Cement and Concrete Research 40 (2010) 546–549

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

ASR pessimum behaviour of siliceous limestone aggregates

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ARTICLE INFO

Article history:
Received 3 November 2008
Accepted 19 August 2009

Keywords:
Aggregate (D)
Alkali-Aggregate Reaction (C)
Calcium Silicate Hydrate (C-S-H) (B)
Concrete (E)
Pessimum effect

ABSTRACT

Siliceous limestone aggregates have “pessimum” behaviours similar to those observed for pure siliceous aggregates such as flint or opal. For high alkali contents concretes based on fine and coarse reactive siliceous limestone aggregates swell less than concretes based on fine reactive siliceous limestone aggregates and non-reactive coarse aggregates. The reduction of the swelling is more significant for a “micritic” limestone containing highly reactive free silica than for a “sparitic” limestone containing less reactive free silica. The consumption of a part of the alkalis by non-expansive processes such as chemical sorption on silanol sites of reactive silica and pozzolanic C–S–H is expected to explain the reduction of the swelling.

1. Introduction

Pure reactive siliceous aggregates such as flint or opal have a “pessimum” effect: for a given level in alkalis, the swelling of concretes based on these aggregates increases first with the reactive aggregate content to reach a “maximum” value and finally decreases for a reactive aggregate content superior to the “pessimum” (Fig. 1).

Hobbs [1] distinguished 4 areas on the “pessimum” curve (Fig. 1):

- Areas A and D: the reaction occurs but is too weak because of a lack in reactive silica (area A) or in alkalis (area D) to induce a swelling phenomenon.
- Area B: the reaction occurs with an excess of alkalis. The swelling increases with the reactive silica content.
- Area C: the reaction occurs with an excess of reactive silica. The swelling decreases with the reactive silica content.

Concretes based only on reactive flint aggregates (both fine and coarse) have compositions generally located in area D: in spite of a high level in alkalis (over 5 kg of Na_2Oeq per m^3), these kinds of concretes constituted by reactive pure silica don't swell.

The aim of this paper is to verify the possibility of reaching area D for reactive siliceous limestone aggregates in spite of their low reactive silica contents compared with the pure reactive silica aggregates.

Our methodology consists of comparing the swelling of high alkali concretes with different contents in fine and coarse reactive siliceous limestone aggregates (a “micritic” and a “sparitic” siliceous limestone aggregate).

2. Materials and methods

2.1. The siliceous limestone aggregates

Two limestone aggregates, a ‘micritic’ with a high content in reactive silica (SL1 aggregate) and a ‘sparitic’ with a low content in reactive silica (SL2 aggregate) were used. A pure limestone (N aggregate) which doesn't contain reactive silica has also been used as a non-reactive reference.

2.2. The concrete compositions

The concrete composition is given in Table 1, and according to the French standard NF P 18-587 the concrete aggregate is classified as susceptible to ASR.

The alkali content of the OPC is equal to 0.8% by weight of Na_2Oeq. To obtain 5125 kg/m^3 of Na_2Oeq in the concretes we add 1 M sodium hydroxide in the concrete water.

Nine concretes based on siliceous limestone fine aggregates which contain either non-reactive or reactive limestone coarse aggregates were made. The aggregate components and the symbols of these nine concretes are in Table 2.

2.3. The swelling test

The swelling test was realized in accordance to the French standard NF P 18–587 [2]. The concrete specimens are prisms of $7 \times 7 \times 28$ cm^3. The swelling test is realized at 38 °C and 100% of relative humidity. The relative longitudinal variations of the prisms ($\Delta L/L$) are measured after 35 weeks (8 months). If this variation is superior to 400 µm/m (0.04%) the aggregate is considered as reactive.

