A NEW APPROACH TO CHARACTERIZE THE CHEMICHAL REACTIVITY OF THE AGGREGATES

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The ASTM C-289 Chemical Method has been rein-vestigated, taking into account the published com-plaints and introducing additional ideas. The new test is called the kinetic test, simply because the time is now a parameter.
The granulometric distribution has been changed and the measurement of Na_2O replaces that of OH^- in order to determine the alkalinity reduction.
The limits between the innocuous and delete-rious aggregates have been established, based on field record performance and/or on conventional concrete (coarse aggregates) or mortar bar tests (sand) issued from 150 aggregates.

INTRODUCTION

In the alkali aggregate reaction field, two main types of approach have been developed to determine the potential reactivity of the aggregates : expansion tests on mortar bars or concrete prisms and direct determinations on aggregates, like the petrographic examination (ASTM C 295 standard) or the ASTM C 289 Chemical method.

This chemical method has had a world-wide success, because it is quick, easy to do and does not require a large quantity of material. However, from the time it first appeared as a standard (1952), many authors have reported that it suffers from several defects : lack of reliability and too narrow a range of application, are the main ones. The detailed bibliography cannot be reported here, see for example : evaluation of test methods for alkali-aggregate reactivity (1) ; the text of the standard itself says : "while not completely reliable in all cases…".

We have tried to overcome or at least improve this situation, establishing a five point research programme. Explaining the reasons why such parameters have been investigated and the synthesis of the results obtained, are the main objectives of this paper. Each point will be the purpose of a separate section but, a very brief summary of the ASTM C 289 standard will be given first.

THE ASTM C 289, STANDARD TEST METHOD
FOR POTENTIAL REACTIVITY OF AGGREGATES

First issued in 1952, the current edition was approved in March 1987. Its scope is reported : "this test method covers chemical determination of the potential reactivity of an aggregate with alkalies in portland cement concrete as indicated by the amount of reaction during 24 h at 80 °C between 1N sodium hydroxide solution and aggregate that has been crushed and sieved to pass a 300 μm sieve and be retained on a 150 μm sieve".

The amount of reaction is evaluated by the measurement of the silica dissolved into solution (Sc) and the reduction in alkalinity (Rc), being the difference between the alkalinity of the original NaOH solution and, theoretically, the remaining OH^-, following completion of the test, (determined by HCl titration, using the phenolphtalein end point). Aggregates are considered innocuous, potentially deleterious or deleterious, depending on the location of the representative point of the Sc, Rc values in the diagram (Fig.1).

GRAIN SIZE OF THE MATERIALS

The material passing the 150 μm sieve is discarded and, to ensure that all material finer than 150 μm has been removed, the sample is washed. Several experimental facts disagree with this decision to remove the fine particles ; a well known case will be quoted :
- the deleterious reactivity of the Potsdam sandstone from the Beauharnois dam (Canada) is not revealed, using the conditions prescribed in the standard (2). From petrographic examinations, it appeared to us that the failure of the method to show correctly the reactivity of this sandstone was related to the elimination of the fine and soft particles, which are also the reactive ones.

This aggregate consists of very large, compact and spherical crystals of quartz embedded in a very porous thin layer of minute particles of silica and argilaceous matter. One can easily imagine, that when the coarse aggregate particles are crushed, the fracture will preferentially occur within this porous and soft interstitial phase. These dusty loose particles, now being at the surface of the reduced size grains, will be easily detached from each other, will form the fine size fraction and will therefore be preferentially eliminated during the sieving and washing processes. Experimental verifications have been made by preparing two batches of samples : one, according to the standard and a second where the finest particles are retained, the particles therefore ranging from 0 to 300 μm : Sc in this case is much higher (3). Also the reactivity of these aggregates was not shown by the mortar bar test ASTM C 227, presumably for the same reason.

In fact this is not an exception ; it can occur with many other types of aggregates presenting heterogeneities and including "strong" and "weak" materials ; this very broad definition can relate to a large variety of situations : hard and soft minerals, compact and porous or layered materials, well crystallized and microcrystalline or amorphous materials. In all these cases, the weak materials which will be drastically disturbed by the crushing process, will be easily discarded in the subsequent step of sieving.

We have not really made investigations to check if the 300 μm limit was a good choice or not ; we have only tried a few experiments, limiting the particles size at 100 μm. In such a case almost all the minerals become highly reactive, liberate large quantities of silica into solution, findings which are in agreement with P.G. Bellew previous results (1) ; therefore we abandoned this limit and maintained the 300 μm one.

