

THE ALKALI-AGGREGATE REACTION QUANTITATIVE ASPECTS

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Analytical quantification of the alkali-aggregate reaction is made difficult by the fact that it involves basically a partial "solubilization" of the silica in the aggregates. This difficulty can be eliminated by thermogravimetry, using the derivative curve, because this makes it possible by cascade to use lime to determine the cement. The excess of "soluble silica" (or even other oxides), which represents the share of the aggregates participating in the reaction, can in this way be determined in nitric acid. A calculation protocol has been developed and validated.

The results obtained on structures affected by AAR show that the silica mobilized ranges from 0.2 to 1 % of the mass of concrete, depending on the severity of the phenomenon, and that it is almost always accompanied by alumina and ferric oxide.

INTRODUCTION

The alkali-aggregate reaction is a destructive process that can occur in concrete with no intervention of the external medium other than providing water. This phenomenon, known for a half century, involves only the constituents of the material, which react chemically with one another, slowly destroying its cohesion.

Very schematically, it can be stated that the excess pH engendered by the presence of the alkalis in the cement paste causes partial dissolution of the silica of the aggregates, all the more easily in that it is poorly crystallized. There then forms a silico-calco-alkali gel subject to swelling, which can exert a considerable pressure at the paste-aggregate interface, leading to loss of cohesion of the material and its characteristic cracking.

Since its discovery in the United States in 1940 (Stanton (1)), the alkali-aggregate reaction has been the object of very many works, including 9 international symposia. They were initially descriptive, then explanatory and especially experimental, with a view to forestalling the phenomenon by a judicious choice of the constituents of the concrete.

Its insidious character and the practically total absence of cures have made the alkali-aggregate reaction a sort of fatality of which one can only record the damage; and so, rare have been the researchers to consider the problem of quantifying the phenomenon, especially from a physico-chemical standpoint.

The first quantitative approach basically concerned measurements of swelling on laboratory specimens, intended to test aggregates or cements (Le Roux and Fasseu (2)), and occasionally on structures, mainly to track the mechanical evolution of the structures affected (Godart (3)).

The second approach, based on optical or scanning electron microscopy, makes it easy to visualize the gel produced by the reaction, but the observable field is limited to a few hundreds of micrometres and, apart from image analysis, there is no method for quantifying the extent of this gel other than a subjective estimate. In addition, some sample preparation modes, such as the fresh break for scanning microscopy, favour failures along the surface of least resistance, revealing zones where the cracks have the greatest chances of having developed. This last point, while it hinders quantification, has the advantage of allowing very early detection of the phenomenon (Larive and Louarn (4)).

Between these two extremes, chemical analysis in the broad sense should be able to yield quantitative indications on the degree of progress of the reactions in question from the silica mobilized. Moreover, this type of approach is the very basis of the chemical tests performed on aggregates for the purpose of prevention (ASTM C 289 and derivative documents).

METHOD OF QUANTIFICATION

Use of the normative calculation

Controlled attack of concrete and the associated normative calculation were developed more than fifteen years ago at the LCPC* not only to guarantee the quality of determinations of cement content in hardened concretes, but more especially to reveal, in a convenient way, possible degradation by external media. The principle is simple.

The purpose of the normative calculation is to process the chemical analysis of a material to extract from it its quantitative mineralogical composition, starting from its true or assumed qualitative composition. It consists of constructing each mineral species from its formula and from a specific pilot oxide (MgO for dolomite, residual CO₂ for calcite, for example). If the assumed composition of the material is exact, the calculation balances, in other words the sum of the species constructed is close to 100 %, and there must not be positive or negative remainders in the balances corresponding to the oxides of the chemical analysis (to within the analytical uncertainties) (Deloye (5)).

