

EXPANSION BEHAVIOR OF GROUND GLASS CULLET USED AS AGGREGATE OR CEMENT REPLACEMENT

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Abstract

The possibility of exploiting recycled glasses of different composition and origin as aggregates or cement replacement in cementitious composites has been investigated. Experimental data, so far collected on mortar samples, show that glasses chemical composition plays an important role in generating highly expanding products that can hinder the use of such glasses even at low size distributions, i.e. as cement replacement.

Keywords: glass recycling, alkali-silica reaction, glass oxides composition

1 INTRODUCTION

Alkali silica reaction (ASR) is surely one of the most deleterious event that can occur in concrete: the reaction products are expansive and lead to crack formation with disruptive effects. Accordingly, high quality aggregates need to be used in building engineering as prescribed by the European standards EN 12620 “Aggregates for concrete” and EN 13139 “Aggregates for mortar”, which introduce characteristics and limits to obtain CE certification. This official recognition is particularly important if the use of recycled and unconventional aggregates is considered. Their exploitation has been recently encouraged by specific laws (in Italy, for example, by the Ministerial Decree 14/09/2005 “Technical standard for building construction”) and presents environmental advantages, such as safeguard of not renewable raw materials and decrease of landfill disposal.

Recycled glass has been used as concrete aggregate[1,2,3], however, its amorphous nature can promote and develop ASR. As recycled glass may come from many sources, for example urban separated collection, industrial waste, television screen (cathode-ray tube, CRT), etc., it is very important to investigate how glass composition and dimension influence ASR. It has been recently reported that ground glass with dimension $<38 \mu\text{m}$ [4] or $<10 \mu\text{m}$ [5] exhibit pozzolanic behavior, whereas glass coming from televisions cathode-ray tube, even at dimension $<50 \mu\text{m}$, forms expanding products [6].

In this work, different types of glass (soda-lime, borosilicate, leadsilicate glasses), whose origin will be specified afterwards in details, have been studied to test their reactivity towards alkalis: all glasses have been used as aggregates or partial cement replacement. Cullet used in this research comes from alimentary, pharmaceutical and house-ware glasses. These glasses, on account of their use in contact with food or substances for personal uses, must fulfill safety requirements concerning hazardous elements leachability, according to Italian Ministerial Decree 21/03/1973 “Hygienic dispositions for packages, containers and tools for direct contact use with food and personal use substances” and following issues. Moreover, Italian laws (Italian Ministerial Decree 05/02/1998 “Selection of non hazardous waste for simplified recycling procedures according to art. 31, 33 of Decree 05/02/1197 N.22” and following modifications published on Italian Ministerial Decrees 09/01/2003, 27/07/2004, 5/04/2006) allow to use glass cullet as recycled material for new glass production and manufacturing of cement matrix conglomerates. Some of these glasses do contain heavy metals which could be progressively leached from cementitious composites; however, many studies [7, 8] have proved that suitable formulations of cement composites can efficiently restrain this process.

By reporting the results of expansion tests in accelerated curing conditions, as well as SEM observations and EDS semiquantitative analysis, the aim of this paper is to investigate if the chemical composition of the investigated glasses can influence expansive gel formation according to the different role exerted by the glass.

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2 MATERIALS AND METHODS

2.1 Glasses

Five different types of glass waste were used: soda-lime glass (hereafter referred as SC-U) coming from beverage containers cullet (kindly supplied by Bormioli Rocco, Fidenza (PR) Italy), ucoloured borosilicate glass (BS-U) and amber borosilicate glass (BS-A) coming from pharmaceutical containers cullet (kindly supplied by Bormioli Rocco, Fidenza (PR) Italy) and leadsilicate glass (CR), coming from production of tableware, giftware and home décor items in crystal (kindly supplied by CALP, Colle di Val d'Elsa (SI) Italy). The chemical composition (wt%) of the investigated materials, as derived by Inductively Coupled Plasma Spectrometry ICPS (ICP-OES Perkin Elmer, Optima 3200 XL), is reported in Table 1: values below 50xLLD have been omitted. Samples for the analysis were prepared according to the following procedure: 1) 200 mg of dry glass powder (grain size < 125 μ m, dried at 105°C) were hot treated with an excess of HNO₃ and HF, till complete evaporation: the residue was treated with HNO₃ (1N) and bi-distilled water; 2) acid digestion of 100 mg of powder at 200°C for 20 min with the aid of microwaves.

