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ALKALI-AGGREGATE REACTION: A METHOD TO QUANTIFY THE REACTION DEGREE

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ABSTRACT

In this study, we propose a new chemical method for quantitative measurement of the reaction degrees of the Alkali-Silica Reaction. It is applied to a crushed natural reactive aggregate kept in contact with an alkaline solution, lime-saturated by an appropriate amount of portlandite. This chemical system is designed to model the basic capillary pore solution of concretes, in contact with reactive aggregates.

Two reaction steps are taken into account in the mechanism: formation of Q_3 (silanol) active sites made by breaking up siloxane bonds of the reactive silica, and dissolution of these Q_3 active sites.

We show that the active sites formation prevails on dissolution below a given OH^- concentration of the solution. This is in agreement with the observation of a "pessimum content" of alkalies, often described in the literature. Moreover, the kinetic laws developed from this method give realistic values of the reaction times.

We also observe a large decrease in density of the altered aggregate as the Q_3 active sites are formed. This molecular volume increase evidences a structural mechanism as the main cause of initial microcracking of the aggregates, which might not be exclusive of a secondary swelling of the gels formed.

Keywords: Alkali-aggregate reaction, reaction degrees, aggregate, alkali, swelling, durability.

INTRODUCTION

Research on Alkali-Aggregate Reaction (AAR) was often focused on the silica-rich gels formed between reactive siliceous aggregates, Ca(OH)_2 and alkali salts, in relation with concrete expansion. Many accelerated tests were developed and much work was done on AAR diagnosis.

- the ultraviolet fluorescence of gels where calcium or alkalis have been exchanged with uranyl ions allows identification of the AAR gel, using optical microscopy (Guedon et al. 1992);
- petrographic and electron microscope examinations can identify the reactive minerals, the altered aggregates and the reaction products (Le Roux 1991);
- the mineralogical analysis of concrete with the determination of the soluble silica can give information on the AAR occurrence (Deloye and Divet 1992).

But these diagnosis methods of AAR are generally not quantitative. Moreover the specific identification of AAR in structures is often difficult, because of the simultaneous occurrence of different causes of expansion. So the potential remaining expansion tests on concrete cores (Palmer 1992) can be biased by other swelling processes like delayed ettringite formation (DEF).

With the aim of developing a diagnosis technique being both specific and quantitative, we try here to have a deeper insight on the AAR mechanisms and kinetics, and to relate expansion to the reaction degree, more than to the reaction products properties.

First we use a chemical concrete sub-system, involving the main AAR reagents : ground aggregate, Ca(OH)_2 and KOH. These reagents, kept in contact in a closed vessel at given temperatures and pressures, can be considered on a kinetic point of view like a "micro-reacting model" representative of the chemistry of reactive aggregates in contact with the concrete capillary pores alkaline solution. This micro-model allows an accurate determination of the reaction kinetics, described by the evolutions of both solid and liquid phases, and the corresponding rate laws. We describe thereafter :

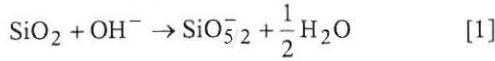
- the assumptions made on the two AAR kinetics steps taken in consideration,
- the definition of the reaction degrees,
- the studied aggregate type and composition,
- the micro-reactor technique,
- the liquid phase evolution and silica polymerisation degree,
- the solid phase evolution, either chemical (silanol groups formation) or physical (aggregates density).

In a next study, aggregates sampled from concrete cores will be characterised in the same way.

CHEMICAL MECHANISM OF ALKALI-AGGREGATE REACTION

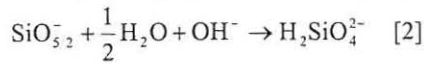
The AAR mechanism was described using different models (Dent Glasser and Kataoka 1981, Poole 1992, Wang and Gillot 1991, Dron 1990) and can be written following two main steps:

- Formation of active sites, due to a first siloxane bonds breaking up by hydroxide ions attack, to give silanol groups.

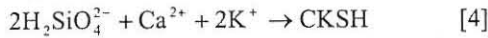


where, from a structural point of view, SiO_2 represents Q_4 silicon tetrahedra sharing 4 oxygens with 4 neighbours, and SiO_5^- represents the Q_3 silanol active sites negatively charged in a basic medium.

