CHEMICAL BEHAVIOR OF NATURAL OPAL AND SILICA GLASS IN BASIC SOLUTIONS. APPLICATION TO AAR.

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The phenomenom of alkali-aggregate reaction taking place within hydraulic concrete is caused by a chemical interaction between the basic cement pore solution and the amorphous siliceous aggregates. The object of this paper is to bring some light to the alkali reaction mechanism by submitting two amorphous solids (opal and silica glass) to an alkaline attack, at 38°C and for a few weeks, in various basic or reconstituted cement pore solutions. A kinetical analysis of the ponderal evolution of both solids and the evolution of dissolved silica, enabled us to follow the inherent reactivity of the solids being studied and to propose silica glass as reference aggregate for the study of alkali-reaction. A micro-structural analysis led to some observations which can be linked to the dissolving mode.

INTRODUCTION

Study of alkali-aggregate reaction is complicated. Indeed, concrete or mortar are heterogeneous systems in which many reactions with different speeds are superimposed. Problem is also to isolate products of reaction and mechanisms to study. The idea of this work is to try to simplify the study model of alkali-aggregate reaction : two amorphous solids (natural opal and synthetic silica glass) are submitting to an alkaline attack in various basic or reconstituted cement pore solutions in polyethylen containers. Some works were already carried out, in particular by Struble (1), who looked at the mortar-bar expansion levels according to the type of the reaction of aggregate in cement pore solution (levels of dissolved silica and reduction in pH).

Originality of our work was to look at the level of dissolved silica in solutions in relation to the attack of aggregate determined from the dissolution percentage of solids and from the observation of samples by Scanning Electron Microscopy. We have observed the products of reaction at SEM and analysed their composition by EDS (Energy Dispersive Spectrometer). Indeed our operating process has an advantage : we have access straight to the solids covered with products of alkali-aggregate reaction.

OPERATING PROCESS

It was chosen with the aim of controlling all parameters which are involved in alkali-aggregate reaction. It was implied that we studied this reaction out of concrete to isolate it from others reactions taking place within concrete.
1°/ This is why we put a given mass (0.78 g) of two amorphous solids in 150 milliliters of seven solutions (concentrated solutions of sodium, potassium and calcium), at 38°C and for a few weeks, in polyethylen containers : after 1, 4, 12 or 24 weeks, we filter and therefore we separate samples and precipitates from solutions (figure 1).

- The two siliceous aggregates are : a natural opal from Massif Central (France) and a synthetic silica glass. These samples are studied either in grain form (grain of 10 mm in diameter for opal and fiber of 2 mm in diameter and roughly 10 cm in length for silica glass) or in podwer form (160 to 315 μm) obtained by crushing.
- The solutions of attack are made from datum of Andersson et al (2) :

TABLE 1 - Composition of attack solutions

Composition	pH
[Na] = 180 mg/l	11,89
[K] = 570 mg/l	12,16
[Ca] = 20 mg/l	11
[Na] = 180 mg/l [K] = 570 mg/l [Ca] = 20 mg/l	12,36
[Na] = 1800 mg/l	12,89
[K] = 5700 mg/l	13,16
[Na] = 1800 mg/l [K] = 5700 mg/l [Ca] = 20 mg/l	13,35

The mixed solutions with the three bases in determined proportions represent the rough reconstitution of cement pore solution.
2°/ The operating process enables us to have access straight to the dissolved solids, to the formed precipitates and to the attack solutions and therefore this process leads to a better study of their evolution :

A kinetical analysis of dissolving mode.

