PESSIMUM BEHAVIOUR OF SILICEOUS LIMESTONE AGGREGATES

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Abstract

Siliceous limestone aggregates have "pessimum" behaviours similar than those of pure siliceous aggregates as opal and flint. For an alkali content of 5.125 kg/m3, concretes based on reactive siliceous limestone fine and coarse aggregates swell less than concretes based on reactive siliceous limestone fine aggregates and non-reactive coarse aggregates. The reduction of the swelling is more efficient for a "micritic" limestone with 8% of high reactive free silica than for a "sparitic" limestone containing 6% of less reactive free silica. In the future, we will try to elaborate non-expansive siliceous limestone concretes thanks to the "pessimum" effect and the use of mineral additions as fly ashes and silica fume.

Keywords: Limestone, ASR, Pessimum, Free Silica, Expansion Test

1 INTRODUCTION

Pure silica reactive ASR aggregates 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 an reactive aggregate content superior to the "pessimum" (figure 1).

Hobbs [1] distinguished 4 areas on the "pessimum" curve (figure 1):

- areas A and D : the reaction occurs but is to 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 with reactive flint aggregates have compositions generally located in area D: in spite of a high level in alkalis (superior to 5 kg of Na_2O_{eq} by m^3), these kinds of concretes constituted by reactive pure silica fine and coarse aggregates don't swell.

The aim of this paper is to verify the possibility to reach the D area for reactive siliceous limestone aggregates although their reactive silica contents are weak by comparison with the pure reactive silica aggregates.

Our methodology consists to compare swellings of high alkali concretes with different contents in reactive siliceous limestone fine and coarse aggregates. A "micritic" and a "sparitic" siliceous limestone aggregates are tested.

2 MATERIALS AND METHODS

2.1 The siliceous limestone aggregates

Two siliceous limestone aggregates respectively with a high content in reactive silica (SL1 aggregate) and with a low content in reactive silica (SL2 aggregate) are used. A quantitative mineralogical analysis of these two aggregates has been given by Monnin et al. [2]. 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. This composition is in accordance to the French standard NF P 18-587 [3] which allows a qualification of the concrete aggregate reactivity towards ASR.

The alkali content of the OPC is equal to 0,8% of Na_2O_{eq}. To obtain 5.125 kg/m^3 of Na_2Oeq in the concretes we add 1M sodium hydroxide in the concrete water.

Nine concretes based on siliceous limestone fine aggregates which contain respectively non-reactive and reactive limestone coarse aggregates are made. The granular compositions and the symbols of these nine concretes are in table 2.

2.3 The swelling test

The swelling test is realized in accordance to the French standard NF P 18-587 [3]. The concrete specimens are prisms of 70×70×280 mm. The swelling test is realized at 38°C and 100% of relative humidity. The relative longitudinal variations of the prisms (DL/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.

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 [2]. We present thereafter a synthesis of this paper. The mineralogical composition of the aggregates is given in table 3. The geologic age of these limestones is included between 345 and 355 millions years. According to the classification of Dunham [4]:

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

The SL1 aggregate have a higher content in potential reactive free silica. The main silica type is xenomorphic quartz of authigenic origin with a grain size lower 50μm. Another part of the silica is finely divide 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 much so dispersed. The main silica is automorph quartz with a limit size of 150μm. A light acid treatment reveals the presence of some structural flaws. In many aggregates, fibrous chalcedony is frequently observed in a variable proportion and often enclosed in a massive calcite grains. Chalcedony generally contains many inclusions of dolomite. The last silica types observed occasionally are the microcrystalline quartz and lamellar silica.

In Table 4, the free silica types are summarized and their relative proportion estimated 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 xenomorphic silica which is strongly reactive. On the other hand, SL2 is mainly constituted by automorphic quartz which is not the most deleterious type. Only the frequently observed chalcedony seems to be the main source of reactivity for this aggregate.

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".

In our methodology we substitute the non-reactive coarse aggregates "N" of concretes based on reactive fine aggregates "sl1" and "sl2" by the reactive coarse aggregates "SL1" and "SL2" (table 2). Table 6 gives the free silica contents provided by the coarse aggregates for each tested concretes. These concrete coarse aggregates free silica content "CA-SiO_2" is calculated according to the free silica content of SL1 and SL2 limestones (table 3). The substitution of the non-reactive coarse aggregates N by the reactive coarse aggregates SL2 then the reactive coarse aggregates SL1 causes an increase of the "CA-SiO_2" content.

