A NEW METHOD FOR QUICK DETECTION OF REACTIVE AGGREGATE IN
MORTAR AND CONCRETE

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This study suggests a new way for quick
detection of reactive siliceous and silicated
aggregates. The principle of the method
consists of hydrolysing an ester in the
interstitial liquid of the concrete so as to
release the corresponding acid. The acid causes
the gelling of the colloidal solution and
serves to reveal the reactive aggregates.
Different techniques can be used to evaluate
the quantity of gel (permeability measurements,
compressive strength, volume variations, etc.).

INTRODUCTION

Under the action of the pH of the interstitial liquid in
concrete, and in the presence of alkaline ions, reactive
siliceous aggregates release a greater or lesser proportion of
their constituents. A colloidal solution forms which is rich
in silica and tends to progressively turn into a gel. The
expansion of the gel can cause cracking of the concrete and
lack of adherence at the cement paste - granulate interface
(1) (2) (3). Two previous papers (4) (5) have been devoted to
the main mechanism of alkali-reaction. Here we study, in
particular, a technique of detection of reactive aggregates.

Numerous tests have been performed over the years,
intended to identify the aggregates likely to deteriorate
rapidly in contact with alkalis. Some of these tests have been
adopted by standards organizations such as ASTM, ACNOR, AFNOR,
etc; others are still under study. In this paper, we do not
suggest another test but, rather, a possible new way of
detecting potentially reactive aggregates.

The method aims to encourage early gelling of the
interstitial siliceous liquid through the action of an acid
electrolyte. The rapid formation of the gel reduces the
response time for tests, which is generally between several
months and a year.

The principle of the method consists of hydrolysing an
ester in the interstitial liquid of the concrete so as to free

the corresponding acid. The acid causes the colloidal solution to gel and serves to reveal the reactive aggregates.

The stages of the process can be outlined as follows.

1) the mortar is prepared and kept in conditions that encourage liberation of the silica;
2) the mortar is impregnated with the ester-water mixture and kept in conditions favourable to hydrolysis of the ester;
3) the characteristics of the evolution of the mortar are obtained by measurements of permeability, compressive strength and volume variations.

In this paper we report the first results obtained during development of this method. The following points were studied:

- the kinetics of ester hydrolysis under various conditions;
- the kinetics of gel formation from a solution containing dissolved silica;
- the consequences of the gelling when it occurs in a Portland cement mortar containing siliceous additives.

OPERATING TECHNIQUES

Study of hydrolysis and gelling kinetics

We used a distillation device comprising 6 flasks, each topped with a sealed condenser. For the hydrolysis study, the same amount of ester-water mixture was introduced into each flask and heated at 90°C with continuous refluxing and shaking. At the end of each given time period, one flask was used to determine how much acid had formed.

The same method was used to study gelling, the flasks containing not only the ester-water mixture but also a known amount of sodium silicate. After each reaction time, the contents of one flask were taken in order to determine the mass of gel that had formed.

Mortar fabrication

All mortars were made with ordinary sand, a Portland cement, and demineralized water. The proportions used were: water/cement = 0.5 and sand/cement = 3. The mortars were set in cylindrical moulds having a diameter of 40 mm. The samples obtained were removed from the moulds after 24 hours and kept in a saturated atmosphere. Depending on the case, the mortars were doped with one of the following: silica gel, ground pyrex, cristobalite or sodium silicate.

Permeability measurements

The permeability was measured by determining the air flow rate through the sample when a pressure gradient was created between the upper and lower faces. To allow changes in the samples to be followed, the results are stated in terms of variations relative to the initial state.
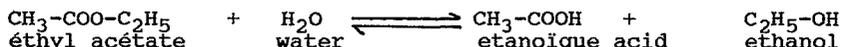
Resistance measurements

Resistance was measured by means of a Mohr and Federhalf hydraulic press, which gave a direct reading of the pressure applied. Loading was increased at a constant rate for all tests.

Volume variations

The apparent volume was found from the upthrust experienced by the sample when it was immersed in mercury. With our apparatus, we can detect volume changes of about 5 mm3 on samples of 40 mm diameter and 55 mm height.

RESULTS

I Kinetics of ester hydrolysis

Ethyl acetate was chosen as the ester, and the hydrolysis reaction is expressed by the following equation:

$$CH_3-COO-C_2H_5 \quad + \quad H_2O \rightleftharpoons CH_3-COOH \quad + \quad C_2H_5-OH$$
éthyl acétate   water   etanoïque acid   ethanol

We followed the hydrolysis kinetics on defined mixtures of ester and water, three cases being taken:
- a mixture of ester and water in stoichiometric proportions,
- a mixture containing excess water,
- a mixture containing excess ester.
The hydrolysis curves are shown in figure (1). It can be seen that the curves have practically the same shape for the first two mixtures (stoichiometric and with excess water). For these two mixtures we note that the major part of the acid is liberated within the first ten hours. After this, the reaction slows down and tends to stop after 24 H. For the mixture containing excess ester, the reaction is slower and equilibrium is far from being reached after 24 H of reaction.

