Recycled brick fines for new alkali activated binder

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Abstract. The construction industry today produces huge quantities of wastes, especially during the deconstruction and demolition of buildings. Ceramics and bricks represent a significant part of this inert waste in Belgium and Northern France. The recycling of bricks is already carried out in the form of aggregates used in road embankments. But this constitutes what is called a "downcycling" operation. The investigated way is here a valorization with higher added value in alkali-activated materials through substitution of blast furnace slag (GGBFS) by brick fines with a grain size $D50 = 20$ µm. It is shown that brick fines can be a precursor equivalent to GGBFS and thus lead to mechanical performances equivalent to control even up to 50% substitution rate in brick fines. Under certain conditions of alkali-activated solution concentration, the addition of 30% brick fines can greatly improve workability time. But this leads to a decrease in mechanical performances, which is still in accordance with specific construction needs.

Keywords: bricks, alkali activated materials, GGBFS, strength, microstructure.

1   Introduction

Bricks and ceramics represent around 2% of the Construction and Demolition Wastes produced in Belgium and North of France. Reusing bricks is undoubtedly better than recycling but C&DW treatment however produces large quantities of fine particles, including brick fines. Bricks are a predominantly aluminosilicate materials which, in the form of fines, can be described as a potentially pozzolanic material [1]. They can be characterized by their quantity of oxides, $SiO_2 + Al_2O_3 + Fe_2O_3 (+ CaO) \geq 70\%$, which includes them in pozzolans and partly in glasses depending on the amount of amorphous phase [2]. Pozzolanicity and fineness are therefore considered as the parameters to characterize the activity of brick fines when used in hydraulic mixtures [3,4].

Alkali-activated material is the result of the reaction between a solid aluminosilicate (precursor) and an alkali-activating solution. This reaction produces a hardened binder, consisting of hydrated alkali aluminosilicates. The precursors are usually aluminosilicate or

calcium-rich materials such as metakaolin and ground blast furnace slag (GGBFS) respectively. The alkali-activating solution is most often sodium or potassium hydroxide, which allows the pH of the solution to be increased, with or without a silicate solution.

Brick fines, due to their high aluminosilicate content and the high percentage of amorphous phase with active silica and alumina, can be identified as a precursor for alkali-activated materials.

Previous research [5, 6] demonstrate the activating potential of brick fines to create a fully alkali-activated material. If the proportion of amorphous phase is sufficient, then the brick fines form a hardened and resistant alkali-activated material.

The use of brick fines can also overcome two disadvantages found in alkali-activated mixtures, which are (i) a very short setting time and (ii) poor workability. According to some studies, a shortening of the setting time is observed [7]. This phenomenon is linked to the larger specific surface area of the fines, which increases the reaction speed. However, the final setting time would be delayed [7]. The fineness would also result in better workability [8]. An improvement in mechanical performance is also noted, with an increase in compressive strength [9, 10, 11]. This higher strength with the addition of brick fines may be due to the presence of amorphous phase in the fines, which contributes to a better reactivity of the mix. Depending on the size of the fines, the alkaline activation can be improved. By increasing the specific surface area of the particles, the alkali-activation process is facilitated. This paper presents the results obtained with commercial bricks and compare the effects of taking into account the possible activity of the brick fines as precursors.

2   Materials and methods

2.1   Blast furnace slag

GGBFS is consisting mainly of amorphous phase. The chemical (Table 1) and physical (Table 3) characteristics of GGBFS show it is a reactive and fine material (d_{50}= 8.5 µm) with a specific surface area of 1 m²/g. The fineness of the material allows for a sufficiently alkali-reactive powder, in addition to its mineralogical nature.

2.2   Alcali-activating solution

The alkali-activating solution is essential for the formulation of alkali-activated materials; it can be assimilated to the mixing water used for the hydration of cement. This solution will be composed of sodium silicate (Na_2SiO_3), sodium hydroxide (NaOH) and water. The choice of activators is mainly related to the performance that can be obtained. By coupling the efficiency of a sodium silicate and sodium hydroxide solution, it is possible to obtain very good performances with GGBFS. Two types have been used:

- Sodium silicate (GEOSIL) is formulated for alkaline activations. Sodium silicate has a molar ratio Ms = 1.7 (SiO_2/Na_2O), a density of 1.57 and a dry mass of 44%.