On one hand, we have followed the ponderal evolution of both solids in various basic solutions (apparent dissolution percentage), and on the other hand, the evolution of silica concentration ([Si] in mg/l) in the attack solutions which were initially without Si. That is why, following the silica concentration in solution is a very good parameter to investigate the dissolution of solids.
These two parameters are then compared. We must transform the dissolution percentage into silica concentration (in mg/l), and therefore we must postulate that the apparent dissolution percentage corresponds only to a dissolved SiO_2 percentage ; any other element is supposed dissolved. We have then compared the levels of measured silica concentrations and the levels of calculated silica concentrations in relation to the time of attack in weeks.
The presence of a possible layer of precipitates on samples after attack in basic solutions is a problem for the calculation of the dissolution percentage and therefore for the calculation of the silica concentration. That is why, we have proceeded to a dissolution of this layer in boiling 2N acetic acid during 10 minutes as Larner did (3). This method enables us to know the quantity of formed precipitates on samples and to deduce then the true dissolution percentage from this quantity.

A micro-structural analysis.

We have tryed, on the other hand, to study the kinetics of dissolution and to visualize the formed products by Scanning Electron Microscopy. Then we have analysed their composition by EDS.

BEHAVIOUR OF NATURAL OPAL

Choice of opal.

In this study we have opt for the use of opal because of its very important reactivity. Sample of opal comes from Massif Central (France). This is a stratified sedimentary rock with very fine grains, composed of low temperature trydimite,quartz and traces of mica, chlorite, calcite, dolomite and feldspar. This is more often than not brown opaque but sometimes vitreous. From Chongxi (4), this material is mainly composed of silica (91.22% SiO_2). The others minor elements are aluminium, iron, titanium, calcium, magnesium, sodium and potassium.

Kinetical investigation of dissolution.

The two parameters used in this kinetical analysis of dissolution (apparent dissolution percentage and silica concentration) in relation to time of opal attack in various basic solutions enabled us to note a number of things:

- The grain opal and the powder opal react in same way. We have logically observed that the powder is dissolved more than the grain keeping in this way the difference from the external surface area.
- The comparison between action of the various solutions shows that the dissolution of samples is all the more important since pH of attack solution is high. Then order of pH is kept with two exceptions :
  - In some case, cement pore solutions dissolved less opal grain than sodium or potassium solutions do, but more than calcium one does. What is the matter ? A weaker dissolution or a more important precipitation of silica compounds ? The presence of calcium acts on the precipitation of silica compounds like C-S-H undoubtedly or, as Gutteridge and Hobbs (5) are showed, on the precipitation of calco-alkaline silicates.
  - We can see that sometimes, attack by sodium solution is higher or not very different from attack by potassium solution whereas pH of the first one is less than pH of the second one. This is in accord with Al Cheikh (6) and Murat (7) who classified solutions with a constant pH of 12.6 in attack of E glass fiber : this attack is faster in sodium solution, slower in potassium solution and very slower in calcium solution. That is why the calcium solution dissolve much less than the others solution.
- The strongly concentrated solutions dissolved solids from six to twenty times than the weakly concentrated solutions (concentration factor of 10 for solutions) do.
- The silica concentration and apparent dissolution percentage of solids increase logically in time. But we observe several steps and decreasing on kinetical curves. Stabilization between two attack times implies two hypothesis :
  - Nothing more is dissolved either by lack of material or by stoppage of the reaction. This stoppage may be due to the formation of barrier layer.
  - Dissolution of silica material is strictly equal to precipitation of silica compounds.

The reduction between two attack times means that the reprecipitation rate of silica compounds is higher than the dissolution of silica material.

- The action of both parameters of dissolution (apparent dissolution percentage and silica concentration) are identical. However the silica concentration calculated from apparent dissolution percentage is always higher than this one measured in solution. Several hypothesis can be advanced to explain this fact but the only plausible one is that reprecipitation of compounds from dissolved elements of samples occurs.
- The true dissolution percentage, calculated after acetic acid extraction, is very close to apparent one. That is why the difference between the two concentrations persists. Then, besides the formation of precipitates on solids, there is important reprecipitation in solution.

Micro-structural analysis of dissolution and of formed products.

