEN AND FINDINGS
	Trials with cement clinkers containing 5% and 10% MIBA.
Tangermsirikul (2003/2004)	MIBA clinkers had similar chemical compositions to the control. Lower compressive strengths were evident, though less susceptibility to sulfate expansion.
Lam et al.	MIBA at content of 2,4,6,8 % in cement raw feed.
(2010/2011)	Clinker containing up to 6% MIBA showed phase composition similar to PC, though 8% led to suppression of the main phases (decreased C_3S) due to P_2O_5 and SO_3 contents.
lietal	2 clinkers: 1 st - control, 2 nd - 9% MIBA + lower limestone, sandstone, fly ash, slag %.
(2016)	Major chemical components of the MIBA and control clinkers were similar, though the MIBA blend had higher alkalis (Na ₂ O and K ₂ O) and P ₂ O ₅ contents.
Pan et al	Cement clinker produced using 3.5% washed MIBA.
(2008)	Allowable MIBA was limited by its chloride content. Setting time increased with MIBA, whilst compressive strength was similar to the control clinker when P_2O_5 was limited.
PC – Portland ce	ment clinker
	Krammart and Fangermsirikul (2003/2004) Lam et al. (2010/2011) Li et al. (2016) Pan et al. (2008)

Table 3: Fresh properties of mortars using MIBA as a cementitious component

REFERENCE MORTAR FRESH PROPERTIES

Consistence

 Cheng et al. MIBA ground <74μm. Minor decreases in flow from 131mm (0% MIBA) to between 109- (2011) 123mm with 10-40% MIBA. Though all mixes were deemed to have satisfactory workability.
Saccani et al. MIBA thermally treated (1500°C, 4hrs), quenched and ground. Increased flow table values of (2005) 75mm (20% MIBA) and 70mm (30% MIBA) compared to control 60mm (0% MIBA).
Tang et al. MIBA ground or ground + thermal treatment (550/700°C). Thermal treatment didn't have a (2014a/2016) significant effect on flow. All flows with 20% MIBA were within +5 to -10 mm of the control.
 Whittaker et MIBA ground to 2μm. More sizeable reduction in flow table results from the control 190mm, al. (2009) to 167mm (10% MIBA) and 136mm (40% MIBA)
Zhang and MIBA ground to 40μm. Slight increases in the water demand with increasing MIBA, rising Zhao (2014) from 26.1% (0% MIBA) to 30.1% (50% MIBA)
Setting Time
Cheng (2012) MIBA ground < 74μm or melted (1450°C) + ground. Initial and final setting times increased (up to 30% longer with 40% MIBA). Melting didn't significantly alter the rate of delay.
Saccani et al. MIBA vitrified (1500°C, 4hrs) + quenched + ground. With 30% MIBA, initial sett increased (2005) from 60 to 100 mins and final set from 170 to 235 mins.
Zhang and MIBA ground < 40μm. Increase in initial and final setting times of approximately 40% for theZhao (2014) highest tested 50% MIBA content.
Fresh Unit Weight

Fresh Unit Weight

Cheng (2012) MIBA ground < 74μm. Minor decrease in the fresh unit weight with up to 40% MIBA, also accompanied by minor increases in the mix air contents.

Bleeding

Cheng (2012) MIBA ground < 74 μ m. Decrease in bleeding with MIBA from 0.1988 mL/cm² (for control 0% MIBA) to 0.1395 mL/cm² (40% MIBA)

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Table 4: Mix designs and density and compressive strength results for aerated concrete

MIX CONSTITUENTS	RESULTS

A. Cement Replaced (Chen et al., 2014; Song et al., 2016; Yang et al., 2015) Other variables: Alkaline solution type and molarity, L/S ratio

Cement	MIBA	Sand	Alkali solution	L/S ratio	Density, kg/m ³	Comp Strength, MPa
4	1	5	Water	0.175	1554	19.5
4	1	5	0.01 mol/L NaOH	0.175	1512	16.0
4	1	5	0.1 mol/L NaOH	0.175	1444	12.5
4	1	5	1 mol/L NaOH	0.175	1324	5.7
3	2	5	1 mol/L NaOH	0.35	1056	2.7
2	3	5	1 mol/L NaOH	0.35	932	1.5

