IONIC EVOLUTION OF PORE SOLUTIONS ASSOCIATED WITH ALKALI-REACTIVITY

A. Le Roux*, A. Zelwer*, R. Dron*, M. Salomon**
* Laboratoire Central des Ponts et Chaussées - Paris - France
** Centre Expérimental de recherches et d'études du Bâtiment et des Travaux Publics.

The internal reactions that occur in mortars and concretes involve complex mechanisms that substantially alter the composition of the liquid phase in the pores. In our study, we examined the particular case of alkali-silica reactions, the indicator for which is the fixation of part of the soluble alkalis.

We worked with two totally siliceous materials, one consisting only of quartz, the other of a natural mixture of opal and quartz. The cements associated with the sandy phase were selected on the basis of their Na2O equivalent contents.

Determinations made at increasing curing times showed that with reactive mixtures, the alkali contents of the pore solutions change substantially, whereas they remain practically constant with non-reactive mixtures. This evolution should be compared to the formation of visible reaction gels on the altered materials.

- INTRODUCTION

The alkali-silica reaction can be interpreted as a manifestation of the coprecipitation of the ions present in the solution when certain thermodynamic and kinetic conditions are met [1].
The Ca_{++}, K_+, Na_+, and OH_- ions are released by the cement during its hydration, while the silicate ions result from attack of the siliceous aggregate by the OH_- ions (Tab. 1).
We know that sodium and potassium predominate in the pore solutions of cements [2] [3]. The product of the (C-K-S-H) reaction appears at different sites according to whether calcium ions or silicate ions are preponderant (Tab. 2).
This release of ions followed by their consumption results in a complex evolution of the instantaneous concentrations, which we propose to monitor by the pressure extraction technique.

- EXPERIMENTAL TECHNIQUE

Initially used only for pure cement pastes, the equipment as designed by one of us (shown in Figure 1) and the first results have been described in papers dating back to 1973 [2][3].

The principle is extraction by the pressure exerted by a tight piston on crushed mortar, placed in a very strong cylindrical die.

The die consists of 3 force-fitted rings made of steels of different types and hardnesses. The hard chrome plating of the piston is honed to a very close tolerance (10 to 20 μm at most). Sealing is by a Teflon disc and the pore solution released escapes between the wall of the mould and the bottom disc, made of very hard steel, that retains the debris.

The work we describe here concerns the reactivity of different types of aggregates with respect to a given cement (the equipment used in the compression technique, originally intended only for pure cement pastes, can not be used directly on concrete) and the translation of this reactivity into the composition of the pore solution.
Because of the conditions imposed by the device, together with the low relative volume of the binding matrix with respect to the aggregates of the concretes, and the proportion of pore solution available in a concrete, the aggregates to be tested must be reduced and calibrated in a specified grading class, without increasing the reactivity of the solid by increasing the specific surface area. Comparison of the reactivities of the different sands therefore calls for an identical or very nearly identical grading and surface condition.

- CHARACTERISTICS OF THE MATERIALS STUDIED

- Cements:
We selected 3 types of cements that were very different in the following respects:
- kinetics of hydration.
- setting time.
- water need.
- and potential composition.

Table 3 below gives the potential composition of each of the cements used and reveals the major differences between them.

These choices allowed us to compare a cement below the 0.6 % threshold in Na_2O equivalent (risk of reactions regarded as non-existent or very low) to a highly alkaline cement as close as possible to the 1.25 % threshold (in Na_2O equivalent), regarded as the alkali content capable of effectively testing the reactivity of aggregates in standardized tests P 18 585 and P 18 587 [6].

- Aggregates:
The choice of aggregates was made on the basis of our previous studies, and also the restrictions we imposed on ourselves by limiting the reaction to be studied to the alkali-silica pair.
Our aggregates therefore had to be chosen from among the various forms of silica likely to be encountered in materials for concretes.
With an identical or very nearly identical grading, there was an absolute limit below which the material could be regarded as pozzolanic. For simplicity, we took this limit to be 100 Êm. There was also an absolute upper limit, near the mm, above which the extraction equipment might risk seizing up.
Finally, we attempted to get close to the limits used in tests P 18 584 and 18 588. This made it easy to compare various possible materials.
These approaches led us to the grading range of 200 to 390 μm finally selected.

