

INFLUENCE OF AGGREGATES AND MINERAL ADDITIVES ON THE COMPOSITION OF THE PORE SOLUTION

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ABSTRACT

Four different mineral additives (granulated blast furnace slag, silica fume, synthetic cristobalite and sericite schist) were added, as partial replacement for fine aggregate, to mortars made with sands of various mineralogical compositions (non reactive quartz, reactive quartzite and opal). The pore solution was extracted by the high pressure extraction method and the evolution of concentrations of OH^- , SO_4^{--} , K^+ , Na^+ , Ca^{++} and silicate ions, measured at 7, 28, 60 and 90 days, was examined.

Opal was observed to lead to a very low alkali and hydroxyl ion level, indicating a very rapid consumption of alkalies to form a gel. In the case of quartz and quartzite, the alkali level was found to increase rapidly giving a peak at early age, then to decrease and finally to stabilize at values somewhat lower than that in the neat cement paste.

Keywords: ASR, pore solution, mineral admixtures

INTRODUCTION

Alkali-silica reaction (ASR) is a heterogeneous reaction between a solid phase represented by aggregates containing reactive species of silica and a liquid phase represented by the alkaline concrete pore solution. Apart from the ambient conditions (relative humidity, temperature...), the occurrence of ASR depends mainly on the ratio between the reactive silica and the Na_2O equivalent content of the surrounding solution. There is a pessimum ratio around 4.5 at which the observed expansion is maximum (Dent Glasser & Kataoka 1981, Wen. 1989, Barret *et al.* 1992).

Mineral additives such as granulated blast furnace slag, pozzolanic fly ash, condensed silica fume and natural pozzolans can be used to limit the risk of ASR (Duchesne & Bérubé. 1992, 1994). These additives not only act by a simple dilution effect, but also by their ability to combine the alkaline oxides and thus reduce the OH^- concentration in the pore solution. Their use in concrete can also lead to a finer capillary pore structure and a lower diffusivity and permeability. The result is usually a reduction of the observed expansion and deterioration.

EXPERIMENTAL

Materials

The chemical, physical, and mineralogical characteristics of the cement (OPC), the fine aggregates and the mineral additives are presented in tables 1, 2a and 2b.

Table 1 : Chemical composition of materials

Weight %	OPC	Qs	Q	O	c	gbfs	s	csf
L.O.I.	0,9	0,1	3,1	6,8	0,2	1	3,5	2,6
SiO ₂	19,9	99,1	90,5	92	99	35	57,4	95,1
Al ₂ O ₃	4,4	0,6	1,4	0,7	0,2	15	19,8	0,2
Fe ₂ O ₃	2,4	0,1	0,3	0,2	0,1	1	7,7	0,3
CaO	62,3	0,1	3,4	0,1	0,5	40	0,9	0,9
MgO	4,7	-	0,1	0,1	0,1	4,5	2,9	0,4
SO ₃	3,6	-	-	-	-	0,2	0,2	0,3
Na ₂ O	0,3	-	0,3	-	0,1	0,5	1,6	0,2
K ₂ O	1,1	-	0,8	-	-	1	4,1	0,6
TiO ₂	0,2	-	-	0,1	-	0,5	0,8	-
MnO	-	-	-	-	-	0,5	0,1	-

Qs = quartz sand, Q = quartzite, O = opal, c = synthetic cristobalite, gbfs = granulated blast furnace slag, s = sericit schist, csf = condensed silica fume

Table 2a : mineralogical and physical characteristics of cement and mineral admixtures

	Material	Mineralogical and physical
C E M E N T	OPC	Class CEM I according to the french standard NF P15-301 C3S = 59.6 ; C2S = 12.7 ; C3A = 7.6 ; C4AF = 7.4 Na ₂ O + 0.658 K ₂ O = 1.2 Fineness = 350 m ² /kg
A D M I X T U R E S	Slag	Granulated blast furnace slag Glass > 95 % Fineness = 280 m ² /kg
	Silica fume	Condensed silica fume Specific area (BET) = 22 m ² /g
	Cristobalite	Obtained from burning of silex Contains 85 to 90 % of cristobalite Fineness = 300 m ² /kg ; average grain size = 25 μm
	Sericit schist	Ground natural rock containing 25% quartz, 14% albite, 42% illite, 14 % chlorite and minor minerals (calcite, magnetite, apatite...) Fineness = 300 m ² /kg, average grain size = 25 μm