Our operating process enables us to observe simply the dissolved samples in various solutions and formed precipitates on the same samples by SEM and to analyse them by EDS :
1°/ The opal attack in different solutions shows dissolution figures which appear very clearly on microscopic pictures, even when the dissolution percentage is weak. The opal attack by basic solutions dissolves silica preferably, and therefore a relative increase of minor elements concentration in solids after partial dissolution of silica (analysis by EDS).
2°/ We could not discern clearly by SEM sodium precipitates after sodium solution attack or potassium precipitates after potassium solution attack.
A single new form could be discerned by SEM in case of potassium attack of opal. That is a matter of silk threads of about 3 μm in diameter and of several hundred of microns in lenght (figure 2). This type of thread was already observed by Chongxi (3) in mortars make up with the same opal (from Massif Central). Analysis by EDS reveals presence of potassium in these threads. We think that it is a matter of a relatively unknown form of gel after dessiccation.
3°/ The calcium solutions have a very limited dissolution action but they lead to a precipitation of calcium carbonates on the surface of all samples (figure 3).
4°/ Only solutions composed by calcium, potassium and sodium give very interesting results. Indeed in this type of solution, there is coexistence of two phenomena : dissolution and precipitation.
The attack of opal by these reconstituted cement pore solutions enables precipitation of a number of compounds :
- Calcium carbonates, observed already in calcium solution attack, precipitate too in these solutions.
- Potassium threads, already observed in potassium attack, are present too (figure 2).
- At last, the characteristic products of the alkali-aggregate reaction are observed :
  - A typical alveolar structure is visible on all samples (figure 4) whether the attack is strong or not. But in weakly concentrated reconstituted cement pore solution, the compound is a calco-alkaline silicate (potassium content about 3%) and in strongly concentrated one, the formed compound is a calco-alkaline silicate with a potassium content up to 30% and then is called C-S-K-H. When we have alkaline presence, the ratio C/S decreases.
  - Massive gels (figure 5) are discerned on all samples too, whether the attack is strong or not. The EDS analysis shows that their composition corresponds to a calco-alkaline silicate with potassium content from 4% to 6%. A beginning texturation of gels is observed in the case of attack of opal grain in strongly concentrated reconstituted cement pore solution.

We can observe that sodium is never present in the composition of reaction products.

BEHAVIOUR OF SYNTHETIC SILICA GLASS

Choice of synthetic silica glass.

The synthetic silica glass was chosen in this investigation for its well-defined structure and chemical composition. This is a glass and therefore an amorphous material. SiO_2 content is 99.99%. It was provided as transparent fibers of 2mm in diameter.

Kinetic investigation of dissolution.

Both parameters (apparent dissolution percentage and silica concentration in solution) in relation to attack time of silica glass enable us to compare the action of various solutions. The pH of different solutions acts on dissolution of silica glass with exceptions like in case of opal.

We can note, on the other hand, that the dissolution of silica glass fiber is much more weaker than this one of others samples and it follows a kinetical law which is directly proportional to the time of attack.
Besides, between strongly concentrated and weakly concentrated solutions (concentration factor of 10), there is only dissolution factor of 2 for silica glass fiber and of 5 for silica glass podwer.

We observe different steps and decreasing on kinetical curves too. We can make the same findings that for opal. The curves of dissolution percentage and silica concentration are similar too. And the calculated silica concentration from dissolution percentage is generally much bigger than measured one in solution. Then there is reprecipitation of compounds from dissolved elements of samples. So, after acetic acid extraction and true dissolution percentage calculation, besides of precipitate presence on solids, there is important reprecipitation in solution, as for opal.

Micro-structural analysis of dissolution and of formed products.

We have observed, as for opal, dissolved silica glass and formed precipitates by SEM and we have analysed them by EDS.

The silica glass dissolution is very clear whatever both the type of attack and the dissolution percentage. In case of fiber, dissolution marks are aligned along the major direction of fiber.

The silica glass attack by sodium solutions does never formed sodium precipitates, the same, the attack by potassium solutions does never give potassium compounds.

On the other hand, calcium carbonates precipitate on silica glass attacked by calcium solutions and by reconstituted cement pore solutions.