1) Nemours sand:
This is a very pure quartz (99.9 % SiO_2) of eolian origin with a natural grading that contains the desired range. From an industrial supply, automatic screening gave us the desired fraction directly. This was our non-reactive sample.

2) Resinite opal:
This comes from a small deposit South of Clermont-Ferrand. It is often found associated with quartz. X-rays characterize it as a cristobalite tridymite opal. From blocks measuring about 20 cm, the preparation required a series of crushing, grinding, and fractionated screening operations to attain the same grading as the control quartz. This necessarily introduced various impurities, in particular iron-bearing impurities from the grinding and crushing operations.

This opal was our reactive sample. Its position on the diagram of the P 18-584 test is eloquent: it has already been used as reference material in many studies, in particular the thesis work of Liu Chong Xi [6], who assigned MAXIMUM reactivity to it.
Finally, each material underwent a measurement of specific surface area by the Dynamic BET. The BET specific surface areas of the opal and quartz sands used in the tests are 2.08 and 0.12 m2/g respectively.
Now, scanning electron microscopy did not reveal any major difference. All of the grains are angular, with conchoidal fracture with no trace of chemical dissolution.

- Formulation of mortars for compression:

The formulation meeting the minimum hydration needs of the cements without causing excessive bleeding is (Table 4):
Substantially increasing the quantity of water quite certainly reduces the reactivity. Several authors have in effect shown that, the lower the W/C ratio or the higher the concentration of [OH-] and [Na2O equ.], the greater the reaction.
We applied a standard formulation for the different cement-aggregate sand pairs, using values as close as possible to those of Table 4.
Fluidization of the pastes by vibration during the turbulent mixing serves to overcome the high initial stiffening and allow instantaneous transfer of the batches into the preservation moulds, sealed in a saturated atmosphere in accordance with a standard procedure.

- Extraction of pore solutions:

The initial quantity of mixing water is always greater than the stoechiometry necessary for complete hydration of the anhydrous cement.
The "pore" solution is rapidly saturated by all the soluble elements released; the equilibria of solubility increase with the age of the concrete.

- DISCUSSION OF THE RESULTS

The main ionic constituents to be considered are:
[Na+], [K+], [Ca++], [OH-], and [Silicates (in the form of SiO2)].
Because of the ionization constants that govern these equilibria, as soon as the pH exceeds 13, the ionic activity of calcium ions becomes very small in the presence of alkalis.

The quantities of Na2O indicated are per 100 grammes of mixture.

Comparison of the evolution of the dissolved alkalis for the 6 cement-aggregate pairs, referred to the potential alkalis of the HS APC cement, very clearly shows, in the diagrams that follow, that there is, in the presence of opal, a quite marked deficit of alkalis in the solution. It is found that the CPA 55 (HTA = a very high initial alkali content) leads to much more fixation of the alkalis. In other words, the richer the initial medium in alkalis, the larger the consumption of alkalis.

Remark: Acidimetric determination of the solutions extracted gives substantially equivalent results for this consumption.
It can be seen that the deficit in total alkalis of the opal-based samples is already significant by the 3rd day. (Figure 2)

Measurements on the extracted solutions also show (Figure 3) that the silica, whatever its form, does not readily go into solution when the cements are poor in alkalis. The measured values are below the threshold of 5 mg/l, whereas they reach more than 30 mg/l with the alkali-rich cement and the opal aggregate. As the curing time increases, these values decrease, reflecting the incorporation of the silica in a structure of the C-K-S-H type. It therefore seems that this is limiting case 1 of the Table 2.