- Dissolution of silica, due to continued hydroxide ions attack on the Q_3 active sites, forming small polymers and mainly monomers $\text{H}_2\text{SiO}_4^{2-}$.



Afterwards, precipitation of $\text{H}_2\text{SiO}_4^{2-}$ by the cations present in the pore solution of concrete is liable to give CSH and/or CKSH gel phases.



DETERMINATION OF REACTION DEGREES

The development of our new chemical method to quantify AAR is based on the measurement of reaction degrees of equations [1] and [2], which are defined as follows:

- the proportion of Q_3 silanol active sites present in the aggregate

$$n = \frac{\text{moles of active sites}}{\text{moles of initial silica}} \quad [5]$$

- the proportion of dissolved silica

$$\alpha = \frac{\text{moles of dissolved silica}}{\text{moles of initial silica}} \quad [6]$$

From n and α , we can calculate n^* :

$$n^* = \frac{\text{moles of active sites}}{\text{moles of remaining silica}} = \frac{n}{1 - \alpha} \quad [7]$$

MATERIALS

The material used in this study was a flint type reactive aggregate coming from the north of France. X-ray fluorescence analysis gave a composition of 99% SiO_2 , and X-ray diffraction detected only quartz lines in this aggregate. The initial active sites value n_0 in the aggregate measured by thermogravimetric analysis was close to 0.08 moles of active

sites by moles of initial silica. In our experiments, the aggregate was crushed to obtain a size range of [0.040-0.315] mm.

DESCRIPTION OF THE MICRO-REACTOR METHOD

The determination of reaction degrees requires solid and liquid phases characterisation at different reaction times. For these measurements, we use a model micro-reactor method, based on a part of the AFNOR P18-589 standard. This method uses the following protocol organised in four stages (fig. 1).

- **Initial stage:** a mix of 1g of crushed aggregate and 0.5g $\text{Ca}(\text{OH})_2$ is introduced in a closed stainless steel container. After 30 minutes of preheating, 10ml KOH solution of given M_0 concentration are added. The container is then autoclaved in an oven to accelerate AAR under controlled temperature and reaction time conditions.
- **Stage 1:** After the reaction, the micro-reactor is constituted of the remaining silica which did not react and of the degraded part of silica $\text{SiO}_{5/2}^-$ to be quantified.

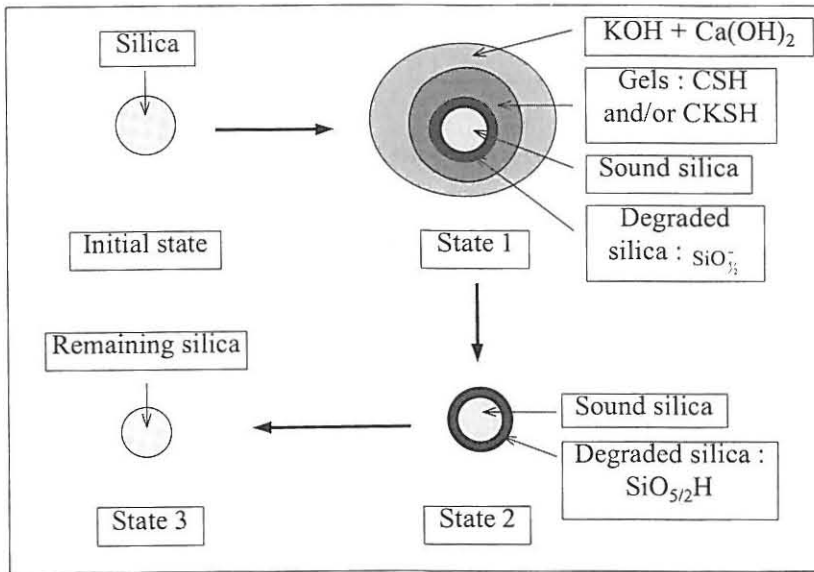
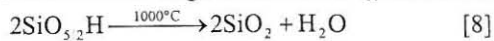


Fig. 1: Description of the model micro-reactor method during the different stages