It is thus not necessary to use a large amount of ester to obtain sufficient hydrolysis in the reaction medium. Proportions of the order of 5 % seem to be perfectly acceptable.

II Kinetics of gelling

We studied the gelling kinetics on mixtures having the same proportions as before: a stoichiometric mixture, a mixture with excess water, and a mixture with excess ester. We added the same quantity of sodium silicate to each of these mixtures and followed the formation of the gel. Figure (2) shows the evolution of the mass of gel with reaction time.

For the stoichiometric mixture the curve shows three fairly distinct zones:
-    an initial, latency zone corresponding to the first thirty minutes, during which no gel is detected although hydrolysis has already started;

- a second zone lasting about ten minutes in which abrupt gelling occurs;
- a third zone in which gelling continues more slowly.

Gelling thus appears to be a fairly abrupt process. It starts when a threshold is reached that corresponds to a few percent of acid having formed. Almost 50% of the final mass of gel appears during the first ten minutes after the start of gelling.

In presence of excess water the curve looks similar to the previous one. The same total mass of gel is obtained but the latency phase is shorter. Gelling starts after about only fifteen minutes as against thirty minutes in the previous case.

In the third case, corresponding to an excess of ester, the curve is more spread out. The mass of gel finally obtained is virtually the same as before, while the quantity of acid formed is smaller.

Thus, the hydrolysis of the ester is an effective way of causing gelling in an interstitial solution containing dissolved silica. So the reaction can serve as an indicator revealing the presence of reactive aggregates.

We repeated the above tests at room temperature. The overall conclusions remain the same, except that the phenomenon is slower. Gelling starts about four hours after the beginning of the experiment and continues for a further four hours. Such time intervals are sufficient for the mortar samples to be impregnated and gelling to be caused *in situ*. The tests on mortar were therefore performed at room temperature.

III Gel formation in mortars containing silica

We sought to examine the consequences of gelling when it occurs in Portland cement. The mortars were doped with siliceous additives and impregnated with the ester-water mixture. The changes were characterized by permeability, compressive strength, and volume variations.

1) Permeability variations

Permeability was measured on the 7th and 22nd day. The relative variations between these two dates are presented in table (1). The measurements concern, on the one hand, mortars kept directly in water without any previous impregnation and, on the other, mortars pre-impregnated with the ester-water mixture.

Case of non-impregnated mortars. When we consider the mortars not impregnated by the ester (column 1), we see that the variation is negative for practically all the samples, permeability tending to decrease as time passes. The greatest decrease was observed with the control mortar containing no additives. These variations of the control mortar indicate

that normal hardening leads to partial closing of the initial cracks to the circulation of gases.

Table 1 – Influence of the impregnation technique on Permeability variations %

Type of mortar (1)	Permeability variations %	
	Non impregnated (2)	Impregnated (3)
Control mortar	-84%	-82%
Mortar with pyrex	-70%	-50%
Mortar with silica gel	-53%	-26%
Mortar with sodium silicate	-69%	destroyed

For mortars containing siliceous additives, the permeability decreases less. So there is no sealing by any gels present in the cracks. On the contrary, it seems that the additives tend to develop an overall dilation of the internal structure of the sample and a simultaneous expansion of the existing network of micro-cracks. It is possible that this may generate new micro-cracks, which would explain the permeability variations observed.

Case of impregnated mortars. When the este-impregnated mortars are considered (column 3), the first observation is that the permeability of the control mortar varies by 85% between the two dates. This variation is of the same order as that of the non-impregnated control mortar (82%). This means that the impregnation technique hardly affects the permeability if the mortar contains no reactive siliceous elements.

The same is not true for the mortars with siliceous additives. These are markedly different from equivalent mortars not having been impregnated. For mortar with silica gel added, for instance, the permeability variations were of - 26% instead of -53%; for ground Pyrex, they were -50% instead of -70%. The most marked variations were obtained with the mortar containing sodium silicate. With this additive, for which the dissolved silica is available immediately, the gel formed is more abundant and its swelling causes the destruction of the sample (Figure 3).

The impregnation treatment thus seems to encourage the appearance of new cracks which have an effect contrary to the normal evolution of the mortar.

In a Portland cement mortar, the silica liberated by the reactive aggregates can be rapidly and artificially transformed into gel, then detected by permeability measurements.

2) Resistance variations

We compared the resistance of the samples kept directly in water with that of equivalent samples that had been pre-impregnated. The results are shown in table (2).

Table 2 - Influence of the impregnation technique on compressive strength.