The investigated glasses used as aggregates were dry comminuted in a laboratory steel jaw crusher to get particles between 0.075 and 2.00 mm, with size distribution close to that of normalized sand (EN 196-1). The investigated glasses used as partial cement replacement were obtained by dry grinding in a laboratory agate ball mill. Chemical analysis of the sand-like and cement-like size materials did not provide significant variation from those of Table 1. Table 2 reports, for all the investigated materials, the values of D₅₀, mean diameter defined as a 50% limit in particles distribution whereby 50% by volume of the particles have a diameter below the 50% limit and 50% by volume of the particles have a diameter above the 50% limit.

2.2 Mortar

A Type I Portland Cement 52.5 R (EN 197-1) was used, whose equivalent alkali content was 0.65 wt%. Mortar samples were mixed with a 1/3 binder/aggregate ratio and water/binder ratio equal to 0.5, following the procedure described in EN 196-1. 40x40x160 mm specimens were cast to investigate their dimensional stability.

Mortar samples containing glass as aggregates (hereafter referred as M/BS-A, M/BS-U, M/CR, M/SC-U), after 1 day at 25°C and 100% R.H., were submitted to accelerated curing at 80°C in a 1M NaOH solution. This procedure closely resembles ASTM C1260 Standard. Glass replaces aggregates for 10, 25 and 35 wt%; reference samples were also prepared for comparison sake.

When glass was used as cement replacement (25 wt%), mortar samples (MF/BS-A, MF/BS-U, MF/CR, MF/SC-U) were cured in the same conditions mentioned above to investigate, again, their possible expansion. Table 3 summarises all the investigated compositions.

2.3 Methods for assessment and analysis

Compression and expansion tests

Mechanical tests were performed at room temperature and at R.H. 50 \pm 10 % by means of 200 kN Volpert Amsler equipment at a 50 mm/min rate.

Expansion was determined by means of a mechanical comparator (0.001 mm accuracy) on samples cooled at room temperature: the detailed procedure is elsewhere reported [9] and is close to that prescribed by ASTM C1260.

Scanning electron microscopy and EDS analysis

Morphological investigations were carried out on fractured surfaces coated with gold by means of a Philips XL 20 electron scanning microscopy equipped by secondary electrons detector. Polished thin sections (about 3 μ m thick) were also prepared by dry cutting with a diamond saw the 40x40x160 mm mortar samples, which were treated with carborundum paper. Small particles were removed by air-blowing and samples were treated with acetone to eliminate water and sputtered with carbon: the resulting samples were analysed with EDS detector (Genesis 2000, Philips). Operating conditions were set at 10 kV with a probe current of 9 \pm 2 nA; the vacuum condition were below 10⁻⁴ Torr. At this stage of experimental work, boron could not be evaluated; the analysis were performed without internal standards and, accordingly, reported values should be considered as indicative of the phases composition and affected by the intrinsic uncertainty related to the undefined volumes of X-ray emission.

3 RESULTS

Figure 1, 2 and 3 report the expansion of bars containing 10, 25 and 35 wt% of glass cullet substituting normalized sand. As can be seen, M/CR and M/BS-U exceed the safety limit (0.1%) suggested by ASTM C 1260 standard at all the compositions while M/SC and M/BS-A almost always remain below this limit. The different behavior of colored and uncolored glasses towards expansion (i.e. BS-A vs BS-U) had been already observed on glasses of different composition [2]. The level of expansion induced by CR is remarkably higher than that of all the other glasses, whichever the amount of aggregate is replaced.

Figure 4 reports the dimensional stability of bars containing 25 wt% of glass powders as cement replacement. It is important to notice that sample MF/CR, after about one week of curing, exceeds 0.1 % expansion, while all the other formulations remain below this limit at the nominal exposure times. Figure 5 reports the compressive strength of the same mortar samples after 14 days of curing. MF/SC-U mortar reaches the same mechanical characteristics of the reference: 10-15 % decrease is determined for MF/BS-A and MF/BS-U and about 30% for MF/CR. The effect of these glasses as cement constituent for new blended cement production has been recently investigated [10] by means of the activity index determination to establish if they can exert pozzolanic behavior: preliminary results indicate soda-lime and uncolored borosilicate glasses as the more promising additions. This behavior is also consistent with an other study [4] where glasses of similar chemical compositions were investigated.

ASR products have been observed in all samples containing glass cullet as aggregates, although they were present at different volume concentrations: their morphology was quite similar in all mortars, and indeed close to those previously reported in literature [11]. Figure 6 reports, as an example, the fracture surface of M/CR sample. Similar products were also found in MF/CR (Figure 7), while all the other MF samples did not contained ASR products.