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 eligible value (0.04%) to be classified non-reactive. In a previous paper we also observed a higher swelling for the SL1 rock in comparison to the SL2 rock [2].

Figure 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: 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).

3.4 Swelling of the concretes versus concrete coarse aggregates free silica contents

According to figure 3 the reduction of the concrete swellings is observed for concrete coarse aggregates free silica content higher than 60 kg/m^3.

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

$$r = \frac{\left[\left(\frac{Dl}{l} \right)_{slN} - \left(\frac{Dl}{l} \right)_{slSL} \right]}{\left(\frac{Dl}{l} \right)_{slN}} \quad (1)$$

with: - sl = sl1 or sl2
- SL = SL1 or SL2 or SL1-2

Figure 4 presents the percentage of reduction of the swelling versus the concrete coarse aggregates free silica contents for the sl1 and sl2 concretes. We observe good linear relationships between these two variables. The effect of reduction is higher for the sl1 concrete: a maximum of 70% for the sl1 concretes for 50% for the sl2 concretes. At least the sl1/SL1 and sl2/SL1 concretes have the same swelling values near 0.08% (table 7).

4 DISCUSSION

The ratios between reactive silica and alkalis are respectively of 9 and 7 for the sl1N and sl2N concretes (table 5). The "pessimum" ratios measured by Hoobs [1] are generally around 6. So these concrete compositions are at the right 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 according to the "pessimum" effect (C area figure 1).

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

The ASR was largely studied. The mechanism was described using different models [7-9] and can be written following three successive steps:

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

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

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:

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

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

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

Afterwards, precipitation of silica ions by the cations of the pore solution of concrete leads to C-S-H and/or C-K-S-H formation.

According to the swelling models developed by Garcia-Diaz et al. [10] and by Ichikawa and Miura [11], step 2 forms expansive alkali silica gels which cause the swelling to the aggregate. The swelling phenomenon needs first the creation of an insoluble tight and rigid barrier constituted by the precipitation of dissolved silica formed by the step 3.

So we can distinguish two kinds of alkalis: expansive alkalis consumed by the step 2 and non-expansive alkalis consumed by the steps 1 and 3.

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/m3 we observe a reduction of the swelling.

5 CONCLUSIONS

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

An idea to elaborate non-expansive concretes based on these aggregates is to combine the "pessimum" effect and mineral additions as fly ashes and silica fume.

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TABLE 1 : Concrete Composition				
Fine aggregate [0-5 mm]	Coarse aggregate [5-20 mm]	Cement OPC 42,5	Water	Alkali Content Na_20 eq
607 kg/m3	1173 kg/m3	410 kg/m3	193 l/m3	5,125 kg/m3

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 3 : Mineralogical composition of the siliceous limestone aggregates according to Monnin et al. [2]		
	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. [2]			
Silica types	Reactivity Potential	SL1	SL2
Automorph quartz	Weak	Not observed	Majority
Xenomorphic silica	Strong	Majority	Not observed
Chalcedony	Strong	Not observed	Frequent
Microcrystalline quartz	Strong	Scarce	Scarce
Lamellar silica	Strong	Not observed	Scarce

TABLE 5: Concrete free silica contents "SiO_2"					
concretes	n/N	sl1/N	sll/SL1	sl2/N	sl2/SL2
SiO_2 (kg/m3)	0	47	139	34	100
SiO_2/Na_2O 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/m3)	0	65,69	78,59	91,49

TABLE 7: Swelling values of the concretes
(35 weeks at 38°C and 100% of relative humidity)

Non reactive cocnrete	nN			
	0,004%			
sl1 concretes	sl1/N	sl1/SL2	sl1/SL1-2	sl1/SL1
	0,27%	0,23%	0,13%	0,08%
sl2 concretes	sl2/N	sl2/SL2	sl2/SL1-2	sl2/SL1
	0,18%	0,17%	0,12%	0,09%