- **Stage 2:** The soluble reaction products K^+ , Ca^{2+} , $\text{H}_2\text{SiO}_4^{2-}$, the CSH, CKSH and $\text{Ca}(\text{OH})_2$ phases are removed by selective acid treatment and filtration. The acid attack is done using 250 ml cold 0.5M HCl solution. The remaining solid is composed of the remaining silica Q_4 and of the protonated silanol Q_3 sites $\text{SiO}_{5/2}\text{H}$.
- **Stage 3:** After a thermal treatment of the remaining solid at 1000°C, the silanol groups are condensed to give back silica Q_4 and release water following :



At stage 3, the weight of the remaining silica allows to determine by difference the quantity of dissolved silica. The water release measurement by thermogravimetry allows the calculation of the quantity of silanol Q_3 sites in the aggregate sample.

CHARACTERIZATION OF THE SILICA IONS IN SOLUTION

To write correctly equation [2] describing the dissolution of silica in the liquid phase during the AAR, the nature and amount of reaction products had to be assessed. After contact with the aggregates, samples of the liquid phase were taken in the autoclaved containers, filtered on 0.45 μm Millipore filters, and analysed using quantitative ^{29}Si NMR high resolution spectroscopy.

TABLE 1: Silica Species Released in Solution after the Reactor Tests at 80°C.
(Quantitative Results within $\pm 10\%$ Uncertainty)

Initial concentration of KOH solution (mol/l)	Reaction time (h)	Q_0	Q_1	Q_{2c}
0.79	2	0	0	0
0.79	18	1	0	0
0.79	54	0.60	0.25	0.15

Table 1 shows the forms of silica in solution at different reaction times (the spectra were obtained by H. ZANNI).

At the beginning of the reaction, the amount of silica into solution is too weak to be detectable. Soluble silica appears first in the Q_0 form ($t=18\text{h}$, 0.79 mol/l KOH). The Q_1 dimers and cyclic Q_{2c} species are formed in a second time. These oligomers are probably produced by polymerisation of the monomers into solution, depending on the alkali concentration. The observed proportions are in fair agreement with the polymerisation equilibria described by Iler (Iler 1979).

It can be concluded that gel formation occurs mainly through solution, by monomer and dimer polymerisation. The expression of the second kinetic step of AAR using equation [2] is thus well assessed.

RESULTS AND DISCUSSION

Study of the Reaction Degrees

The curve giving the proportion of moles of active sites per mole of initial silica (n) as a function of time (fig. 2) starts from a value n_0 which is the proportion of active sites initially present in the aggregate. In our aggregate n_0 equals 0.08 mol active sites/mol initial silica. After a plateau up to 24 hours, n increases with time. This is the result of two successive reactions:

- the creation of active sites by attack of the siloxane bonds following equation [1],
- the consumption of these active sites by dissolution following equation [2].

When n increases, the creation of active sites prevails over the dissolution reaction. For the studied aggregate, n increase by over four times during the reaction (Fig. 2).

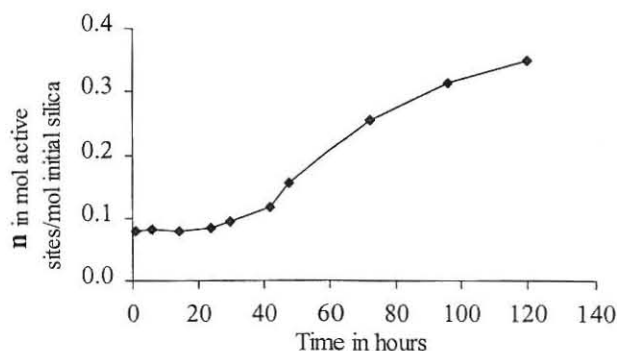


Fig. 2: n as a function of time at pH13.9 and 80°C.

The degree of silica dissolution α as a function of time (fig. 3) follows three steps. The first is a short plateau, about 6 hours long. The second step is an increase of α between 6 and 120 hours, during which the aggregates silica (SiO_2) degradation by AAR produces active sites SiO_2^- which are dissolved to give $\text{H}_2\text{SiO}_4^{2-}$. The third step is an asymptote where α reaches about 0,54 after 120 hours. This high proportion of final dissolved silica shows that equation [2] plays an important part in this experiment where initial hydroxide ions concentration is high. This proportion of final dissolved silica increases when hydroxide ions concentration increases (Bulteel et al. 1999).