B. Coal Fly Ash Replaced (Song et al., 2015; Yang et al., 2015)

Other variables: Comparison to Al powder

Cement	MIBA	Coal fly ash	Al powder	Lime /Gypsum	Water	Density, kg/m ³	Comp strength, MPa
10	0	67	0	20/3	65	1074	13.9
10	5	62	0	20/3	65	846 (↓ 21%)	9.7 (↓ 30%)
10	10	57	0	20/3	65	728 (↓ 32%)	8.4 (↓ 40%)
10	20	47	0	20/3	65	673 (↓ 37%)	7.2 (↓ 49%)
10	30	37	0	20/3	65	637 (↓ 41%)	6.1 (↓ 56%)
10	0	67	0.05	20/3	65	831 (↓ 23%)	7.7 (↓ 45%)
10	0	67	0.1	20/3	65	673 (↓ 37%)	6.5 (↓ 53%)
10	0	67	0.2	20/3	65	603 (↓ 44%)	4.1 (↓ 71%)
10	0	67	0.3	20/3	65	511 (↓ 52%)	2.9 (↓ 79%)

C. CFBC fly ash replaced (Wang et al., 2016)

Other Variables: None

Cement	MIBA	CFBC fly ash	Lime	Water	Density, kg/m ³	Comp strength, MPa
10	0	70	20	65	1116	18.1
10	5	65	20	65	868 (↓ 22%)	17.1 (↓ 5%)
10	10	60	20	65	799 (↓ 28%)	13.2 (↓ 27%)
10	20	50	20	65	656 (↓ 41%)	8.9 (↓ 51%)
10	30	40	20	65	613 (↓ 45%)	6.8 (↓ 63%)

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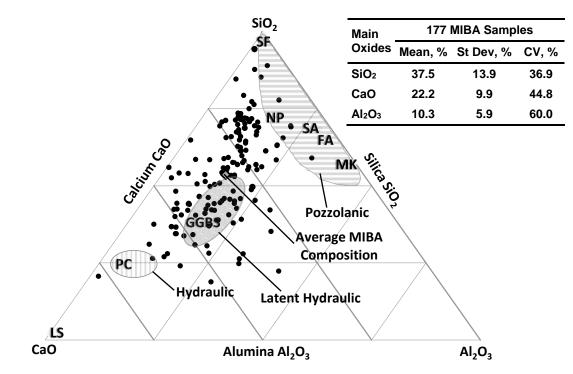
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718 FIGURES