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0008-8846/$ – see front matter
doi:10.1016/j.cemconres.2009.08.011

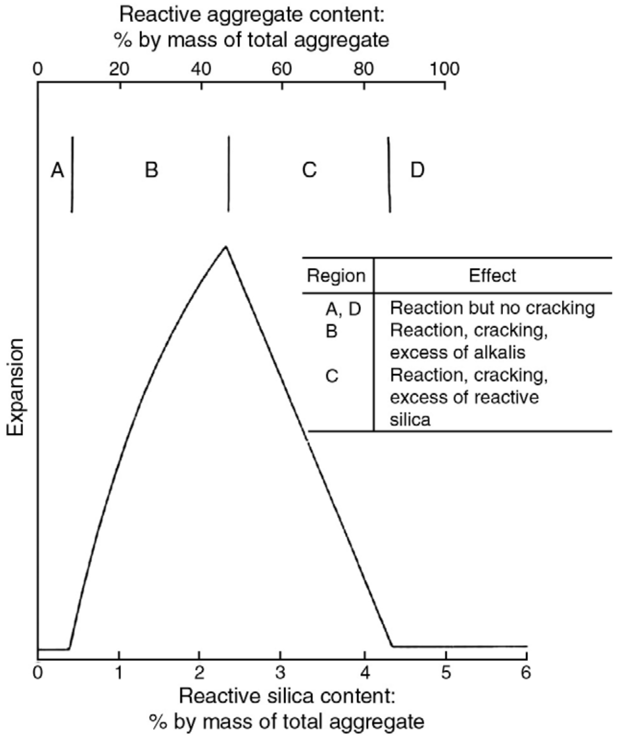

Fig. 1. "Pessimum" behaviour of pure siliceous aggregate according to Hobbs [1].

3. Results

3.1. Mineralogical composition of the siliceous limestone aggregates

The SL1 and SL2 aggregates have been characterized by Monnin et al. in a previous paper [3]. We present hereafter a synthesis of this paper, and a mineralogical composition of the aggregates is given in Table 3. The geologic age of these limestones from the North of Europe is between 345 and 355 million years. This kind of aggregate is implicated in several cases of civil-engineering structures affected by the ASR.

According to the classification of Dunham [4]:

- The siliceous limestone SL1 is a micrite constituted mainly of calcite associated with a smaller quantity of dolomite. Several silicates are detected: phyllosilicates identified as illite and clinochlore. Illite is more important and dispersed within the carbonated matrix. Potassium-feldspar and framboïdal pyrite are also present in lesser quantities.
- The siliceous limestone SL2 is classified as a packstone. This is a "sparitic" rock containing many bioclasts and massive crystallised calcite. Dolomite is more important than in SL1, illite and K-feldspar are present in a lesser quantity than in SL1. Clinochlore was not observed.

The SL1 aggregate has a higher content in potential reactive free silica. The main silica type is anhedral quartz of authigenic origin with a grain size less than 50 µm. Another part of the silica is finely divided silica observed in the interstices of this mudstone associated with the clayey fraction.

The free silica of the SL2 aggregate is more heterogeneous and is not so much dispersed. The main silica is euhedral quartz with a maximum size of 150 µm. A light acid treatment reveals the presence of some structural flaws. In many aggregates, fibrous chalcedony is frequently observed in variable proportions and often enclosed in massive calcite grains. Chalcedony generally contains many inclusions of dolomite. Finally, microcrystalline quartz and lamellar silica are observed occasionally.

In Table 4, the free silica types are summarized and their relative proportion classified from "majority" to "not observed". According to the ASR literature, the potential reactivity of each silica type is classified [5,6]. Consequently, SL1 is mainly constituted by anhedral silica which is strongly reactive. On the other hand, SL2 is mainly constituted by euhedral quartz which is not the most deleterious type. The frequently observed chalcedony seems to be the main source of reactivity for SL2.

3.2. Concrete free silica contents

The free silica content of the limestones (Table 3) allows us to calculate the free silica content "SiO_2" of each concrete composition. Table 5 gives the calculated values as the mass ratio "SiO_2/Na_2O".

Table 1
Concrete composition.

Fine aggregate [0–5 mm]	Coarse aggregate [5–20 mm]	Cement OPC 42.5	Water	Alkali content Na_2O eq
607 kg/m^3	1173 kg/m^3	410 kg/m^3	193 l/m^3	5125 kg/m^3

Table 3
Mineralogical composition of the siliceous limestone aggregates according to Monnin et al. [3].

	SL1	SL2
	Weight (%)	
Calcite	71.4	81.7
Illite	10.3	3.8
Free silica	7.8	5.6
Dolomite	6.7	8.1
K-feldspar	2.0	0.5
Clinochlore	1.5	–
Pyrite	0.3	0.3
SUM	100	100

Table 4
Potential reactivity of silica types and their proportion in both aggregates according to Monnin et al. [3].