Table 2b : mineralogical and physical characteristics of the sands

S A N D S	Quartz sand	Natural well crystallized quartz sand. Non reactive SiO ₂ = 99 % Granularity : 250-600 μm
	Quartzite	Strained quartz with microquartz and phyllit at the grain boundaries Potentially reactive rock Granularity : 250-600 μm
	Opal	Amorphous silica with some quartz Potentially reactive rock with pessimum effect Granularity : 250-600 μm

Preparation and curing of mortars

The composition of the micro-mortars is given in table 3.

Table 3 : composition of mortars

Materials	Standard mortar	Mortar with additive
OPC	774 kg/m ³	774 kg/m ³
Sand (250-600µm)	774 kg/m ³	694 kg/m ³
Mineral additive	-	80 kg/m ³
W/C	0,6	0,6

Five mortars were prepared with each of these two fine aggregates: four were made by replacing 10% by weight of the fine aggregate with a different mineral additive (granulated blast furnace slag (gbfs), condensed silica fume (csf), synthetic cristobalite (c) and natural sericit schist (s)) and one was made without any mineral additive. This fine aggregate replacement procedure was selected in order to keep the amount of cement (which is the main source of alkalies) constant. Pure cement paste and a series of five mortars made with a non reactive quartz sand (Qs) were also prepared as reference mixtures. The selected water/cement ratio was relatively high in order to facilitate the pore solution extraction.

For each of the 15 micro-mortars, three cylinders (h = 9 cm, Ø = 4.5 cm) were prepared using the following procedure: homogeneization of the dry materials, addition of the required amount of water, energetic mixing (10 000 rpm), filling up the moulds under mechanical vibration to avoid heterogeneity and bleeding. The moulds were sealed and kept for 24 hours at 20°C and 95% R.H. After demoulding, the mortar specimens were stored at 38°C and 100% R.H.

Extraction of the pore solution and chemical analysis

The pore solution of the mortars was extracted by the high pressure extraction method (Longuet *et al.* 1973) at 7, 14, 28, 60 and 90 days. About 4 to 12 ml of liquid were collected and immediately neutralized. The chemical analysis was carried out by ICP and ionic chromatography.

TEST RESULTS

Evolution of pore solution composition

The results of the pore solution analyses are illustrated in Figures 1 to 7.

With regard to the evolution of the OH⁻ concentration (Fig.1), the mortars can be clearly divided into three groups :

- the first group includes all mortars prepared with the non-reactive quartz and the reactive quartzite, without silica fume. In this group the OH⁻ concentrations are the highest. They vary between 500 to 600 mmoles/l, i.e. close to the concentration observed in the neat cement paste. These results thus show that the slag, the synthetic cristobalite or the sericit schist did not significantly reduce the OH⁻ concentration;

- the second group includes the mortars containing silica fume and made either with the non-reactive quartz or the reactive quartzite. For these mortars, the OH⁻ concentration lies between 250 and 350 mmoles/l, which is still rather high probably because of the alkali content of the csf itself. Nevertheless these results confirm the well known effect of silica fume in reducing the alkalinity of the pore solution;

- the third group includes all mortars prepared with the opal aggregate for which the OH⁻ concentration decreases from about 180 mmoles/l at 7 days to 75 mmoles/l at 90 days. In these mortars, the reaction with the opal aggregate seems to be the prevailing one and there is no apparent influence of any of the mineral additives with respect to the OH⁻ level. Nevertheless complementary expansion tests carried out on the opal mortars have shown an obvious reduction of expansion with csf when compared with the other additions, indicating that, in fact, there is a rapid consumption of OH⁻ by the csf.