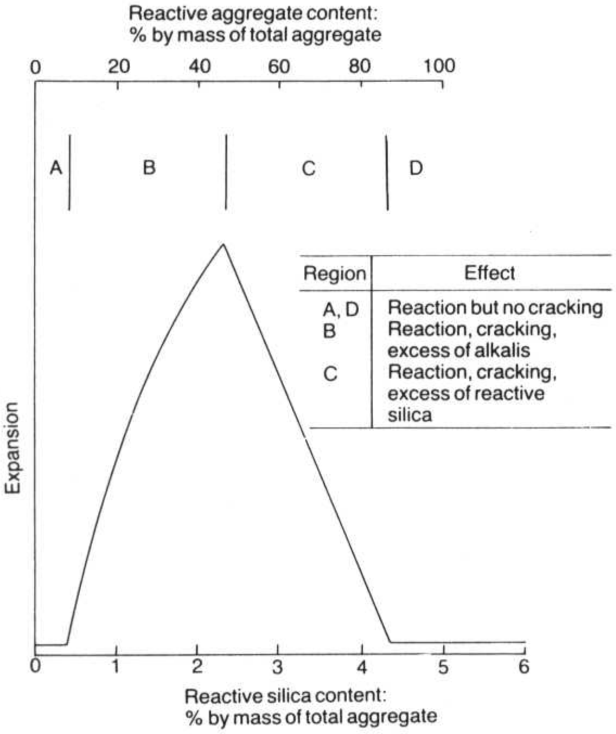

Figure 1: "Pessimum" behaviour of pure siliceous aggregate according to Hobbs [1]