This activator allows for slag to dissolve more slowly and for better diffusion of the reaction products between the grains.

- Sodium hydroxide is packaged in pellet form. It is the activator with the fastest kinetics: it plays an important role at a young age by rapidly dissolving the materials and bringing the ions into solution.

2.3   Brick fines

Brick fines (BF) are prepared in order to obtain a granulometry equivalent cement (reference CEM I 52.5 N). In a first step, a jaw crusher is used to reduce the sample into aggregate form. A sieve (1 mm sieve) is then used. The by-product is then crushed in a ball mill (steel balls). Chemical and mineralogical characterizations have been performed by means of XRF and XRD (Table 1 and 2). Bricks are a material rich in silicon, aluminium, and iron oxide, with a SiO_2/Al_2O_3 ratio equal to 6.

Table 1. Oxides in GGBFS and brick fines.

Oxides (%)	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	K$_2$O	Na$_2$O	MgO	TiO$_2$	Total
Brick fine	1.7	62.8	10.4	16.3	2.1	0.6	2.2	2.4	99.3
GGBFS	42.9	38	10.8	0.5	0.3	-	6.5	0.7	99.5

The minerals found in the bricks are quartz (SiO_2), hematite (Fe_2O_3), feldspars with albite ($NaAlSi_3O_8$) and microcline ($KAlSi_3O_8$). Corundum is used as a standard to enable phase quantification. The percentage of the different minerals and phases is given in Table 2.

Table 2. Mineral phases in brick fines.

Mineral (%)	Brick fine
Quartz SiO$_2$	58.6
Hematite Fe$_2$O$_3$	12.8
Albite NaAlSi$_3$O$_8$	3.9
Microline KAlSi$_3$O$_8$	6.0
Cristobalite SiO$_2$	2.8
Amorphicity	15.9

The proportion of amorphous phase in the studied bricks is around 16%. The dissolution of amorphous phases and softer minerals such as feldspars (albite, microcline), can lead to an increase in free oxides in the mixtures which can precipitate to form C-S-H or even C-A-S-H type gels in the case of alkali-activated materials.

Pozzolanic activity can be determined by the modified Chapelle test which gives the consumption of lime by the material tested (Table 3). This factor indicates how much lime can be fixed by the fines: lime or Portlandite is the main crystallized element formed during

the hydration reaction. The lime consumed by the brick fines studied is around 390-400 $Ca(OH)_2$ mg/g brick fines.

Table 3. Physical characteristics of brick fines.

Brick fine	Brick fines	GGBFS
Specific surface, BET (m²/kg)	833	1
Water absorption (%)	1.1	-
Granulometry (μm)		
d10	1.95	1
d50	19.1	8.5
d90	56.6	30
$Ca(OH)_2$ quantity fixed (mg/g brick fines)	394	-

2.4   Preparation of alcali-activating solution

Tests are firstly carried out to determine which types of activators to use and in what proportions. These tests are carried out on mixes with 0, 50 and 100 % mass substitution of brick fines. Mixtures containing only brick fines do not harden, regardless of the activator concentration used. Brick fines cannot be activated on their own and a precursor must be added to the mixture. Two types of activators are finally used in the mixture: sodium hydroxide and sodium silicate.

Two factors allow the mixture to be optimized: a Na_2O content of between 2 and 8% and a SiO_2/Na_2O ratio of 1 to 1.5. These two parameters are calculated from the amount of GGBFS in the mixture. On the basis of the literature review and these preliminary tests, an alkali-activator solution was chosen which combines these two activators: 5% Na_2O fixed and a SiO_2/Na_2O ratio fixed at 1.45. The first formulations (BL) were carried out with a concentration calculated according to the amount of GGBFS in the mixture (table 4). With these formulations, activation is associated with the amount of GGBFS and the brick fines are considered as an addition but not activatable.

Subsequently, a second series of formulations (BLM) was carried out (table 4). The concentration of the solution was calculated according to the total amount of material (GGBFS and brick fines), so that the percentage of Na_2O increases with the increase in brick fines, the SiO_2/Na_2O ratio remaining fixed. As the level of brick fines increases, the amount of silicate in solution remains constant in relation to the total mass of material but increases sharply in relation to the mass of GGBFS. While it is known that optimal activation of GGBFS occurs between 2 and 8% Na_2O, it is expected that beyond this there will be little effect on mechanical strengths and may even lead to efflorescence and carbonation.