Silica types	Reactivity potential	SL1	SL2
Euhedral quartz	Weak	Not observed	Majority
Anhedral silica	Strong	Majority	Not observed
Chalcedony	Strong	Not observed	Frequent
Microcrystalline quartz	Strong	Scarce	Scarce
Lamellar silica	Strong	Not observed	Scarce

Table 2
Concrete symbols.

		Coarse aggregate			
		Non-reactive limestone aggregate "N"	Reactive siliceous limestone aggregate "SL2"	50% "SL2" + 50% "SL1"	Reactive siliceous limestone aggregate "SL1"
Fine aggregate	Non-reactive limestone aggregate "N"	nN			
	Reactive siliceous limestone aggregate "sl1"	sl1/N	sl1/SL2	sl1/SL1-2	sl1/SL1
	Reactive siliceous limestone aggregate "sl2"	sl2/N	sl2/SL2	sl2/SL1-2	sl2/SL1

Table 5
Concrete free silica contents "SiO_2".

Concretes	n/N	sl1/N	sll/SL1	sl2/N	sl2/SL2
SiO_2 (kg/m^3)	0	47	139	34	100
SiO_2/Na_2O mass ratio	0	9	27	7	19

Table 6
Concrete coarse aggregate free silica contents "CA–SiO_2".

sl1 and sl2 concretes	sl/N	sl/SL2	sl/SL1-2	sl/SL1
CA–SiO_2 (kg/m^3)	0	65.69	78.59	91.49

Table 7
Expansion values of the concretes (35 weeks at 38 °C and 100% of relative humidity).

Non reactive concrete	nN 0.004%			
sl1 concretes	sl1/N 0.27%	sl1/SL2 0.23%	sl1/SL1-2 0.13%	sl1/SL1 0.08%
sl2 concretes	sl2/N 0.18%	sl2/SL2 0.17%	sl2/SL1-2 0.12%	sl2/SL1 0.09%

Table 6 gives the free silica contents provided by the coarse aggregates for each tested concrete. These concrete coarse aggregates free silica contents "CA–SiO_2" are calculated according to the free silica content of SL1 and SL2 limestones (Table 3).

3.3. Swelling of the concretes

Table 7 gives the swelling values of the concretes after 35 weeks at 38 °C and 100% of relative humidity.

The sl1 and sl2 fine aggregates are very reactive. The swelling values of sl1/N and sl2/N concretes are respectively six and four times higher than the maximum allowed value (0.04%) to be classified as non-reactive. In a previous paper we also observed a higher swelling for the SL1 rock in comparison to the SL2 rock [3].

Fig. 2 presents the swelling of the concretes based on the two siliceous limestone aggregates versus the concrete free silica content. The swelling is not a monotonic function of the reactive silica content: a pessimum behaviour is observed. The substitution of the non-reactive coarse aggregates N by the reactive coarse aggregates SL2 then the reactive coarse aggregates SL1 causes an important reduction of the swellings of the concretes. The pessimum effect is more marked for the most reactive SL1 aggregates which have a higher content in potential reactive free silica (Tables 3 and 4).

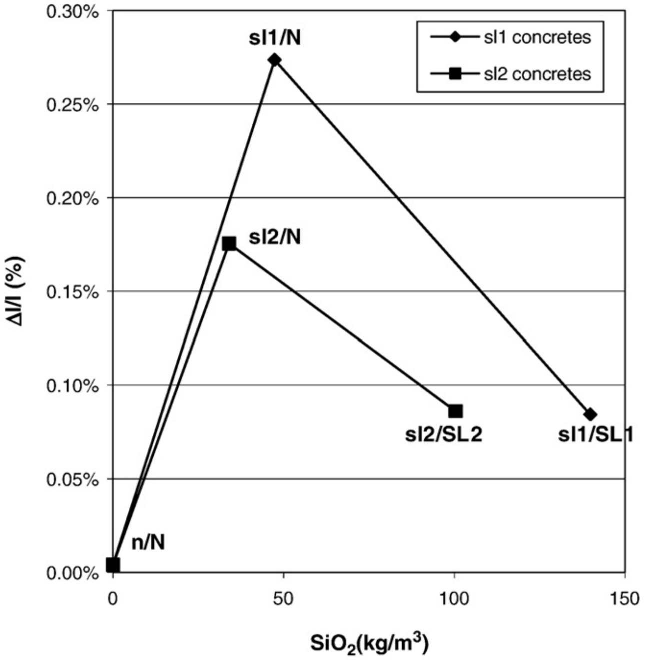

Fig. 2. Concrete swellings versus concrete free silica contents.