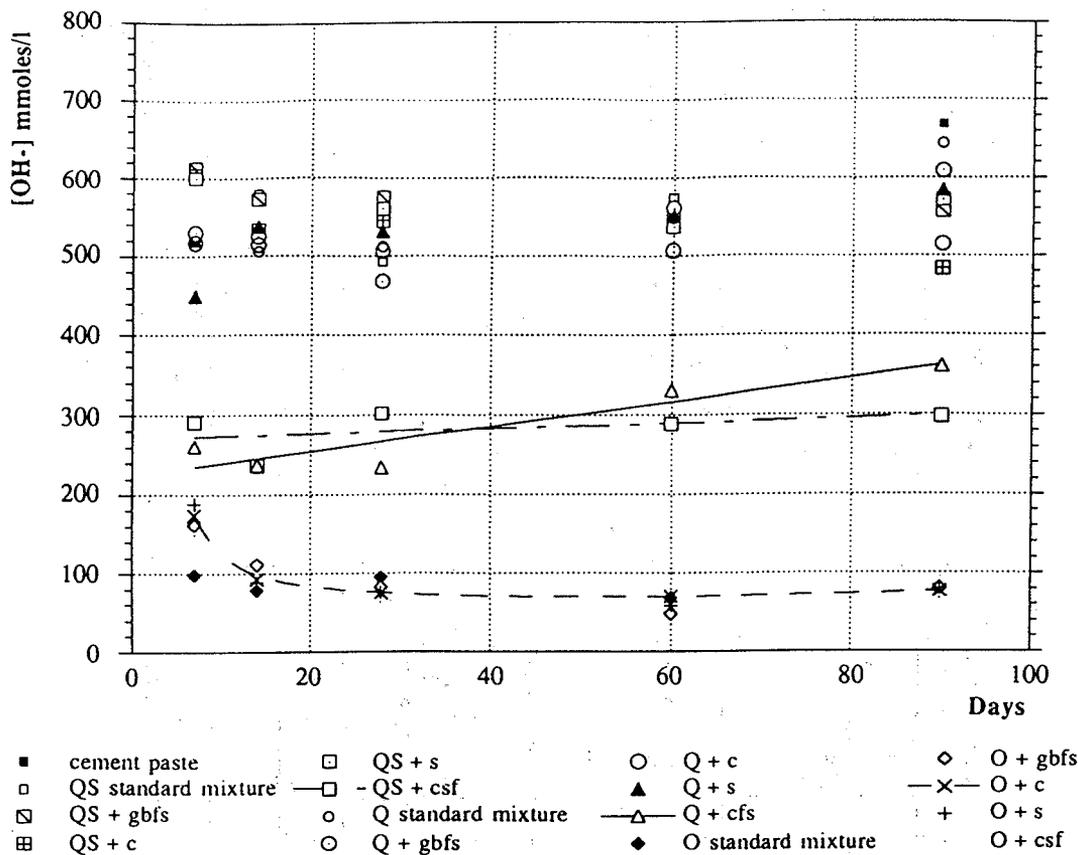


Figure 1. Evolution of OH^- concentration versus time

With regard to the evolution of alkaline oxides in the pore solution (Figures 2 to 7), four groups can be distinguished:

1) neat cement paste which shows a normal increase of the alkali concentration between 7 and 90 days. The value rises from 100 to 330 mmoles/l which is quite normal.

2) all mortars prepared with the non-reactive quartz (with the exception of that containing silica fume) which exhibit a very characteristic peak of concentration at 14 days. At this point in time, the alkali concentration ranges between 400 and 500 mmoles/l and is much higher than that of all the other mixtures including neat cement paste. The concentration drops to approximately 200 mmoles/l at 28 days, close to the value for the quartzite mortars.

3) all mortars prepared with the reactive quartzite. These mixtures do not exhibit a characteristic concentration peak at 14 days, but there appears to be a slightly higher value at 7 days, which would tend to show that there is a peak before 7 days. The concentration decreases slowly from about 260 mmoles/l at 7 days (a value also much higher than that in cement paste at 7 days, 100 mmoles/l) to 200 mmoles/l at 90 days. In the presence of silica fume, the concentration decreases from 150 to 100 mmoles/l.

4) all mortars prepared with the opal aggregate for which the concentration is very low and approximately constant between 7 and 90 days at a mean value of about 20 mmoles/l.

The concentration of SiO_2 which is normally low in cement systems with high calcium content, was also determined. It was found to be in all cases less than 1 mmole/l, even in the presence of silica fume and opal, despite the obviously high amount of silica that is dissolved, particularly in the mixtures containing opal. The small amount of silica in the pore solution is due to the presence of calcium which leads to the precipitation of a siliceous calco-alkaline gel. It results from a dynamic equilibrium between the dissolution and the precipitation processes. Work by Thuret *et al.* (1992) has shown that in the absence of calcium, the silica concentration in a 1N NaOH solution can be about 1.6 moles/l after 1 day, but that the addition of a diluted $\text{Ca}(\text{OH})_2$ solution leads to gelification.