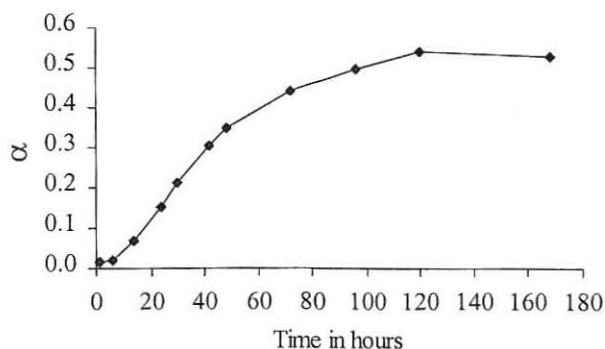


Fig. 3: Degree of silica dissolution α as a function of time at pH13.9 and 80°C.

The relationship between reaction degrees n and α (fig. 4) evidences the competition between equations [1] and [2]. For dissolution rates up to 30% approximately, the number of active sites increases slowly. The active sites formed following equation [1] are rapidly

consumed by dissolution following equation [2]. Afterwards, n increases with α . Then equation [1] forms more active sites than equation [2] can consume.

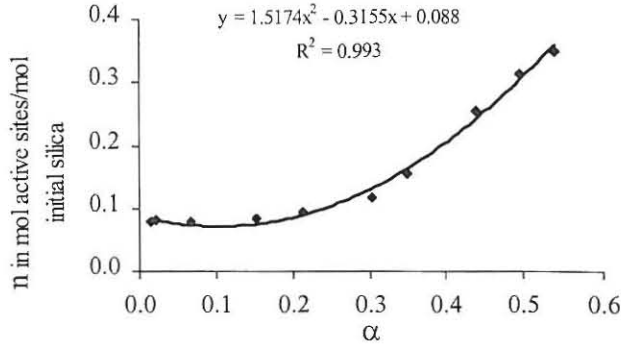


Fig. 4: n as a function of α at pH13.9 and 80°C.

Reaction Time

In a former paper, Bulteel et al. (1999) have shown that the dissolution rate can be approached by a first order law. The limiting step is the siloxane bonds breaking up, which activation energy is equal to 80 kJ/mol. If we apply this result to our example, we can estimate the reaction time of the studied aggregate in contact with the model alkaline solution at 20°C:

$$t(20^\circ\text{C}) = 120 \times e^{\left(-\frac{80000}{8.32} \times \left(\frac{1}{353} - \frac{1}{293}\right)\right)} = 31740\text{h} \approx 3.5\text{years} \quad [9]$$

For this ideal micro-reactor in optimal reaction conditions (large amount of water), the reaction time would be several years at 20°C.

Basic Content Evolution of the Micro-Reactor

The active sites formation and their dissolution (equation [1] and [2]) consume hydroxide ions and lime from solution.

In figure 5 we show the decrease in OH^- concentration during the experiments. The solution is filtered on 0.45 μm Millipore filters and the pH is measured by successive dilutions. The pH values are expressed in OH^- concentration.