In Table 4, the oxide composition (wt%) of the gels determined by EDS on samples containing glass as aggregates is reported: at least eight different areas for all samples have been investigated. The results reported should be considered only as indicative of the gel composition on account of: 1) the intrinsic limits of the technique, unable to define the true volume of X-ray emission and determine boron oxide; 2) the possible evaporation of alkaline ions *in vacuo* when the gels were scanned by the electron beam.

Some observations may be drawn from Table 4: 1) the wt% oxide composition of SC-U gel is quite consistent to those found elsewhere for traditional ASR products [12], particularly for Na₂O and K₂O; 2) there is no direct correlation between the overall expansion and the relevant SiO₂ content in the original glass; 3) gel deriving from SC-U has a lower sodium content than the relevant glass, whereas CR gel exhibits the opposite behavior. A similar behavior can be observed also for BS-U and BS-A, even if in the gels composition reported boron content can not be included; 4) heavy elements (Pb, Fe, Ba, Ti) are present in CR, BS-U and BS-A gels.

Table 5 reports the molar ratios between selected elements present in the gels: in details, alkalis divided by earth-alkalis, the total amount of bivalent cations divided by the total amount of bivalent and monovalent cations with (*) or without considering Pb²⁺ and Ba²⁺ cations.

4 DISCUSSION

The question we would wish to answer with our experimental work is: why do some glasses generate expansion phenomena in cementitious composites while other behave safely or even improve the material characteristics? This problem involves two different aspects that act simultaneously: 1) the rate and extension of glass dissolution in an alkaline environment; this feature will affect the amount of reacted glass particles and thus the amount of reaction products; 2) the chemical composition and the swelling capacity of the gel that is formed from glass dissolution.

As to what concerns the first aspect, experimental results on the rate of glass dissolution of our systems are presently not available: literature data [13], however, predict a high solubility of lead in alkaline environment. It is thus possible to postulate that the high CR solubility has lead to an high amount of gel formation (qualitatively observed by SEM) with deleterious effects on mortar, regardless glass specific surface.

In borosilicate glasses, transition metals (iron, titanium, zinc) tend to reduce the dissolution rate [14] and this lower solubility should lead to a reduced amount of gel thus reducing expansion: indeed M/BS-U expands more than M/BS-A. This effect should be also evident when glass specific surface is higher; however, when BS-A and BS-U are used as cement replacement, no expansion is detected in both cases, meaning that solubility process plays a different role in both glasses. Actually, powdered glass solubility is still regulated by chemical glass composition, but in this case soluble ions

are involved with cement reactions products thus leading to pozzolanic reaction. Accordingly, a higher pozzolanic activity for BS-U than BS-A, when used as cement replacement, has been determined [10].

Concerning the swelling capacity of the gels, some theories have been formulated to correlate expansion to their chemical composition: they usually consider the ratio between alkalis and earth-alkalis elements [15] predicting, for example, high swelling capacity in gels containing large content of alkalis. However, analysing Table 5, we realize that this principle can possibly discriminate BS-A and BS-U expanding behavior, but it is unable to predict CR expansion. Other theories exploit the double-layer model (EDL) [16] to explain gels potential expansion. This theory predicts reduced swelling for gels containing highly charged ions: in our case, the different behavior of BS-U and BS-A on account of the presence of Fe^{3+} cations in BS-A gels could be explained, but, contrarily, the presence of a bivalent cation (Pb^{2+}) has no mitigating effect on CR gels swelling tendency. This theory allows to define a parameter, the charge fraction E_{biv} , defined as the ratio between the sum of bivalent cations (usually only Ca^{2+} and Mg^{2+}) divided by the total amount of mono and bivalent cations [17]: the higher its value, the lower the expansion should be. Table 5 reports two different E_{biv} values, calculated ignoring or considering (*) the presence of Pb and Ba in the gels. Again, CR behavior can not be explained by the use of this index, confirming that the leadsilicate glass behavior is anomalous compared to the other glasses and needs further studies.

According to these preliminary observations, to be confirmed by analysing gels composition with more reliable techniques than EDS and from experimental solubility tests, it seems that the first aspect (solubility, rate of dissolution) prevails in borosilicates glasses: as to what concerns CR, solubility still plays an important role, but a direct effect of lead atoms in the gels expansion may be envisaged.

5 CONCLUSIONS

The main conclusions from the experimental work previously described, can thus be summarized:

- the glass chemical composition has a strong influence on the extent of mortar expansion formulated with glass aggregates: this expansion exceeds the safety limits suggested by ASTM standard when leadsilicate and uncolored borosilicate are used;
- even at fine dimension, leadsilicate glass can lead to undesired effects and can not be safely used as cement replacement;
- from the experimental data so far collected, the main factors influencing the glass expansive characteristics seem to be their rate of solubility, but a specific effect of lead ions cannot be still ruled out for CR.