REACTIVITY OF SILICA AGGREGATES		
MEASURED BY ACCESSIBLE REACTIVE SILICA CONTENT AND ITS DISSOLUTION FLUX IN ALKALINE SOLUTIONS, WITH ALL KINETIC FACTORS CONTROLLED		
STRUCTURAL	FACTORS	
They determine the intrinsic solubility and thus the dissolution flux of the silica allotropic varieties cristallinity prefragmentation -> -> 1 siloxane to 2 silanols	CRISTALLINE VARIETIES quartz, chalcedony tridymite	THE STRUCTURAL FACTORS ARE ACCESSIBLE BY : XRD DTA IRS
	AMORPHOUS VARIETIES silica glass true opal silica gel	Anhydrous or hydroxylated amorphous varieties are determined as cristobalite after 12 hour's calcination at 1200°C
TEXTURAL	FACTORS	
They govern; - the accessibility of the reactive interface to the OH- ions of the alkaline solution - The ability of the silicate ions formed to force a path to migrate to the pore solution where the insoluble C-K-S-H calcium compound forms.	SPECIFIC SURFACE AREA external (grading) internal (BET) MICROCRACKING (textural prefragmentation) size of cristaline grains LOCATION OF REACTIVE PHASES - in grains - at grain joints - in mineral cement	

Table 1

TROUGH-SOLUTION MODEL OF FORMATION OF CALCIUM-POTASSIUM-SILICATE HYDRATE (C-K-S-H)				
The vectors represent the initial diffusion currents				
	INTERSTITIAL	SOLUTION		
REACTIVE	OH- ←	K+ OH-	OH- ←	PARTICLE OF
SILICA	SiO4H3- →	C-K-S-H ↓↓↓↓	Ca++ ←	CALCIUM HYDROXIDE
Ca++ and SiO4H3- ions are incompatible in solution. With K+ and OH- they precipitate into C-K-S-H				
EXTREME CASE 1: Pore solution rich in silicate ions				
	INTERSTITIAL	SOLUTION		
REACTIVE	OH- ←	K+ →	C K	PARTICLE OF
SILICA	SiO4H3- → → → → -	OH- ← Ca++ ←	S H ↓	CALCIUM HYDROXIDE
Ca++ ions cannot reach silica				
The C-K-S-H germinates and grows on surface of the Ca(OH)2 particle and forms a diffusion barrier there				
EXTREME CASE 2: Interstitial solution saturated in Ca(OH)2				
	INTERSTITIAL	SOLUTION		
REACTIVE	C K	K+ OH- ←	OH- ←	PARTICLE OF
SILICA	S H ↓	SiO4H3- → → → → →	Ca++ ←	CALCIUM HYDROXIDE
The C-K-S-H germinates and grows on surface of the silica particle and forms the diffusion barrier there				
FOR BOTH CASES THE DISSYMMETRY IS,THEN, AMPLIFIED				

Table 2

POTENTIAL COMPOSITIONS % ANHYDROUS CEMENTS %			
	CPA HP	CPA HTS	CPA 55
SO4 Ca	6,84	4,32	7,22
C4AF	6,44	6,96	7,51
C3A	12,62	5,11	13,54
C3S	49,32	55,54	47,34
C2S	20,99	25,58	20,04
Na2O	0,08	0,12	0,36
K2O	0,44	0,44	1,32
Free CaO	0,29	0,30	0,54
Carbonates	0,30	0,55	0,25

Table 3 - ALCALIS & POTENTIAL CONTENTS

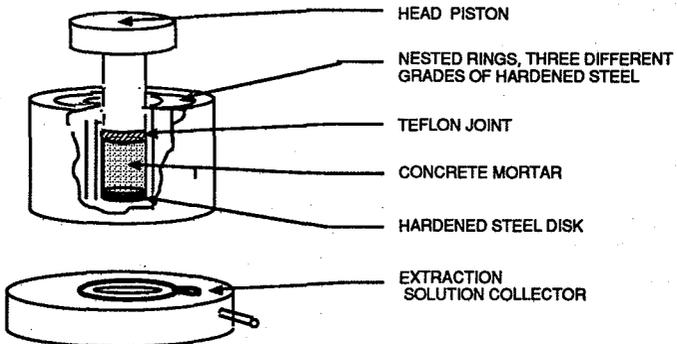| STANDARD CEMENT-SAND-WATER RATIOS	
Components	Mass (g) TOTAL 320
Water	78,22
Cement	120,89
Sand	120,89
Water/Cement	0,65
Cement/ Sand	1,00
Water / Solid	0,32