The application of such a calculation to a sound concrete assumes that a controlled attack, by a 0.25 N solution of nitric acid, cold, on a sample ground to 315 µm, does not reach the siliceous and silicate-containing part of the aggregates but does dissolve their calcareous part (dolomite included) and the cement. The complete analysis of this filtrate, accompanied by thermogravimetry, allows determination of the cement by at least two independent methods: soluble silica (or another tracer oxide), on the one hand, and the CETIC** formula (made iterative to allow for the true carbonation), on the other. When the true composition of the cement is given as hypothesis, the normative calculation is balanced, for each oxide (it can even be used to discover the composition of an unknown cement by a recurrent method). If the calculation can not be balanced, it means that the concrete has undergone chemical attacks by the ambient medium (sulphate, magnesia, chlorides, partial dissolution of binder by pure water, etc.), and the remainders corresponding to each oxide (positive or negative) provide information on the type and the intensity of the attacks (Longuet and Deloye (6)).

* LCPC Laboratoire Central des Ponts et Chaussées

** CETIC Comité d'Etude Technique de l'Industrie Cimentière

Problems specific to the alkali-aggregate reaction

Used as is on a concrete affected by the alkali-aggregate reaction, the normative calculation detects it through an excess of cement accompanied by abnormally high carbonation. In effect, the hypotheses concerning the soluble/insoluble balance of the sound concrete are found to be faulty, since a part of the silica from the aggregates is solubilized by the nitric acid. The phenomenon is indeed detected, but it would be incorrect to speak of quantification, since there persists an uncertainty on the calculated cement content. The CETIC formula counts the silica of the reaction as part of the cement, and assigns to it the corresponding lime, which the calculation takes away from the calcite of the aggregates, the CO₂ of which becomes ... "CO₂ of carbonation" (See table 1).

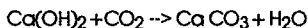
SAMPLE No.	% CO ₂			% CEMENT	
	CALCULATED	BY THERMOGRAVIMETRY	BY CETIC FORMULA	BY LIME	BY SILICA
Sound concrete n° 1	0,67	0,72	16,3	16,1	16,2
Sound concrete n° 2	0,66	0,49	17,2	17,1	17,2
Sound concrete n° 3	0,76	0,51	12,5	12,2	12,2
Sound concrete n° 4	0,05	N.E.*	15,6	15,6	15,5
Sound concrete n° 5	0,20	0,32	18,3	18,3	18,3
Sound mortar n° 6	0,79	0,93	25,0	24,8	25,0
Sound mortar n° 7	1,52	1,43	25,3	25,1	25,3
Diseased concrete n° 8	1,14	0,88	15,8	14,5	16,0
Diseased concrete n° 9	2,53	0,87	17,4	15,8	19,1
Diseased concrete n° 10	0,81	0,49	20,0	19,7	21,2
Diseased concrete n° 11	1,55	0,53	17,9	17,1	20,1
Diseased mortar n° 12	1,35	1,27	27,3	24,1	38,8

* Cannot be estimated

TABLE 1 : INCIDENCE OF DECLARED CO₂ ON CEMENT CONTENT

Independent determination of carbonation

Reasons of physical logic suggest that the carbonation front within a concrete is steep: when the binder starts to carbonate at a given point, since the reaction



releases water and water is necessary for carbonation, the carbonation propagates and becomes total in this location a very short time later. Samples taken in the core of the concrete may therefore be regarded as having a very low carbonate content; moreover, thermogravimetry readily confirms this hypothesis on concretes free of limestone. The same applies to those that contain some.

Because of the tenuousness of the crystals derived from the carbonation of the binder of a concrete, during a test in a thermobalance, the corresponding CO₂ is evolved at a slightly lower temperature than that from the calcite of the aggregates. This observation was made thanks to recent progress of the method, in particular through the use of the derivative thermogravimetric curve to determine, with the greatest possible precision, the temperature limits of the various evolutions of gases, making it possible to distinguish between the CO₂ of carbonation and the CO₂ from the calcareous part of the aggregates (Platret and Deloye (7)).

Systematic application of this technique has shown that in sound concretes the CO₂ of carbonation measured by thermogravimetry is practically identical to that derived from the normative calculation by iteration using the modified CETIC formula.