6 REFERENCES

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- [1] Bignozzi MC, Sandrolini F (2006): Wastes by glass separated collection: a feasible use in cement mortars and concrete. In: Limbachiya MC, Roberts JJ (eds): Proceedings of the International Conference Sustainable waste management and recycling Kingston University, London, 17-24 September 2004, , Thomas Telford, London, UK.
 - [2] Jin W, Meyer C, Baxter S (2000): Glas-crete: concrete with glass aggregate. *ACI Materials Journal* (97 - 2): 208-213
 - [3] Shi C, Zheng K (2007); A review on the use of waste glasses in the production of cement and concrete. *Resources Conserv Recycl* (52): 234-247.
 - [4] Shao Y, Lefort T, Moras S, Rodriguez D (2000): Studies on concrete containing ground waste glass. *Cement & Concrete Research* (30): 91-100.
 - [5] Bignozzi MC, Sandrolini F, Franzoni E, Andreola F, Barbieri L, Lancellotti I (2004): Recycled fillers for Self Compacting Concrete: CRT glasses (Italian). In: Morselli L (eds): Proceedings of Ecomondo, Rimini (Italy) 3-6 November 2004, 185-192, Maggioli, Rimini, Italy.
 - [6] Shayan A, Xu A, (2006): Performance of glass powder as a pozzolanic material in concrete: a field trial on concrete slabs. *Cement & Concrete Research* (36): 457-468
 - [7] Chen QY, Tyrer M, Hills CD, Yang XM, Carey P (2008): Immobilisation of heavy metal in cement based solidification/stabilisation: a review. *Waste Management* doi: 10.1016/j.wasman.2008.01.019
 - [8] Bar-Nes G, Katz A, Peled Y, Zeiri Y, (2008): The mechanism of cesium immobilization in densified silica fume blended cement pastes. *Cement & Concrete Research* (38): 667-74

- [9] Saccani A, Bonora V, Monari P (2001): Laboratory short-term ASR: a contribution. *Cement & Concrete Research* (31): 739-42
- [10] Bignozzi MC, Sandrolini F (2008): Effects of different glasses composition on ecosustainable blended cements. In: *Proceedings of the Conference Excellence in Concrete Construction Through Innovation* Kingston University, Kingston upon Thames, UK. September 9-10, 2008, Taylor & Francis, in press.
- [11] Shayan A (1992): The pessimum effect in an accelerated mortar bar test using 1M NaOH solution at 80°C. *Cement & Concrete Composites* (14): 249-55
- [12] Hou X, Kirkpatrick RJ, Struble LJ, Monteiro PJM, (2005): Structural investigation of ASR. *Journal American Ceramic Society* 88 (4): 943-949
- [13] Carmona N, Garcia-Heras M, Gil C, Villegas MA (2005) Chemical degradation of glasses under simulated marine medium. *Materials Chemistry & Physics* (94): 92-102
- [14] Trocellier P, Djanathany S, Chene J, Haddi A, Brass AM, Poissoneet S, Farges F (2005): Chemical durability of alkali-borosilicate glasses studied by analytical SEM, IBA, isotopic-tracing and SIMS. *Nuclear Instruments & Methods in Physics Research B* (240) 337-344.
- [15] Chatterji S (2005): Chemistry of alkali-silica reaction and testing of aggregates. *Cement & Concrete Composites* (27): 788-795
- [16] Monteiro PJM, Wang K, Sposito G, dos Santos MC, de Andreade WP (1997): Influence of mineral admixtures on the alkali aggregate reaction. *Cement & Concrete Research* (27): 1899-1909

TABLE 1: Main element composition of bulk materials by ICP in wt%.

Oxide	Investigated glasses				
	LLD	BS-U	BS-A	SC-U	CR
SiO ₂	0.07	68.1	65.3	70.2	61.7
Al ₂ O ₃	0.04	5.64	5.88	2.06	°
B ₂ O ₃	0.001	11.56	10.70	0.69	0.72
MgO	0.0007	°	°	1.47	°
CaO	0.002	1.53	1.42	11.10	°
Na ₂ O	0.04	8.06	8.02	13.1	3.96
K ₂ O	0.024	1.24	1.16	1.21	6.96
ZnO	0.006	0.82	0.78	°	0.9
BaO	0.001	2.95	2.86	0.12	°
Fe ₂ O ₃	0.014	°	0.78	°	°
TiO ₂	0.0003	°	2.89	°	°
PbO	0.0043	*	*	*	25.3
Sb ₂ O ₃	0.007	*	*	*	0.26
Sum	-	99.90	99.79	99.95	99.53
° below 50 x LLD * not determined					

TABLE 2: Mean diameter of glass powders.