Table 4

HEAD PISTON

NESTED RINGS, THREE DIFFERENT GRADES OF HARDENED STEEL

TEFLON JOINT

CONCRETE MORTAR

HARDENED STEEL DISK

EXTRACTION SOLUTION COLLECTOR

Figure 1

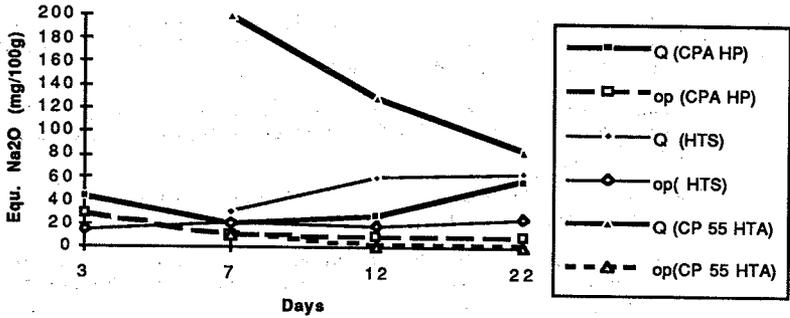**Cements-sands pairs: Development of Na2O**

Figure 2

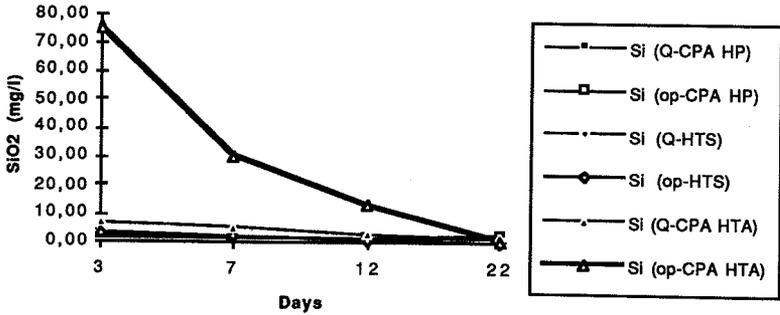**Cements-sands pairs: Development of SIO2**

Figure 3

- REFERENCES

[1]   Dron, R., and Brivot, F., June 1992, "Thermodynamic and kinetic approach of the alkali-silica reaction", to be published in Cement and Concrete Research.

[2]   Zelwer, A., June-July 1973, "Etude électrochimique de la phase aqueuse interstitielle au cours de l'hydratation du Silicate Tricalcique", Publication CERILH N⁻ 227, Revue des Matériaux de Construction et des Trav. Publics, N⁻ 681, pp. 20-39.

[3]   Longuet, P., Burglen, L., and Zelwer, A., January 1973, "La phase liquide du ciment hydraté", Publication CERILH N⁻ 219, Revue des Matériaux de Construction et des Trav. Publics, N° 676, pp. 35-41.

[4]   Zelwer, A., and Buil, M., Sept.-Oct. 1989, "Extraction de la phase liquide des ciments durcis, "Bull. Liaison Lab. Ponts et Chauss., N⁻163, Inf. 3414, pp. 3-97.

[5]   Diamond, S., Barneyback, R.S. Jr., and Struble, L.S., 1981, "On the physics and chemistry of alkali-silica reactions", 5th Int. Conf. on Alkali-Aggregate Reaction in Concrete, Paper 252/22, Cape Town.

[6]   Liu Chong Xi, 26 June 1986, "Contribution à l'étude des réactions Alcalis-Granulat. Application au barrage de Sandouping, Chine", Thèse de Docteur-Ingénieur en Géologie, Un. P. et M. Curie et E. Nat. Sup. Mines, Paris.

[7]   Ranc, R., and Sorrentino, D., January 1990, "Réactions silico-alcalines - Mise au point de méthode fiable", An. ITBTP, N⁻ 480, Série : Essais et Mesures, 225.