There is no reason not to use thermogravimetry with the derivative curve to determine the degree of carbonation of a concrete affected by the alkali-aggregate reaction, making it possible to establish a protocol for the normative calculation that takes into account, in a rigorous way, the reactions involving only the internal constituents of the concrete. Such a protocol gives access to the part of the aggregates made soluble in the nitric attack by the occurrence of an alkali-aggregate reaction.

PROTOCOL TAKING ACCOUNT OF THE INTERNAL REACTIONS OF THE CONCRETE

- Preliminary remarks

- The analytical approach of dedolomitization (Deloye and all. (8)) had shown in 1980 that the CETIC formula, modified or not, accounted (except for carbonation) for the composition by weight of the constituents of the concrete just at the time of mixing, from which the anhydrous cement content could be derived. In fact, by its very principle, it counts as "cement" any part of the chemical analysis that is not included in the siliceous aggregates (insoluble in the acid attacks), the calcareous aggregates (calcite and dolomite), the carbonation, or the water of hydration. But it should be noted that this determination is based on a series of subtractions of which "cement" is the remainder.

- If an internal reaction in the concrete transforms part of the aggregates, normally insoluble by acid attacks, into a soluble product, even if it includes some proportion of cement, the CETIC formula will not distinguish between the cement and the portion of the aggregates involved in the reaction. The calculation will therefore yield the sum "anhydrous cement plus solubilized aggregates".

- Under these conditions the difference between the cement content calculated by the CETIC formula and the cement content that would be determined from the lime not included in the calcareous portion of the aggregates would in fact be the quantity of aggregates solubilized in the alkali-aggregate reaction, but it should be noted that this quantity can be determined only from a cascade of differences, with the resulting cascade of uncertainties.

- Protocol of calculation

In a first stage, the usual iterative mineralogical calculation described previously is applied as is to the analysis of the concrete to compare the results obtained for the cement content and the carbonation, respectively, to the nominal proportion of binder and the value of CO₂ of carbonation determined by thermogravimetry (with temperature subdivisions based on the derivative curve).

If these results are in agreement (even if the calculated cement content is less than the nominal value), it can be asserted that there has been no internal solubilization of the concrete, and that in consequence it is free of any quantitatively detectable alkali-aggregate reaction (even if some disquieting symptoms have been observed by scanning microscopy). Barring unforeseen events that would then make a very thorough investigation necessary, the results of the calculation can be regarded as definitive.

In the contrary case, where a "calculated" cement content that is abnormally high with respect to the nominal proportion in the concrete (which is highly improbable) is found together with a CO₂ of carbonation that is much greater than the value indicated by thermogravimetry (or even in some cases by ordinary common sense), one can be sure that the results concerning the siliceous aggregates have been thrown off in this first calculation because of the solubilization of some part of them.

The complete calculation must then be performed, with a declared value imposed for the CO₂ of carbonation (that determined by thermogravimetry using the derivative curve). The difference with respect to total carbon dioxide then gives direct access to the calcareous portion of the aggregates (including the breakdown between calcite and dolomite, by iteration if necessary), and this allows the precise breakdown of the CaO determined by the analysis between the aggregates and the binder (this last by difference). This allows the use of this oxide as a tracer to calculate the cement content. Given both the importance of lime in the chemical composition of cement (more than 60 % in an Portland cement, against 20 % for silica) and the rigorous stoichiometry of the carbonates (calcite and dolomite), this method of calculation improves the precision of the proportion of cement in the hardened concrete, especially if its chemical composition is known (FIG.1).

This calculation, then, leads to a positive difference between the result of the modified iterative CETIC formula and the cement content calculated from the lime. This difference, also found (to within the analytical variability) in the difference from 100 % of the general assessment, represents the portion of the siliceous or silicate-containing aggregates having reacted, stated with respect to the mass of the concrete.

Finally, the chemical composition of this portion involved in the alkali-aggregate reaction can be found in the positive remainders of the oxides at the end of the mineralogical calculation.

Incidence of declared carbonation

An ancillary calculation was performed to estimate the influence of the variability of the proportion of "declared" CO₂ of carbonation in the second part of the calculation on the results.