Glass	D50 (µm)
BS - U	29.9
BS - A	28.2
SC - U	9.9
CR	33.1

TABLE 3: Weight composition (g) of the investigated mortars.

Type	Cement	Binder	Water	Silica Sand	Coarse Glass
REF	450	0	225	1350	0
MF/BS-U	338	112	225	1350	0
MF/BS-A	338	112	225	1350	0
MF/SC-U	338	112	225	1350	0
MF/CR	338	112	225	1350	0
M/BS-U 10	450	0	225	1215	135
M/BS-A 10	450	0	225	1215	135
M/SC-U 10	450	0	225	1215	135
M/CR 10	450	0	225	1215	135
M/BS-U 25	450	0	225	1013	337
M/BS-A 25	450	0	225	1013	337
M/SC-U 25	450	0	225	1013	337
M/CR 25	450	0	225	1013	337
M/BS-U 35	450	0	225	878	472
M/BS-A 35	450	0	225	878	472
M/SC-U 35	450	0	225	878	472
M/CR 35	450	0	225	878	472

TABLE 4: Oxide wt% gel composition.

Oxide	CR	SC	BS-U	BS-A
SiO ₂	45.81	54.85	59.05	56.43
Al ₂ O ₃	0.36	2.03	8.10	6.95
CaO	22.05	35.64	5.29	4.30
MgO	0.44	-	-	-
Na ₂ O	14.77	4.21	22.39	21.23
K ₂ O	3.69	3.27	4.02	2.12
PbO	12.88	-	-	-
TiO ₂	-	-	-	5.44
Fe ₂ O ₃	-	-	-	0.53
BaO	-	-	1.15	1.0

Data normalized at 100 %
excluding volatiles

TABLE 5: Element molar ratios.

Molar ratio	CR	SC	BS - U	BS - A
(Na+K)/Ca	1.34	0.29	18.00	11.49
$\Sigma(b)/\Sigma(bm)$	0.43	0.78	0.05	0.08
$\Sigma(b)/\Sigma(bm)^*$	0.48	0.78	0.06	0.09

* considering Pb and Ba cations

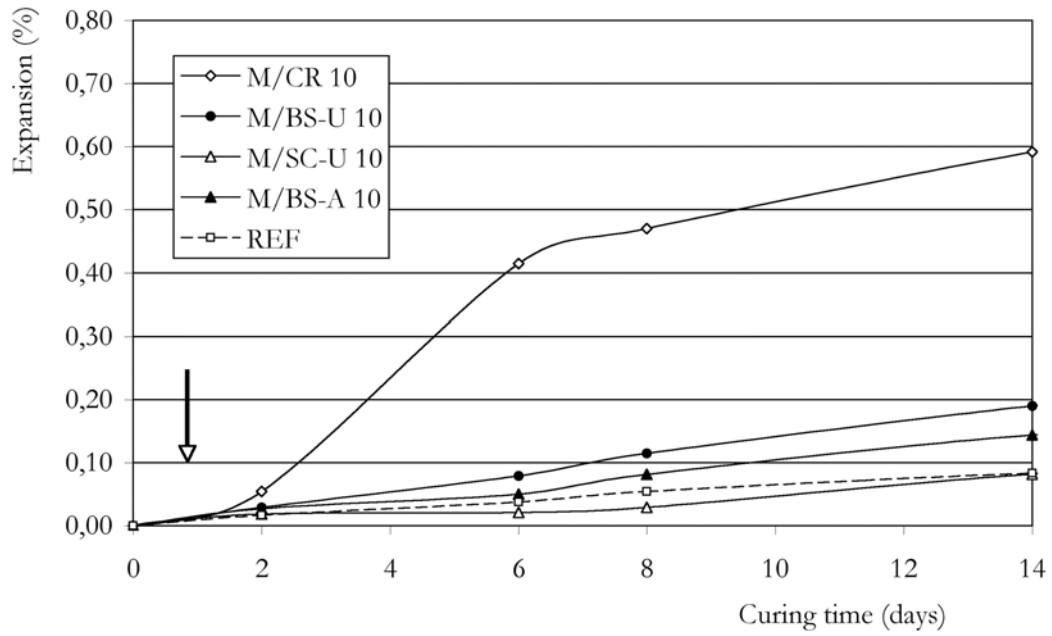


Figure 1: Relative expansion of mortar bars with coarse glass cullet replacing 10 wt% of aggregates (arrow: expansion limit at 14 days according to ASTM C1260).