The attack by these last solutions produces precipitation of silico-alkaline gel like C-S-K-H and of typical alveolar structures. Then attack of pure silica glass by cement pore solutions enables precipitation of characteristic products of alkali-aggregate reaction as in opal attack.

CONCLUSION

The object of this work was to bring some light to the alkali reaction mechanism by submitting two amorphous solids (natural opal and synthetic silica glass) to an alkaline attack, at 38°C and for a few weeks, in various basic or reconstituted cement pore solutions.

The findings of this investigation are :

- Sodium solutions dissolve amorphous solids more than potassium solutions. But silico-alkaline precipitates formed by cement pore solution attack are only composed by potassium.
- Calcium acts on alkali-aggregate reaction : it is only in solutions with both calcium and alkaline that the characteristic products of this reaction, which are renowned for their expansion, appear.
- A precipitation of compounds on solids but also in solution was observed.
- Kinetical study is very important and necessary because it enables us to integrate slowly reactive aggregates as that was pointed out by Sorrentino et al (8). Indeed, time is factor too often forgotten.
- The synthetic silica glass can be used as reference aggregate for the study of alkali-reaction because of its very high reactivity and its well-defined structure and chemical composition.
- The products formed in our operating process are similar to these ones formed in mortars. That is why we think that our operating process enables to re-create the real environment and to have access straigth to the products of alkali-aggregate reaction. We can think that our operating process may be a simple test of aggregate reactivity. But it requires more investigations.
- The operating process proposed in the present paper allows too the recovery of the solutions of attack for quantitative analysis of the elements it contains (Ca, Na, K). On the other hand, solids resulting from the alkaline attack can be characterized by other techniques (e.g infrared spectroscopy, ...).

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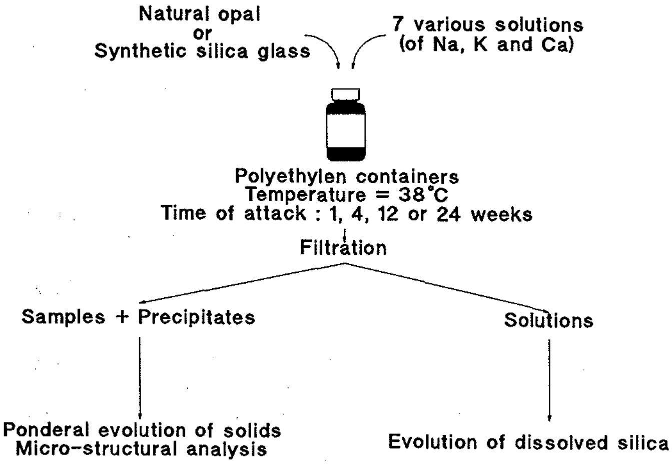
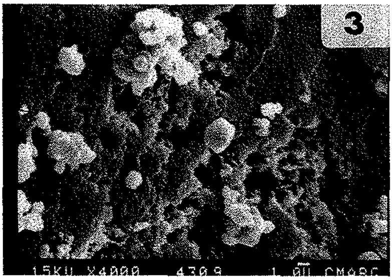
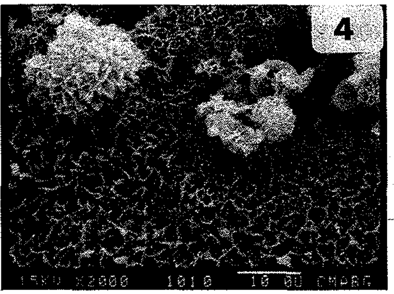


Figure 1 Operating Process





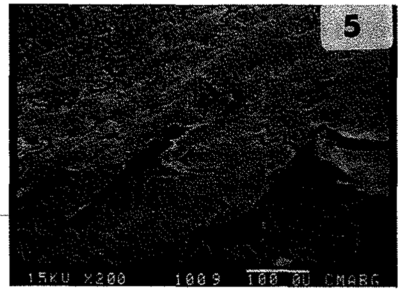


Figure 2 Thread of potassium
Figure 4 Alveolar structure

Figure 3 Calcium carbonate
Figure 5 Massive gels