The solution was prepared 24 hours in advance to avoid the exothermic reaction associated with the dissolution of sodium hydroxide. The sodium silicate, sodium hydroxide and water are weighed and mixed for several minutes. The solution is prepared and stored in a ventilated hood. Working with higher temperatures would result in increased reaction kinetics and

therefore faster hydration: as one of the effects expected with the addition of brick fines is precisely the slowing down of the hydration, tests were carried out at room temperature.

Table 4. Design of mixes.

BL	GGBFS (g)	BF (g)	Na_2SiO_3 (g)	NaOH (g)	Water (g)	W/B	SiO_2/Na_2O	$\%Na_2O$
0%	1500	0	377	14.2	550.4	0.45	1.45	5
10%	1350	150	340	13	562.7	0.45	1.45	5
20%	1200	300	302	11.5	575.2	0.45	1.45	5
30%	1050	450	265	10	587.7	0.45	1.45	5
50%	750	750	188	7.2	612.9	0.45	1.45	5
BLM	GGBFS (g)	BF (g)	Na_2SiO_3 (g)	NaOH (g)	Water (g)	W/B	SiO_2/Na_2O	$\%Na_2O$
0%	1500	0	377	14.2	550.4	0.45	1.45	5
10%	1350	150	377	14.2	550.4	0.45	1.45	5.6
20%	1200	300	377	14.2	550.4	0.45	1.45	6.25
30%	1050	450	377	14.2	550.4	0.45	1.45	7.14
50%	750	750	377	14.2	550.,4	0.45	1.45	10

The high Al/Si ratio is essential for the incorporation of fines into alkali-activating mixtures with GGBFS. Alkaline activation is essentially a reaction of the aluminosilicates with the sodium silicate in the alkali-activating solution causing polymerization of these elements and giving the material its strength.

3 Results and analysis

The behaviour of the two types of mixes BL and BLM is different. For BL formulations, the workability is impacted from 30% substitution. For BLM mixes, the setting time is affected from 50% substitution onwards and it is the end of setting that is mainly affected. The addition of brick fines to alkali-activated materials at levels above 30% extends the workability time.

Spreading tests (EN 1015-3) indicate that the workability changes little with a low addition of brick fines (below 30%). In contrast, spreading tests with continuous mixing show a change in behaviour with BL mixes and workability increases with the substitution of 30% brick fines. The "freezing" phenomenon can be delayed with a continuous mixing protocol as well as by lowering the concentration of the activating solution and increasing the brick fines content. The workability time (EN 196-3), which is a handicap of alkali-activated materials, can therefore be extended in this case.

The alkali-activation kinetics of the mixtures changes according to the mixtures. For the BL 10% formulation, the precipitation of secondary C-A-S-H is delayed by more than one day. With the BLM mixtures, at 10% brick fines, the hydration kinetics is similar or even faster than that of GGBFS. With the addition of brick fines at 50%, the induction period is slightly longer. The hydration kinetics are delayed by the addition of brick fines, but this can be compensated for by increasing the concentration of the activating solution.

Alkali-activation kinetics and hydrate generation are increased when the activator solution is more concentrated for the same brick fines substitution rate. Conversely, alkali-activation kinetics and hydrate generation decrease with increasing brick fines substitution rate for a constant activator solution concentration.

Thermogravimetric analyses show that the hydrates formed in alkali-activated GGBFS materials are identical to those formed during brick fines substitution: C-A-S-H, hydrotalcite and carbonates. The total mass loss at 90 days of the samples with 10% fines is identical to the GGBFS for the higher concentration activator solution but decreases when the activator solution is at a lower concentration. There is less hydrate formed with the samples containing 50% brick fines, especially for the BL 50% sample which is the least concentrated in activator solution.
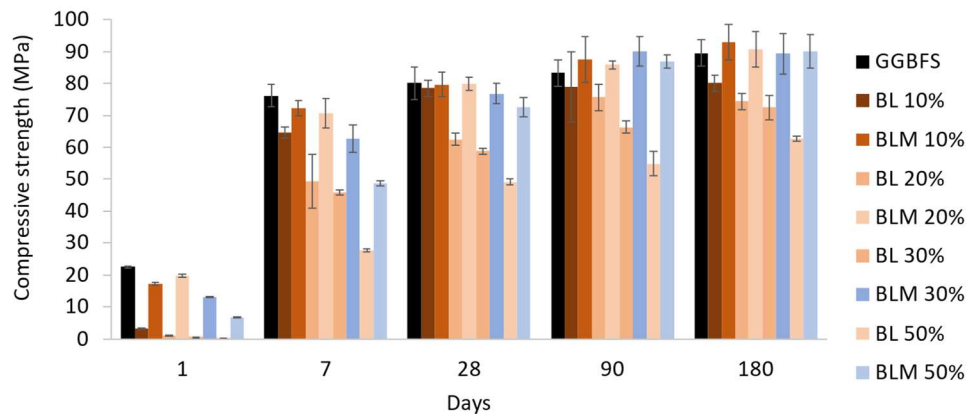
Fig. 1. Evolution of compressive strength of BL and BLM mixes with time (EN 196-1)