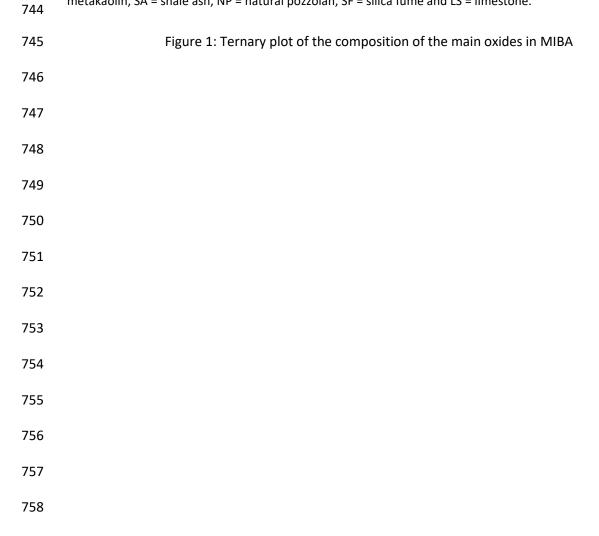
- 719 Figure 1: Ternary plot of the composition of the main oxides in MIBA
- 720 Figure 2: LOI values of MIBA samples in ascending order
- 721 Figure 3: Density results of MIBA for (a) unspecified treatment/screened/sieved samples (b) samples
- subjected to metal recovery treatment and (c) samples ground to cement size fraction.
- 723 Figure 4: Particle size distribution curves of MIBA samples screened and ground as a cementitious
- 724 component
- 725 Figure 5: Effect on cement paste compressive strength with MIBA subjected to (a) standard
- 726 processing and (b) additional chemical or thermal treatments.
- 727 Figure 6: Compressive strength development of mortars using MIBA subjected to (a) standard
- 728 processing and (b) additional thermal treatment.
- 729 Figure 7: Compressive strength development of concrete using MIBA subjected to (a) standard
- 730 processing and (b) additional thermal treatment.
- 731 Figure 8: Compressive strength of CLSM after 28 days using MIBA as a cement (CSA) replacement
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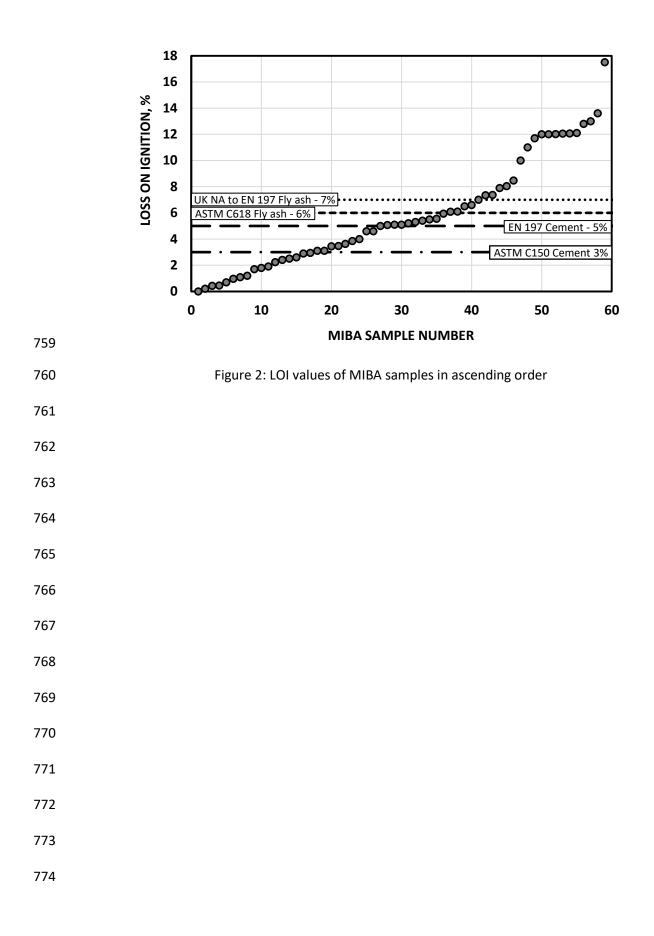
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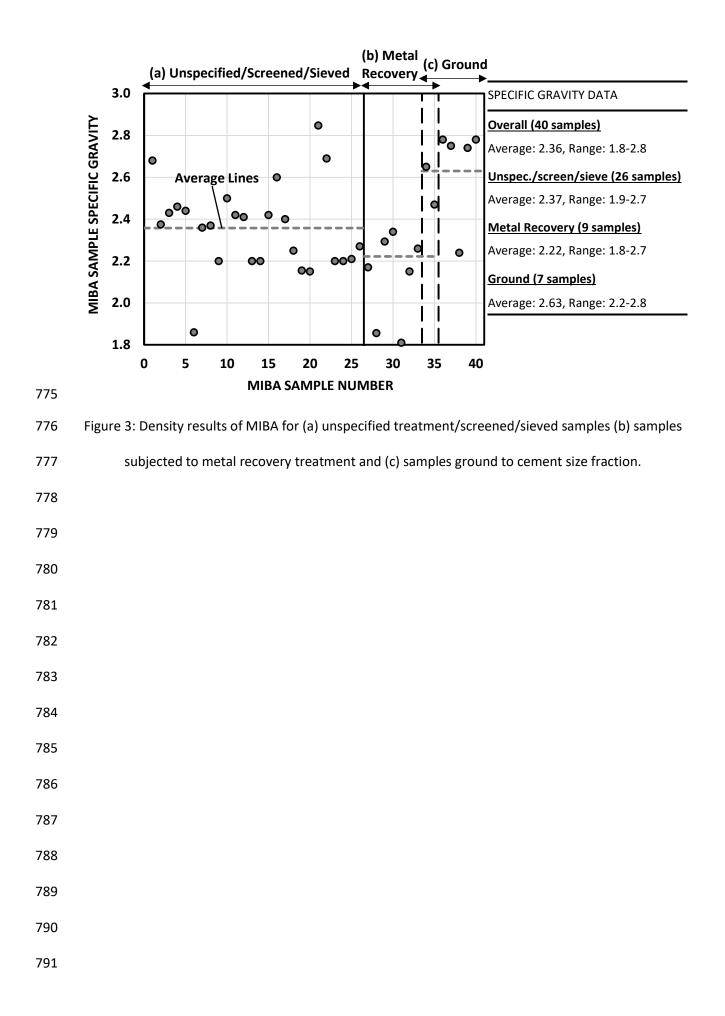
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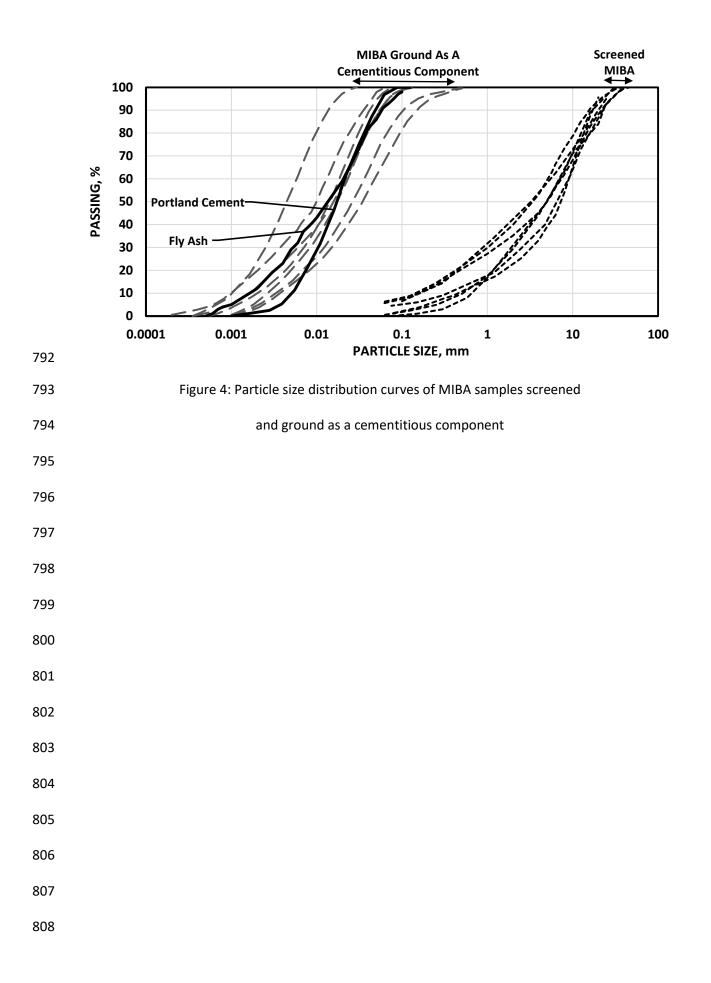