3.4. Swelling of the concretes versus concrete coarse aggregate free silica contents

Fig. 3 shows a reduction of the concrete expansions for CA–SiO_2 values higher than 60 kg/m^3.

To quantify this reduction we measure the percentage "*r*":

$$r = \left[\frac{\left(\frac{\Delta 1}{1}\right)_{s1N} - \left(\frac{\Delta 1}{1}\right)_{s1SL}}{\left(\frac{\Delta 1}{1}\right)_{s1N}}\right] \tag{1}$$

sl = sl1 or sl2, SL = SL1 or SL2 or SL1–2.

Fig. 4 presents the percentage of reduction of the swelling versus the concrete coarse aggregate free silica contents for the sl1 and sl2 concretes. We observe good linear relationships between these two variables. The reduction is greater for the sl1 concrete: reaching a maximum of 70% for the sl1 concretes, and a maximum of 50% for the sl2 concretes.

4. Discussion

The "pessimum" ratios between reactive silica and alkalis measured by Hobbs [1] are generally around 6. The ratios are 9 and 7 respectively for the sl1N and sl2N concretes (Table 5), so these concrete compositions are in excess of the "pessimum" (sl1 concrete) and near the "pessimum" (sl2 concrete).

The increase of the reactive SiO_2 by the substitution of the non-reactive coarse aggregates N by the reactive coarse aggregates SL2 and SL1 causes a reduction of the swelling as both concretes are now beyond the "pessimum" value (area C in Fig. 1).

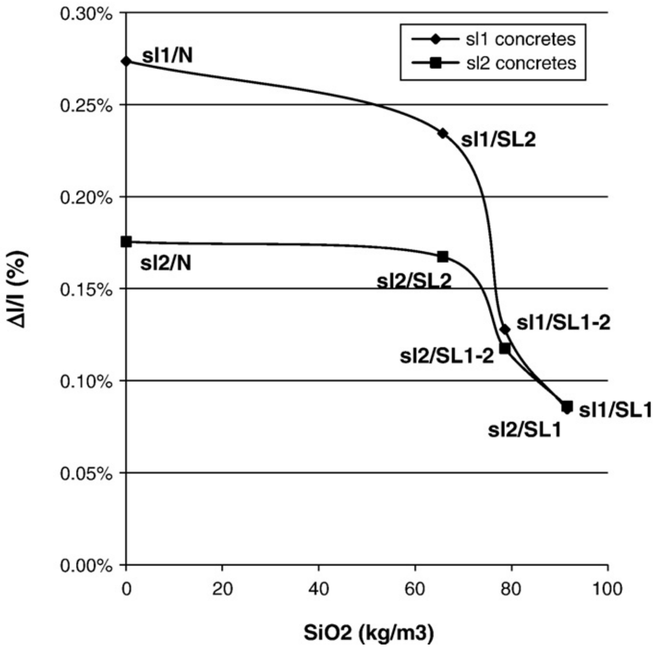

Fig. 3. Concrete swellings versus concrete coarse aggregate free silica contents.

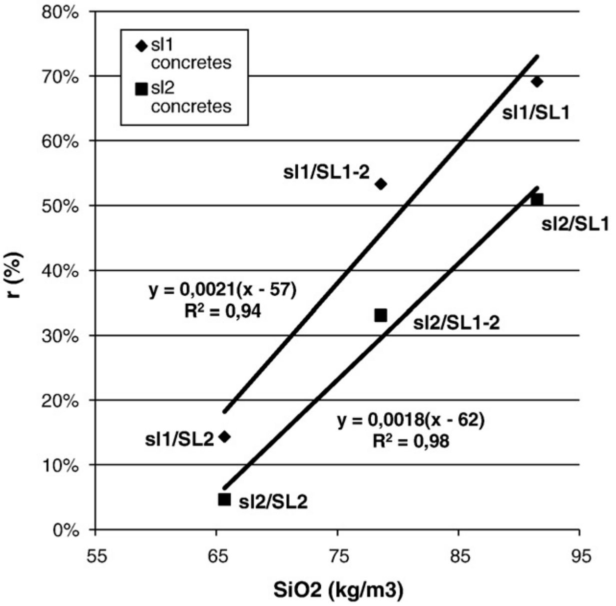

Fig. 4. Concrete swelling reduction versus concrete coarse aggregate free silica contents.