In terms of mechanical performance (Fig. 1), a different behaviour between the two mixes is noted. For the BL formulations, the compressive strength is very low in the early stages but improves in the long term while remaining below that for GGBFS alone. Compressive strengths exceed 60 MPa at 180 days, regardless of the level of brick fines, and above all the loss of strength is not proportional to the level of substitution, thus showing a beneficial role for brick fines. For BLM mixes, the strength increase is faster and the performance is equivalent to GGBFS, even with 50% brick fines, from 28 days. This demonstrates that brick fines can be considered as an activatable mineral addition.

Poral distribution has been evaluated by means of Mercury Intrusion Porosimetry. During phase precipitation, porosity decreases with time and the pore size distribution becomes concentrated in pores smaller than 0.1 μm in diameter after 90 days (Fig. 2). The pore size distribution is equivalent between the control and the samples with 10% fines as well as the BLM 50% sample. The proportion of finer pores is lower for the BL 50% sample. The microstructure refinement is little impacted by the addition of brick fines when the mixtures are formulated with high concentrations of activating solution.
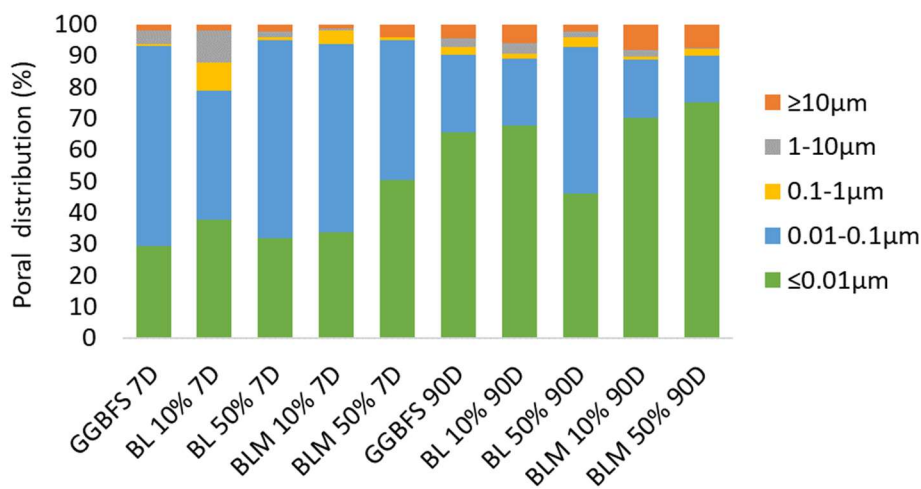

Fig. 2. Poral distribution of BL and BLM mixes at 7 and 90 days.

4 Conclusions

Results show that, for formulations with a lower concentration, the mechanical performance at a young age is very low but improves afterwards and can be partially compensated for after 90 days. This loss of strength is in favour of an increase in the workability of the material. The setting time of these formulations is longer, provided that a continuous mixing protocol is put into practice. In these formulations, the use of brick fines can also be envisaged while allowing a reduction in the activating solution used. The two types of mixes (BL and BLM) therefore have different strengths. Formulations based on the activation of brick fines with a concentration of activators calculated on the total mass of material show the best performances.

This type of mixture allows for optimal valorization and activation of the brick fines. In all cases, the development of an alkali-activated binder based on GGBFS and using a large proportion of brick fines (up to 50%) is viable. The use of brick fines allows a significant economic and ecological gain since the value of the brick fines is lower even including the

cost of crushing the brick aggregates and allows the recovery of a waste product rather than its disposal.

Acknowledgements

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