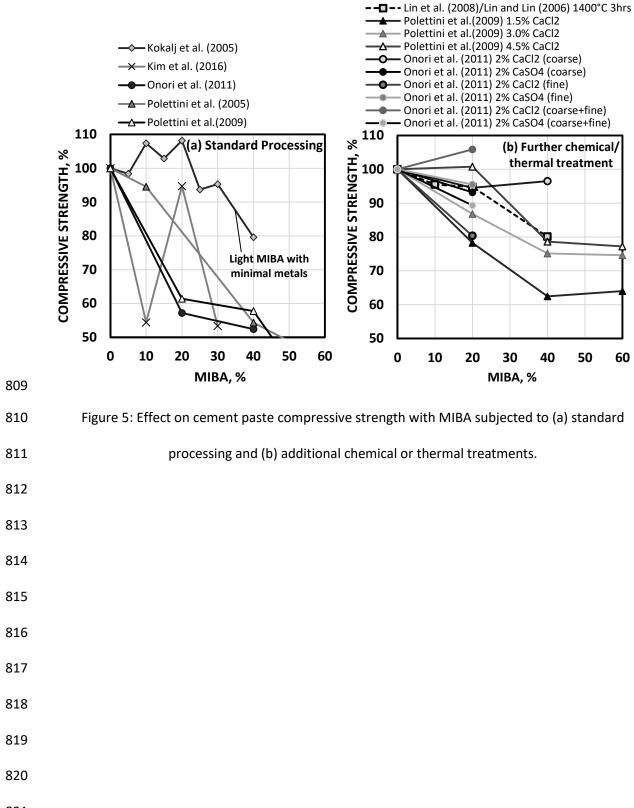
Note: PC = Portland cement, GGBS = ground granulated blastfurnace slag, FA = fly ash, MK = metakaolin, SA = shale ash, NP = natural pozzolan, SF = silica fume and LS = limestone.