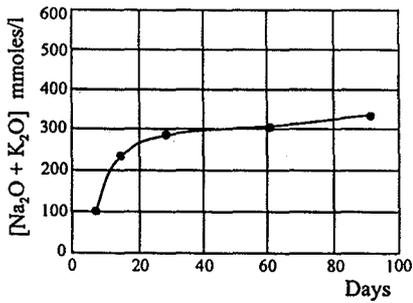


Figure 2. Neat cement paste.

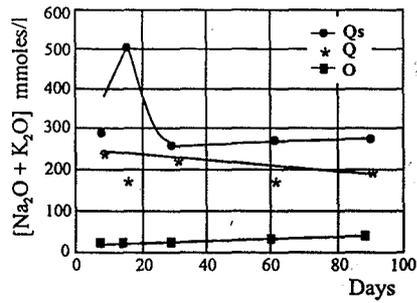


Figure 3. Mortars without mineral admixture.

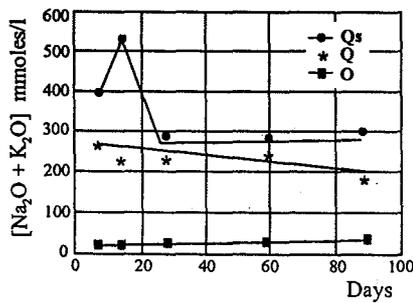


Figure 4. Mortars containing blast furnace slag.

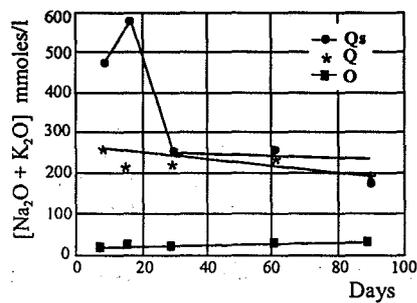


Figure 5. Mortars containing synthetic cristobalite.

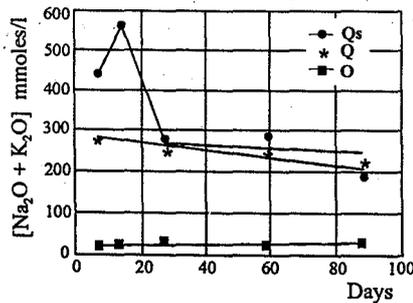


Figure 6. Mortars containing sericit schist.

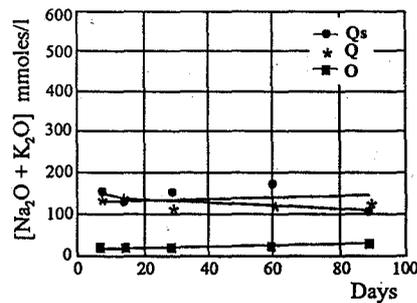


Figure 7. Mortars containing silica fume.

The CaO concentration was observed to be approximately constant at around 1 mmole/l for the cement paste and for all mortars prepared with the non-reactive quartz and the reactive quartzite. With opal, the concentration was higher at a value around 10 mmoles/l, except for the mixture containing silica fume where the values during the 90 day period varied between 3 to 5 mmoles/l. The reason for this is the lower alkali concentration which allows a higher amount of Ca^{++} in the pore solution, the solubility of calcium being very low in the presence of alkalis. Figure 8 illustrates the variation of the CaO concentration with the composition of the mixtures which can be divided into three groups :

- first group : cement paste, quartz sand and quartzite mortars ;
- second group : opal mortars with silica fume ;
- third group : opal mortars containing slag, sericitschist and cristobalite and opal mortars without addition.

The difference between the second and the third group is probably due to pozzolanic activity of silica fume which partly consume the free calcium ions.