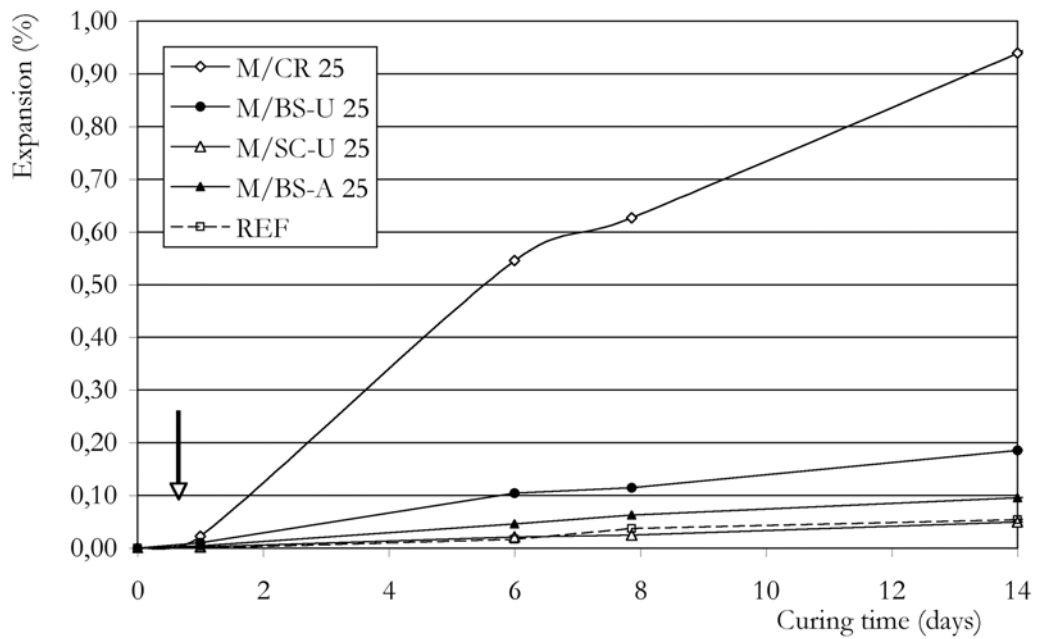


Figure 2: Relative expansion of mortar bars with coarse glass cullet replacing 25 wt% of aggregates (arrow: expansion limit at 14 days according to ASTM C1260).

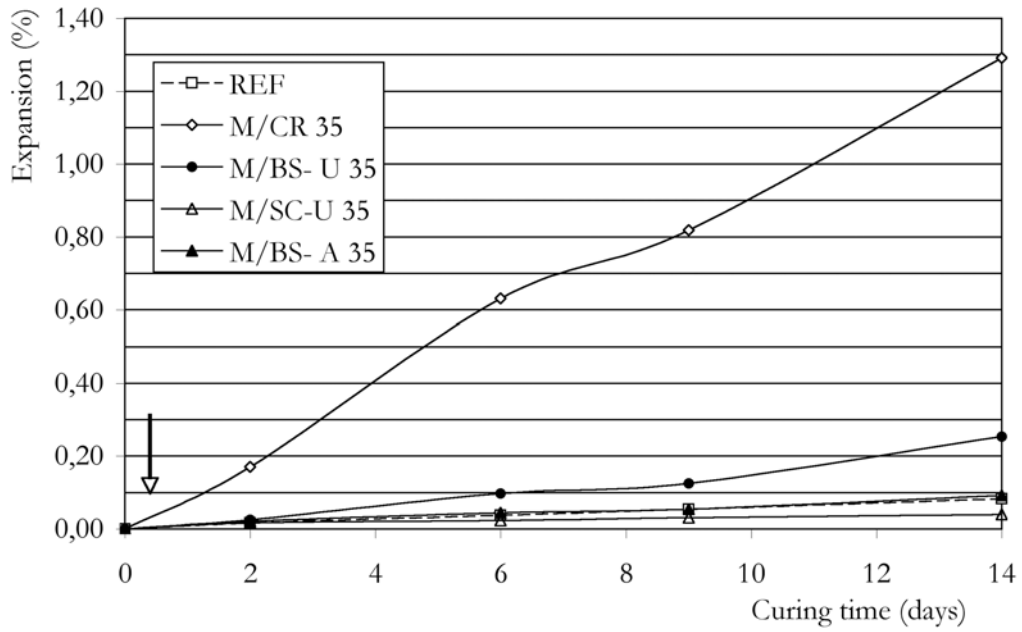


Figure 3: Relative expansion of mortar bars with coarse glass cullet replacing 35 wt% of aggregates (arrow: expansion limit at 14 days according to ASTM C1260).