For these reasons, the test we now practice is made on particles ranging from 0 to 300 μm. This choice means, that special attention has to be paid to the sample preparation. As the production of over-ground particles has to be avoided, we recommend following section 7.2 of the ASTM Chemical method, i.e : reduce the material retained on the 300 mm sieve by repeated passes through a disk type pulverizer, with sieving after each pass. From a practical point of view, several types of grinder, manual or mechanical, are suitable but as soon as a few percent of a fine particles are generated, they must be removed from the grinding circuit, sieved on a 100 μm sieve, weighed each time for control ; once the grinding has been completed, they should be mixed and homogeneized with the larger particles. The percentage of particles smaller than 100 μm should range 35 to 45.

AN ADDITIONAL IMPORTANT PARAMETER : THE TIME

When making mortar bar or concrete prism tests, the length changes are measured as a function of the time ; on the contrary to the chemical method where the duration of the alkaline attack is constant and lasts for 24 hours. Time is not a parameter and this is surprising ! It is interesting to draw in the same figure(Fig.2) the expansion of equivalent concrete prisms, made of two deleterious aggregates : the siliceous limestone Spratt's aggregate (Ontario, Canada), which is now considered as a reference aggregate of the alkali silica reaction, and the Sudbury's aggregate, also from Ontario, which represents the slow / late alkali-silica / silicate reaction, abbreviated as SLEASS (4) The same shapes of curves have been obtained by Rogers and appear in figure 4 of the previous reference.

The expansion kinetics for the Sudbury's aggregate is slow during 3 months but the ultimate expansion is probably as high if not higher. From this, we have made the assumption, that the dissolution kinetics of the silica from these two types of aggregates could follow the same laws : fast dissolution rate for the siliceous limestone, slow initial rate but ultimate, large quantity of reaction for the polyphasic Sudbury's aggregate.
In order to check the validity of this assumption, the following experiments have been made : ground aggregates (0·300 μm) have been placed at 80°C, in a thermoregulated vessel, made of teflon and stirred with a 1N or 2N NaOH solution. This type of experiment is now being used as an industrial quality control test, to determine the reactivity of hydraulic binders (Portland clinkers, Aluminous cements).
The quantity of silica released as a function of the time, of sodium and OH⁻ consumed by the silica network, have been determined at selected times, using the I.C.P to analyse silica and a flame photometer to determine the sodium.The results obtained with three aggregates : Spratt, Sudbury and the Thames Valley sand from the U.K are very interesting when presented in the same figure (Fig.3).

It clearly shows that the reaction kinetics of silica dissolution from Sudbury's aggregate is slow during the first few days, but the dissolution rate, which is almost linear, remained constant for the 35 days of the experiment. This experimental fact fits with P.G. Bellew assumption, that the % of reactive minerals may be as high as 70%, in such types of material (5).

The conclusion to be drawn from this is that the deleterious character of the Sudbury's aggregate can be revealed by the chemical test, but that the 24 hours is not long enough : 30 mmols/L silica were found.

Based on this type of findings, we have decided to include time as a parameter. Instead of using 24 hours only, we now make tests at three ages, at least : 24, 48 and 72 hours. The reason why we call it a KINETIC test is to emphasize on the importance of time and we consider this as an important progress factor. This will help to evaluate correctly the aggregates developing a slow alkali silicate reaction, which was not the case with the regular ASTM C 289 method. Preliminary investigations were made up to 144 hours but it was then shown that there was no need to go this far. However, if the answer is not quite clear after 72 hours, an additional experiment at 96 hours should be made.

THE REDUCTION IN ALKALINITY : Rc

The validity of determining an alkalinity reduction, Rc, by an acidic titration with HCl, using phenolphtalein as an indicator, has been questioned many times in the literature ; due to this, Rc has been abandoned by many authors, who simply determine Sc. A 50 or 100 mMols limit for Sc has been proposed (1), but for reasons explained in section 7, this is unfair for some families of aggregates, especially those containing large quantities of flint. We will not detail all the complaints on this subject ; some basic explanations were discussed by L. Dent, Glasser and Kataoka (6). From this it appears that the choice of the parameter OH-, is neither correct from a theoritical point of view, because it is involved within two reactions, nor from a practical point of view : since the HCl titration, using the phenolphtalein does not indeed measure the OH$^-$ concentration, but the concentration of some anions, including part of the carbonates and silicates and others, if they are partially or totally soluble (chlorides, sulfates). The titration to the phenolphtalein end point not being independent of dissolved silica, means that Rc is a function of Sc, this shows that the choice of this second parameter Rc is incorrect.

Following the advice provided in this publication (6) and in several later papers, we now measure the Na$^+$ concentration remaining in the liquid phase after the alkaline attack. The results are expressed as the molar Na_2O / SiO_2 ratio (see the y axis of figure 4). Flame photometry is a suitable method and, as it is often also calibrated for K_2O, it additionnally provides the K_2O concentration, due to the release of alkalies by minerals. We have already observed, although the approach is still rough and on a qualitative basis, that the aggregates which liberate K_2O during this NaOH attack are the same which give "releasable" alkalies, determined in a $Ca(OH)_2$ solution maintained at the boiling point for 7 hours. We

consider that it is worthwile to develop this point further.