However because of the low content in reactive silica of the siliceous limestone aggregates in comparison to pure siliceous aggregates such as flint or opal, the addition of reactive silica from the siliceous limestone coarse aggregates is not enough to obtain non-expansive concretes (D area Fig. 1). The swelling values of sl1/SL1 and sl2/SL1 concretes are two times higher than the allowable value to be classified as non-expansive.

The ASR chemical mechanisms have been widely described [7–9] and can be summarised as four successive main steps:

- Step 1: neutralization of surface silanols of the reactive silica by the alkali base:

$$SiO_{5/2}H + K^{+} + OH^{-} \rightarrow SiO_{5/2}K + H_2O \tag{2}$$

using a simplified notation, $SiO_{5/2}H$ and $SiO_{5/2}K$ represent the Q_3 tetrahedron sharing 3 oxygens with 3 neighbours.

- Step 2: breaking up of siloxane bonds by hydroxyl ions to form Q_3 tetrahedrons:

$$SiO_2 + K^{+} + OH^{-} \rightarrow SiO_{5/2}K + 0,5H_2O \tag{3}$$

- Step 3: dissolution of silica due to continued hydroxyl ions attack on the Q_3 tetrahedron to form silica ions and small polymers:

$$SiO_{5/2}K + K^{+} + OH^{-} + \frac{1}{2}H_2O \rightarrow H_2SiO_4^{2-} + 2K^{+} \tag{4}$$

- Step 4: “gelation” of expansive ASR silica gels from the silica saturated pore solution.

ASR gels are highly polymerised and dominated by Q_3 and Q_2 silica tetrahedron [10–12]. The stoichiometry of the ASR gels varies according to the local pore solution concentrations in alkalis and calcium [13,14]. Before the ASR gel formation, the dissolved silica reacts first with portlandite and high-C/S C–S–H of the cement paste to form low-C/S C–S–H similar to pozzolanic C–S–H [12]. According to the swelling models developed by Garcia-Diaz et al. [15] and by Ichikawa and Miura [16], the swelling phenomenon for an aggregate by ASR gel formation requires the creation of an insoluble tight and rigid barrier by C–S–H precipitation on the periphery of this aggregate.

Pozzolanic C–S–H with low C/S ratios can fix by adsorption a part of the available alkalis of the pore solution [17]. So we can distinguish two kinds of alkalis:

- expansive alkalis consumed by the steps 2 to 4 to form the ASR expansive gels,
- non-expansive alkalis consumed by a non expansive surface adsorption process:
  - adsorption by the reactive silica (step 1),
  - adsorption by the low-C/S C–S–H.

For the sl1-N and sl2-N concretes the level of the expansive alkalis is enough to cause a maximum of swelling. The addition of reactive silica by the substitution of the non-reactive coarse aggregates by the reactive coarse aggregates increases the consumption of the non-expansive alkalis to the detriment of the expansive alkalis. Finally for reactive silica additions superior to 60 kg/m^3 we observe a reduction of the swelling.

5. Conclusion

Siliceous limestones in concrete have “pessimum” behaviours similar to those of pure siliceous aggregates such as opal and flint: for a given high alkali content, concretes based on fine and coarse reactive siliceous limestone aggregates swell less than concretes based on siliceous limestone fine aggregates and non-reactive coarse aggregates.

However, contrary to the pure siliceous aggregates, the contents in reactive silica of the tested sparitic and micritic siliceous limestones are too low to consume a maximum of alkalis in non-expansive adsorption processes and to obtain non-expansive concretes.

Acknowledgements

This study received financial support from “Holcim Aggregates Belgium” and “Belgian Cements Company Ltd”.

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