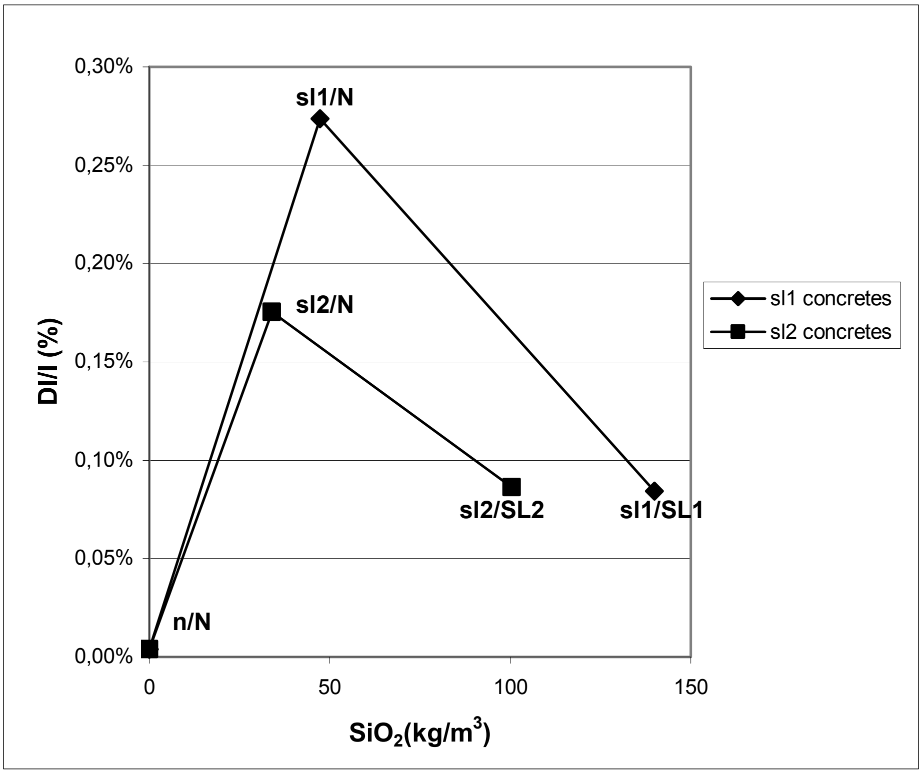

Figure 2 : Concrete swellings versus concrete free silica contents

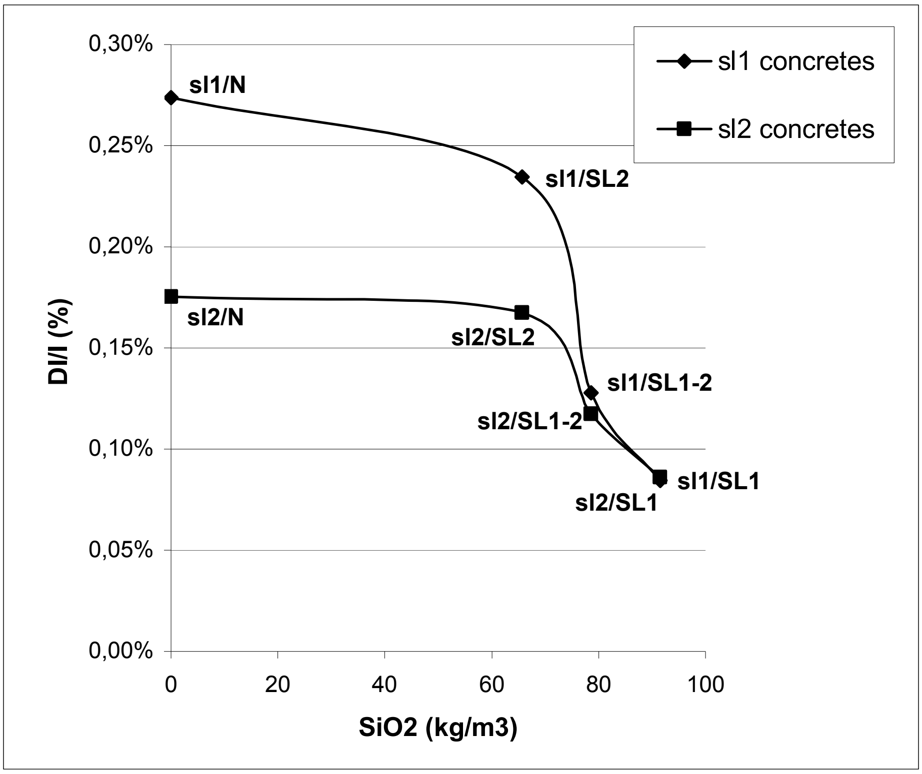

Figure 3 : Concrete swellings versus concrete coarse aggregate free silica contents

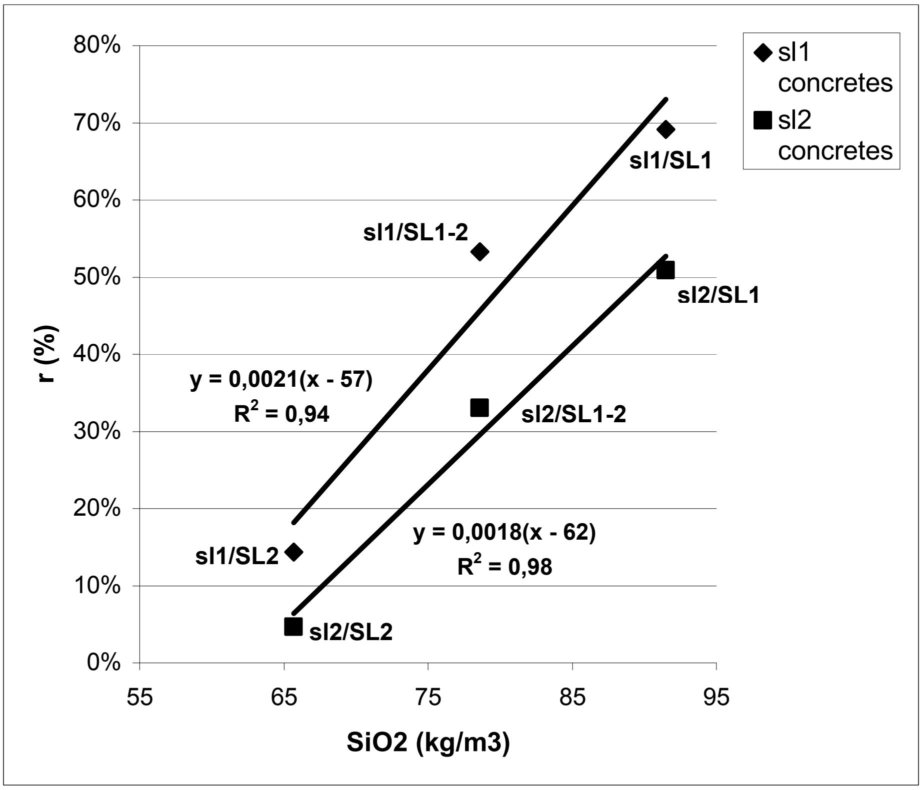

Figure 4 : Concrete swelling reduction versus concrete coarse aggregate free silica contents