SILICEOUS LIMESTONES

This type of aggregate is common in Canada, especially on the East coast ; the Spratt's aggregate already mentioned, belongs to this group : the rock consists of calcite and small amounts of dolomite with an insoluble residue of 10%, which itself consists of quartz with small amounts of illite and pyrite.

Practising the ASTM C 289 on the whole aggregate, does not show its deleterious nature : we found 25 mMols silica, which agrees with previous results. The problem originates from several reasons : - a low silica content compared to the very high $CaCO_3$ level, - a very high Rc if using the experimental HCl titration, because Rc includes part of the carbonates ; this shift of the representative point into the upper part of the diagram (Fig.1) could move it out of the deleterious region.

To overcome these problems, a solution has been tried, which consists of making the NaOH attack on the siliceous insoluble residue and not on the entire aggregate. The quantity of silica dissolved is usually extremely high, the insoluble residue being essentially made of reactive silica ; however the interpretation of the results remains delicate because the true reactivity of the materials is far from being that of the insoluble residue, even if corrected to the % of the insoluble residue.

Using the modified conditions, explained above in sections 3, 4 and 5, we have applied the kinetic test to the Spratt's aggregate first and repeated it with French limestones (Tournaisis). The results expressed in the new diagram, figure 4, show that their deleterious behaviour is easily evidenced.

A special mention shall be made for aggregates which contain a few percent of calcite and simultaneously slowly reacting forms of silica or silicates. A problem may arise in this case, which leads to an underestimation of the soluble silica. At the beginning of the alkaline attack, the silica concentration is low : a few millimols ; at the same time, minute amounts of lime will be released from the calcium carbonate, but this is enough to be over saturated with respect to CSH, which may then precipitate. This precipitation of CSH will remove calcium and silicates ions from the liquid phase, therefore the measured soluble silica will be underestimated. This type of reactivity has seldom been met, until now, with French aggregates, but seems more common in Canada.The lesson to draw from this is that, to avoid any misinterpretation of the test, a complete chemical analysis of the aggregate and an XRD pattern are essential and detailed petrographic determinations are strongly recommended.

AGGREGATES AND COMBINATIONS OF AGGREGATES BEARING A PESSIMUM EFFECT

The pessimum effect has been known since the earliest AAR research, but has received a great deal of attention by researchers from the UK (Hobbs, Sims, Jones, Nixon …), because it is a typical case they have to deal with.

The pessimum can be simply defined as the reactive silica content or reactive aggregate content corresponding with the maximum expansion. It occurs in the distressed structures in the UK with some aggregates containing flints and cherts, when these types of sands or gravels (Trent Valley, Bristol Channel, isle of Wight), were used in combination with a non reactive limestone or coarse granite aggregate ; otherwise their field performance record is good.

The ASTM C227 mortar bar test produces misleading results, as recently documented by Sims (7) : "the mortar bar test is insensitive to those circumstances encountered in the UK which depend upon the occurrence of a critical combination of constituents and conditions". We can add, that the accelerated tests are also in trouble, for the same basic reason, that they are not able to give a flexible answer. The Canadian concrete prism test and the broadly equivalent French standard P 18 587, may be right or wrong, but their answer is in any case incomplete. What is indeed evaluated, is a particular combination of the coarse agrregate with a non reactive sand but nothing else ; it neither gives the reactivity of the coarse aggregate, nor the reactivity of any other combination ! Therefore, the extension of the results to any other composition may be dangerous. One has to be very careful with this type of aggregates and one has to think in terms of reactivity of the combination of the aggregates. Concerning the expansion tests, the only valid approach will be the evaluation of the job mix concretes. (Presently under investigation in France).

The ASTM C 289 chemical test is also insensitive to the pessimum effect and because these rock types contain highly reactive forms of silica from a chemical point of view, (large amounts of silica are released into solution during the first hours of the alkaline attack ; see curve figure 3), they would be classified as deleterious or potentially deleterious, which is unjustified most of the time.
We have taken these observations into consideration and, working with a large series of aggregates showing such a type of reactivity (there are plenty in France), we are now able to give a better image of the reality.
The upper part of the new diagram represents the reactivity of the aggregate alone ; this means that, if used alone or in combination with aggregate of an equivalent reactivity, there will not be an expansive reaction, but it is important to note that it is not an innocuous aggregate, as in the section part of the diagram. If combinations of this type of aggregate are to be made with aggregates of a different reactivity, it will be a necessity to make the tests on this particular combination. The kinetic test can do this. We have prepared and tested a series of mixes, with varying % of Thames Valley sand and another non reactive material ; the representative curves are located in the three parts of the diagram, depending on the respective proportions of the materials and this apparently complicated situation represents the reality.