Type of mortar	Compressive strength (en MPa)	
	Non impregnated	Impregnated
Control mortar	17	18
Mortar with cristobalite	19	22
Mortar with silica gel	31	33
Mortar with sodium silicate	21	destroyed

For non-impregnated mortars, it can be seen that the addition of small proportions of siliceous elements leads to increased resistance. The resistance of the control mortar after 14 days is 17 MPa, whereas those of the mortars with cristobalite, silica gel and sodium silicate are 19, 31 and 21 MPa respectively.

For the pre-impregnated samples, the resistance is slightly higher in three cases: the control mortar, the one with silica gel and the one with cristobalite. This result indicates that, if the amount of additive is small, the gel formed does not necessarily destroy the mortar structure and may even help to increase its resistance.

When large amounts of silica are added, however, (mortar with sodium silicate additive) the gelling destroys the coherence of the sample and can even cause it to break up. As a follow-up to this work we intend to study the variations of resistance for increasing quantities of siliceous additives; perhaps we shall find evidence of the existence of the "pessimum content" suggested by various authors (6) (7).

3) Volume variations

Figure 4 shows the variations of the apparent volume for the impregnated samples.

Generally speaking, the volume increases fairly quickly. The maximum swelling is always obtained between the second and seventh day. A direct relationship can be observed between the swelling and the formation of gel in the mortar. Beyond this maximum, the swelling subsides, a fact which can possibly be attributed to slow contraction of the gel.

CONCLUSION

We have shown that it is possible to use the hydrolysis of an ester to cause rapid gelling of the interstitial solution of concrete containing reactive siliceous aggregates.

The kinetic study of the phenomenon shows that the colloidal solution is destabilized as soon as a small proportion of acid is liberated. The gel appears after a latency phase and develops quickly in a few minutes. The gel forms relatively early in the presence of excess water.

Using Portland cement mortars doped with siliceous additives, we examined the effect of gel formation on the permeability, compressive strength, and apparent volume. We observed that the formation of gel led to additional micro-cracking and an increase in dimensional variations. In some cases the swelling was considerable and could result in the destruction of the sample. As far as resistance was concerned, we noted that gel formation did not always lower the resistance but could, on the contrary, help to increase it. The determination of the compressive strength would not, therefore, be a good criterion for detecting granulate reactivity.

Finally, our results show that it should be possible to detect reactive aggregates in concrete by following the two steps indicated, i.e. gelling of the colloidal silica liberated by the aggregates, followed by an examination of the consequences of the gelling by appropriate techniques. Different techniques should be used together: macroscopic observations, permeability measurements and dimensional variations, notably in the volume.

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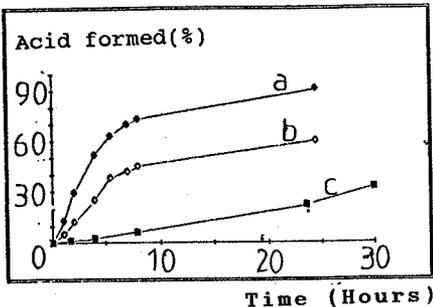
a) mixture with excess of water
b) stoichiometric proportions
c) mixture with excess of ester

Figure 1: Hydrolysis curves
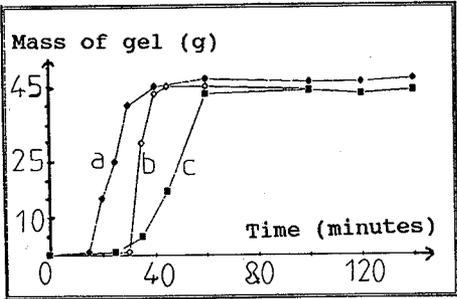
a) excess of water
b) stoichiometric
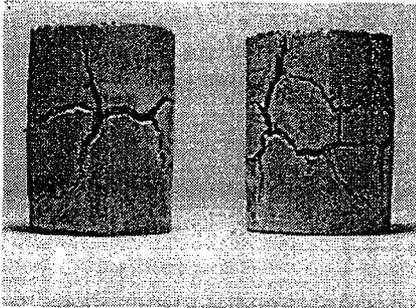c) excess of ester
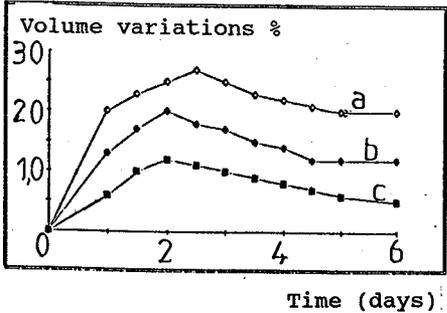
Figure 2: Gelling curves

Figure 3 Impregnated mortars

a) 2 % sodium silicate
b) 1% sodium silicate
c) 0,5% sodium silicate

Figure 4: Volume variations