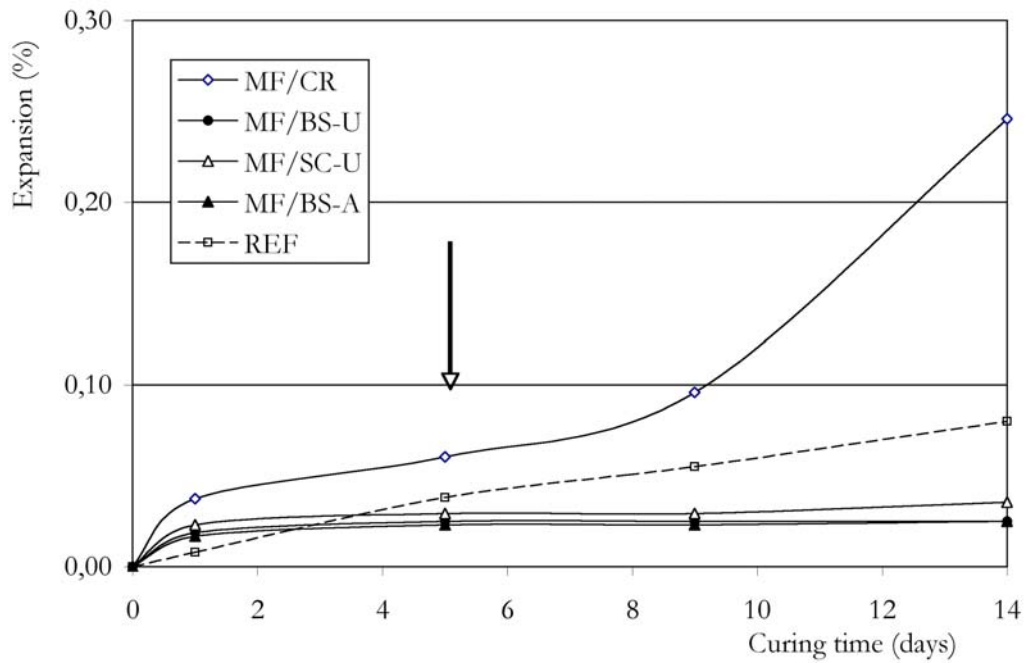


Figure 4: Relative expansion of mortar bars with powdered glass cullet replacing 25 wt% of OPC binder (arrow: expansion limit at 14 days according to ASTM C1260).

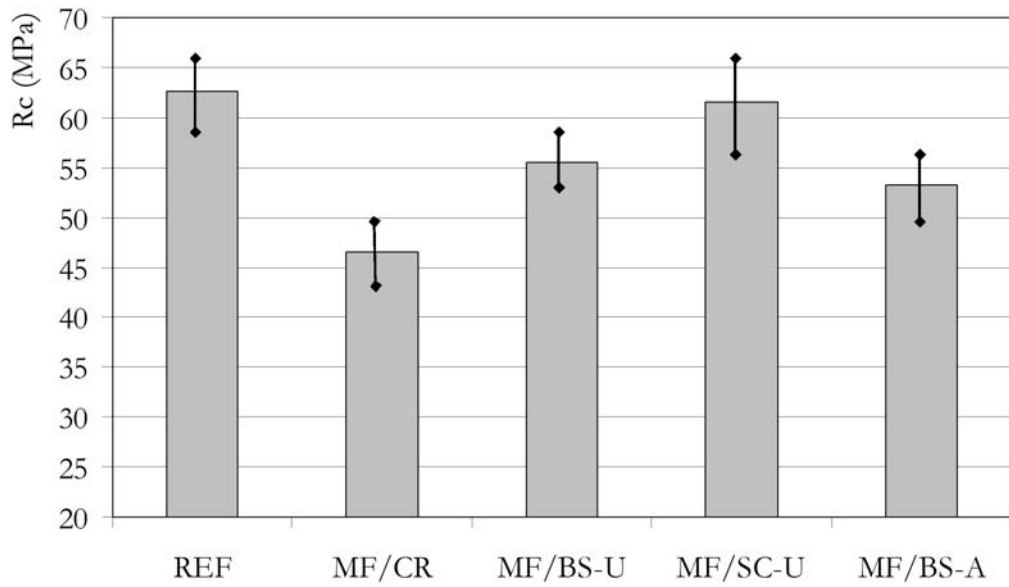


Figure 5: Compressive strength after 14 days of mortar bars with powdered glass cullet replacing 25wt% of OPC binder (confidence limits at 80% of probability).