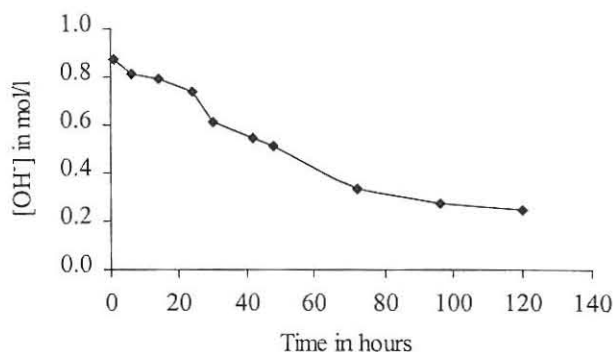


Fig. 5: Hydroxide ions concentration as a function of time by measure of the pH

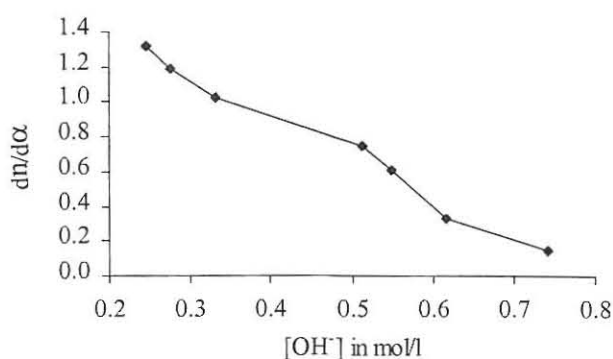


Fig. 6: $dn/d\alpha$ as a function of hydroxide ions concentration

Influence of Hydroxide Ions Concentration on the Mechanism.

The relationship between n and α (fig. 4) can be approached by an experimental law:

$$n = 1.5174 \times \alpha^2 - 0.3155 \times \alpha + 0.088 \quad [10]$$

If we derive the equation [10], we can estimate the $dn/d\alpha$ ratio. Figure 6 shows that the slope $dn/d\alpha$ increases when the hydroxide ions concentration decreases: as AAR progresses, the hydroxide ions concentration decreases and the active sites formation prevails.

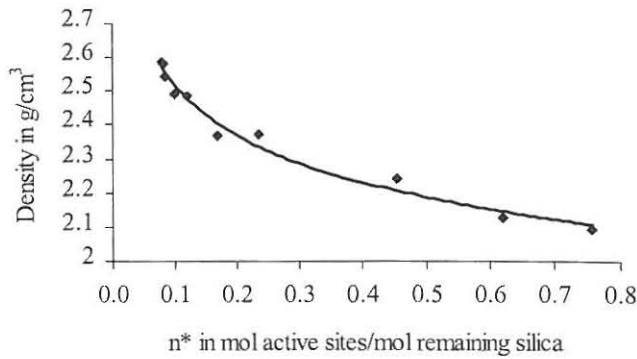


Fig. 7: Density as a function of n^*

New Comprehension Elements of the Origin of Swelling.

Figure 7 shows the density of the aggregate as a function of the number of moles of active sites per moles of remaining silica n^* . The density measurement is carried out by toluene pycnometry on the silica after elimination of the reactions products (stage 2 on fig. 1). This curve shows that the density of the silica falls during the structural transformation of Q_4 sites into Q_3 . This local volume increase can be considered as a main source of damage of the aggregate. The silanol groups formation inside aggregates is liable to raise internal swelling forces, because structural transformations are so powerful as to overcome the traction strength of the aggregates, and be at the origin of the large aggregates cracks often described in AAR damaged concretes. This mechanism is expected to be not exclusive, and could be followed by cations diffusion towards the negative silanol groups, to maintain the electrical charges balance. Afterwards, swelling of gel could add lower energy osmotic forces to enhance the first concrete swelling.

CONCLUSION

This work develops a new chemical method for quantitative measurement of the rate and degree of AAR. The model micro-reactor method described in this paper allows to evaluate two reaction degrees:

- “ n ” moles number of Q_3 active sites made by siloxane bond breaking up inside the aggregate,
- “ α ” moles number of monomer $H_2SiO_4^{2-}$ and small polymers obtained from Q_3 active sites dissolution.

The active sites formation prevails on dissolution when the hydroxide ions concentration falls. This is in agreement with the occurrence of the so-called “pessimum content” observed in concretes when the {reactive silica/basic content} ratio varies. The kinetic laws developed from our approach give realistic values of the reaction times.

The structural transformation of Q_4 sites into Q_3 silanol groups which involves an important local molecular volume increase is expected to be the main source of initial

damage of the aggregates, so powerful as to overcome the traction strength of the aggregates, and is expected to be at the origin of the large cracks often observed inside the aggregates in AAR damaged concretes. This mechanism could be enhanced afterwards by cations diffusion inside the cracked aggregates to balance the negative charges of the silanols, and also gel swelling.

Future work will be focused on measurements on aggregates extracted from concrete cores kept on site.

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