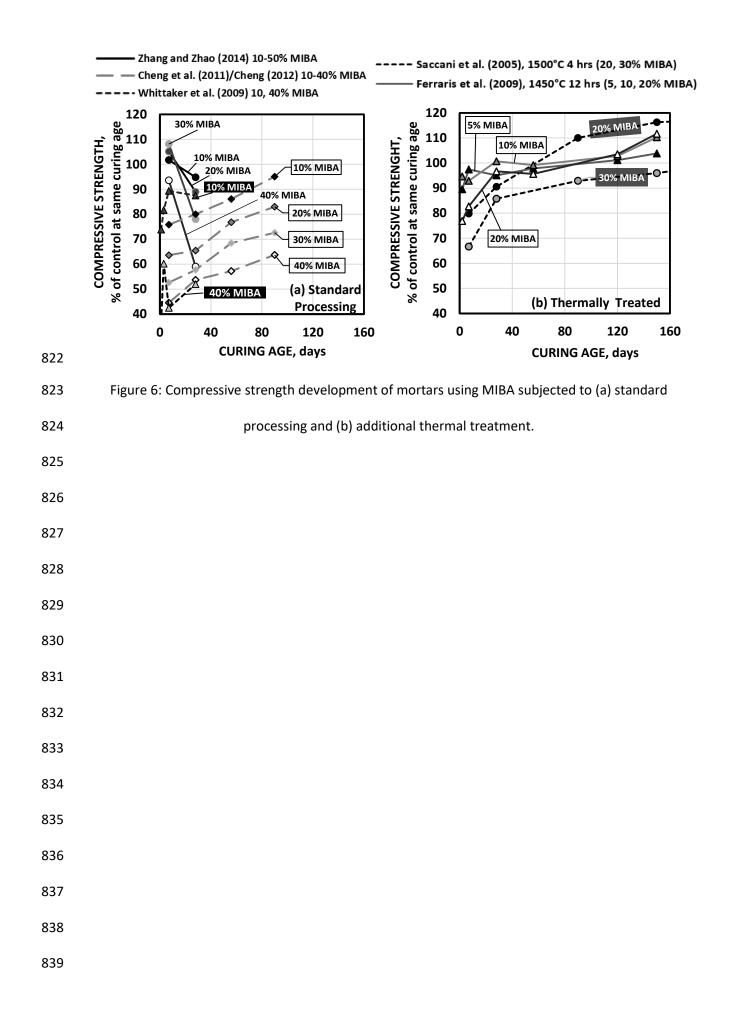


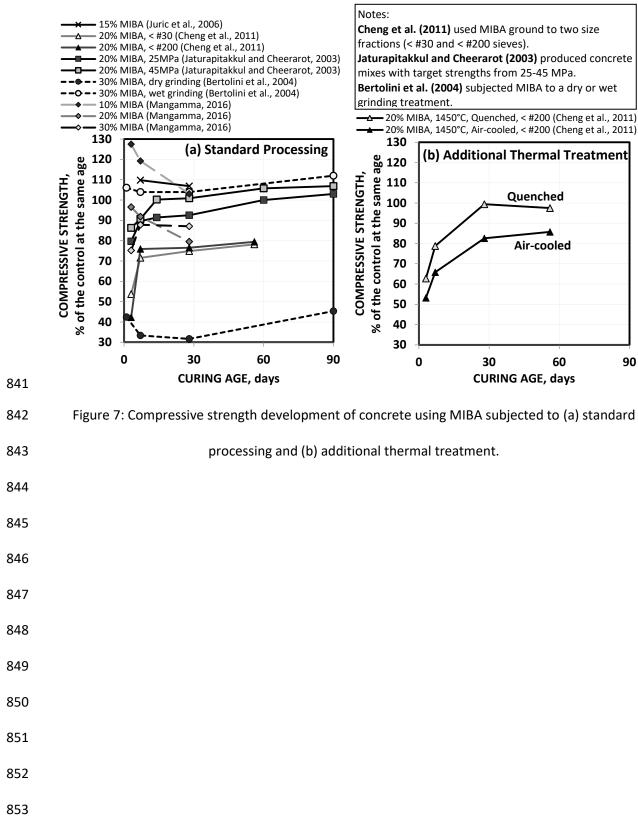


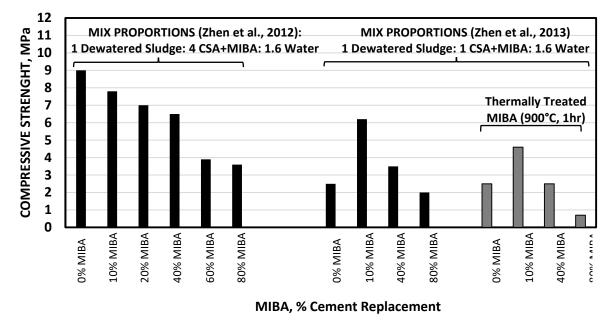












857 Figure 8: Compressive strength of CLSM after 28 days using MIBA as a cement (CSA) replacement