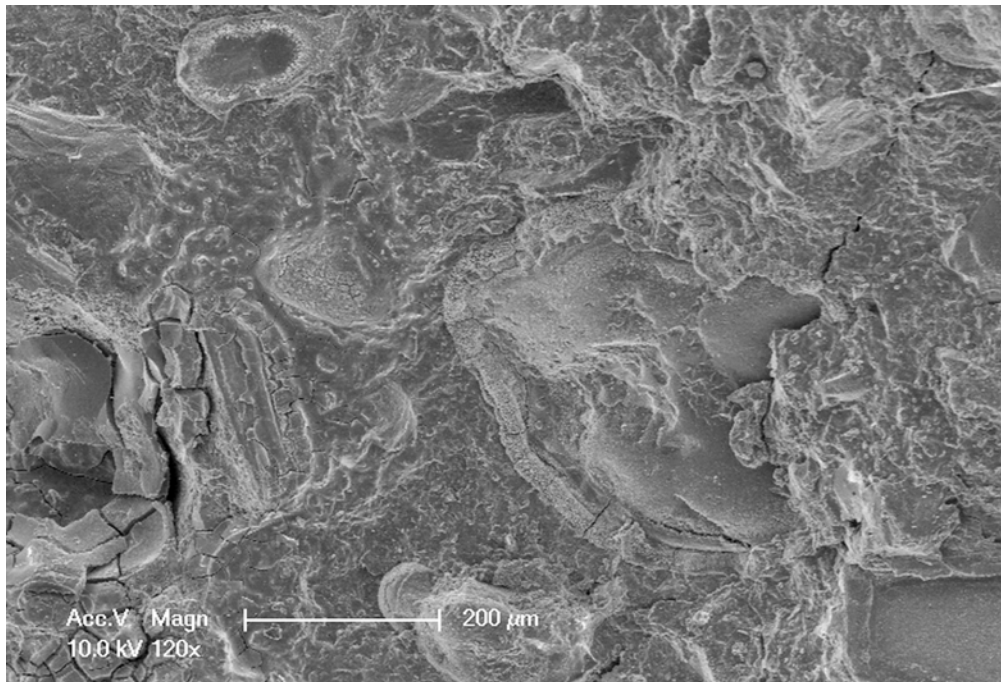


Figure 6: ASR products M/CR (35% of sand replacement) at 14 days of curing.

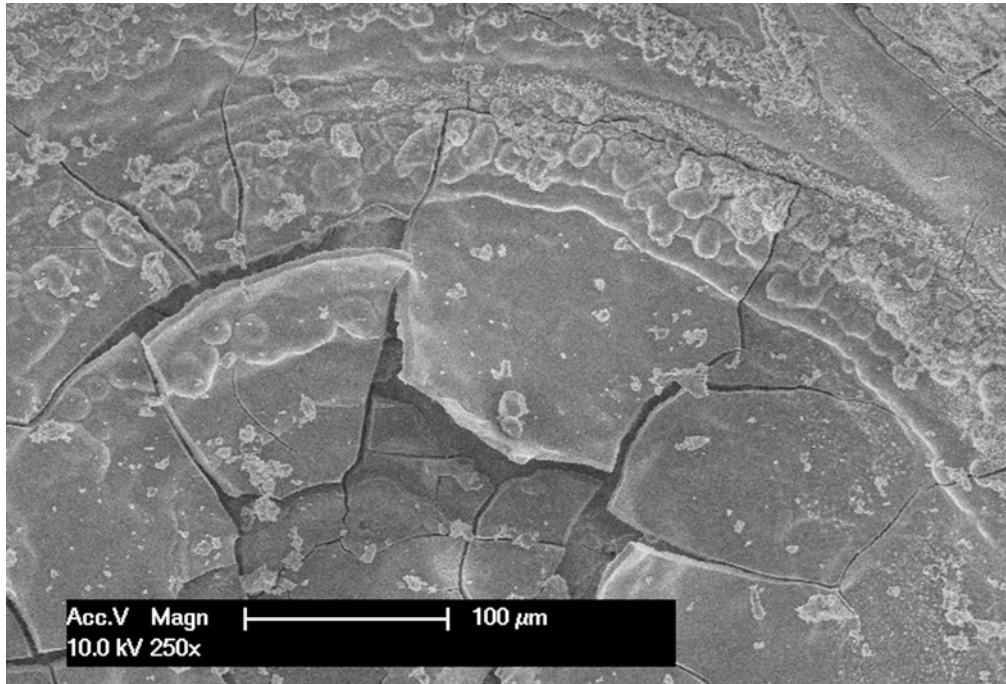


Figure 7: ASR product in MF/CR mortar at 14 days of curing.