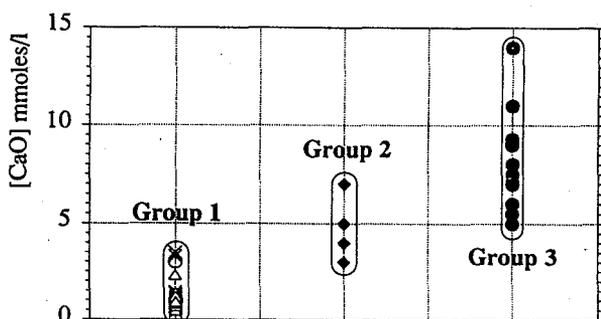


Figure 8 CaO concentration of the pore solution in the three groups of mortars

The opposite trend is observed with the concentration of the SO_4^{--} ions which clearly decreases in the presence of opal from an average value of 10 to 18 mmoles/l to about 0.2 to 1 mmole/l. Also due to solubility equilibrium, precipitation of SO_4^{--} within the solid phases is increased.

As shown by Shayan (Shayan *et al.* 1993) ettringite formation is promoted by silica fume addition. Due to their ability to consume alkalis which leads to higher Ca^{++} concentration in the pore solution, opal aggregates can act in the same way. Higher Ca^{++} concentration reduces ettringite solubility which in turn leads to a decrease of SO_4^{--} concentration in the pore solution.

DISCUSSION

In a recent publication on the mathematical modeling of ASR (Sellier *et al.* 1995), it was explained that the global kinetics of ASR is governed by the diffusion rate of the alkalis either in the reactive silica or in the mortar matrix, and that the chemical process ends when the diffusion of alkalis towards the reaction sites is no longer possible (generally when all the alkalis have been chemically bound in the silica gel). It was further shown in this publication, by mathematical calculations, that the probability of the presence of alkalis at a given reactive site increases rapidly at first, due to the slow diffusion of the alkalis in the silica, and then rapidly decreases as the alkalis diffusing from the mortar to the reaction site are chemically combined in the gel being formed.

This phenomenon can be linked to the variation of the amount of alkalis in the pore solution for the mixtures prepared with the quartz aggregate (Figures 3 to 6) which shows a similar trend of a rapid increase immediately followed by a decrease (thus

indicating that, even with innocuous quartz, some reaction with the alkalis is occurring). The same type of phenomenon should of course also be observed for the reactive aggregates, but the peak is expected to occur earlier, probably in the very first minutes or hours for the very reactive opal, and during the first few days for the quartzite which is less reactive than opal but more than quartz. It should be noted in this respect that, as previously indicated, there seems to be a higher concentration of alkalis at 7 days in at least three of the mixtures containing quartzite (Figures 3 to 5). Furthermore, it is clear from the test results that the presence of aggregates (such as quartz and quartzite) tends to cause an increase in the alkali content of the paste in the first days of hydration, which again shows (as the model briefly described indicates) the influence that aggregates can have on the kinetics of the processes involved.

CONCLUSION

Tests were performed to determine the composition of the pore solution in mortars prepared with three different fine aggregates (non reactive quartz, reactive quartzite and opal) and four different mineral additives (granulated blast furnace slag, condensed silica fume, synthetic cristobalite and sericit schist). The composition of the pore solution was found to be influenced both by the type of aggregates and the mineral additives.

Opal was observed to lead to a very low alkali and hydroxyl ion level, indicating a very rapid consumption of alkalis to form a gel. In the mortars made with quartz, and perhaps also with quartzite (although, in this case, more tests with measurements made at early ages will be required to investigate the phenomenon), the alkali level was found to increase rapidly at first (to values higher than in the neat cement paste), then to decrease, and finally to stabilize at values somewhat lower than that in the neat paste. This phenomenon shows that, despite its innocuity, the quartz consumes some of the alkalis. It also indicates that the dissolution kinetics is linked to the kinetics of the gel forming reaction.

Under the particular test conditions that were used, slag, cristobalite and sericit schist had no influence on the pore solution composition, probably due to the low replacement level in the case of slag and to poor reactivity in the case of synthetic cristobalite and sericit schist. Silica fume, however, had a strong influence, its use causing a significant decrease of alkali and hydroxyl ions in the solution.

Limiting ASR by the use of mineral admixtures is a complex problem in which different parameters must be taken into account, and, as shown in this paper, particularly the reaction kinetics of the aggregates and of the mineral additives. Further investigation using both laboratory tests and mathematical calculations (with models such as that proposed by Selier *et al.*) should allow a better understanding of the phenomenon.

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