The capability of the kinetic test to easily detect the aggregates showing a pessimum content and to provide the range of proportion of the mixes giving the pessimum expansion is of a great importance.

CONCLUSIONS

A quick chemical test is very attractive to characterize the potential reactivity of the aggregates ; the world-wide known ASTM C 289 Chemical method has revealed cases of failure. Based on the published complaints and our knowledge in the cement hydration field, the main problems have been investigated ; an improved version of this test is now proposed, which is termed kinetic test to emphasize the importance of the time.

The following points have been considered : granulometric size, alkalinity reduction, time. The modifications included in the kinetic test allow its application to a much larger number of aggregates : the slowly reacting aggregates developing an alkali silicate reaction and the siliceous limestones can be correctly evaluated.

A great advantage of this test is its capability to detect the aggregates showing a pessimism effect. Its detailed answer fits much better with reality. Those aggregates whose curve lies in the upper part of the diagram are chemically highly reactive. If used alone or in combination with aggregates showing the same type of reactivity, i.e curve belonging to the same upper area, they will not produce a deleterious expansion. But if any time a combination is used which associates these particular aggregates and aggregates of a different reactivity, (curve belonging to a different region of the diagram), great care will have to be taken ; the tests will necessarily have to be repeated, with the combination of the aggregates, not with the aggregates separately.

Up till now, this test has been applied to about 150 aggregates, with a very high degree of success.

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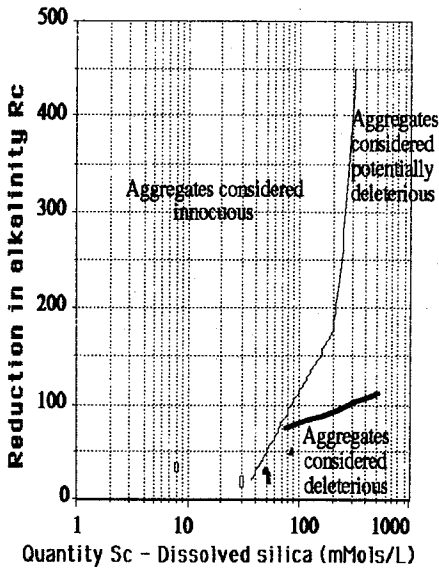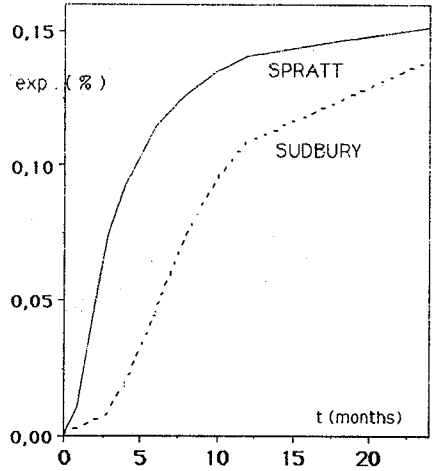
Fig. 1 : Diagram of the ASTM C-289
chemical method

Fig. 2 : Concrete expansion data
with Spratt (ASR) or Sudbury aggre-
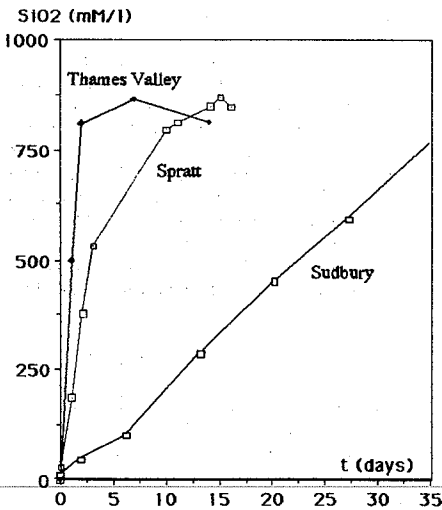gates(alcali silicate reaction)
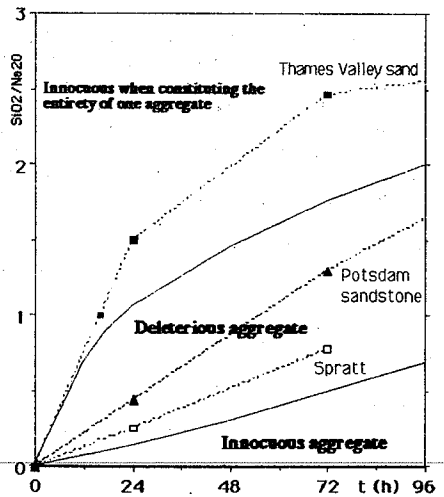

Fig. 3 : Dissolution rate of silica
from three aggregates.

Fig. 4 : Diagram of the kinetic
test.