It is clear that any increase of CO₂ declared as "of carbonation" entails a proportional increase of the calculated cement content.

In effect, to CO₂ there corresponds CaO, used to determine the cement content with the help of a coefficient that simply takes account of the molecular masses, giving the formula

$$\% \text{ CEMENT} = K \cdot \text{CO}_2 \quad \text{with} \quad K = \frac{100}{\text{Lime content of the cement}} \times \frac{56}{44}$$

The coefficient of proportionality K goes from 2.15 for a cement containing 60 % lime to 2.10 for an Portland cement that contains 65 %, today a very common value. In terms of proportion of cement in the concrete, an accidental increase of 1 % in the CO₂ of carbonation would lead by calculation to an apparent excess of the order of 45 Kg/m³, 3 to 4 times the tolerances allowed in production.

The foregoing considerations mean that a variation of $\pm 0.2\%$ on the content of CO_2 of carbonation is not significant with respect to the cement content, given the tolerances on the proportions.

With respect to the excess soluble silica content, calculation of the influence of the declared CO_2 of carbonation is more complex because it involves a larger number of parameters. It is, despite everything, a linear function inversely proportional to the quantity of CO_2 , the root of which corresponds in principle to the content of CO_2 of carbonation obtained by the usual iteration of the CETIC formula. Exactly the same applies to excesses of alumina or of ferric oxide.

To avoid tiresome theoretical developments that would not even take account of the variability of the silica content of the cement or the tolerances on the proportion of cement in the concrete, a series of complete mineralogical calculations was performed on three concretes affected by the alkali-aggregate reaction, of which all the parameters were well known.

As was to be expected, the excess SiO_2 content decreases as the CO_2 of carbonation increases but, since in the case of a severely affected concrete, the convergence of CO_2 is situated in the vicinity of 3% or 4%, for a variation of $\pm 0.2\%$ around the true carbonation, the excess silica varies not more than 0.1%. For alumina or ferric oxide the corresponding differences are not even perceptible ($\pm 0.02\%$, substantially smaller than the analytical variability).

It follows from the foregoing calculations that excesses of silica less than 0.2% can only with difficulty be regarded as reflecting any effect on the concrete of a quantitatively significant alkali-aggregate reaction; on the other hand, values greater than 0.3% of the mass of the concrete can be regarded as valid to within 0.2 points.

EXPERIMENTAL RESULTS AND DISCUSSION

Validation of the protocol

Systematic recording of the results of the chemical and thermogravimetric analyses, in computerized data bases, made it possible to develop and validate the calculation protocol described above from actual cases analyzed at the LCPC over a period of approximately five years. These cases concern both laboratory specimens of which the composition is perfectly known, some of which were used for researches on the alkali-aggregate reaction, and bridges affected to various degrees by the phenomenon.

First of all a check on sound concretes (Table 1) revealed that, for a balanced mineralogical calculation, the CO_2 of carbonation determined by thermogravimetry correctly matched the value obtained by iteration of the modified CETIC formula, the cement content of the calculation is in agreement with the cement content determined from the soluble silica and from the residual lime, and finally there is no excess in the remainders for silica, alumina, and ferric oxide (to within the variability of the chemical analyses or $\pm 0.03\%$ on the oxide balances).

For pathological cases that have caused major damage to structures, the complete calculation reveals a remainder of silica between 0.5% and 1% of the mass of the concrete, a highly significant value, almost systematically accompanied by alumina and ferric oxide, and sometimes SO_3 , and finally the difference between the result of the CETIC formula and the cement content calculated from the lime often exceeds 1%.

Kinetics of the alkali-aggregate reaction on specimens in the laboratory

In the context of the researches conducted at the LCPC on the alkali-aggregate reaction*, specimens of mortar were made with 25 % of a given CPA type cement doped to 1.25 % of Na_2O equivalent and two aggregates: a quartzite considered reactive and a limestone known for its stability. The grading ranged from 160 μm to 2.5 mm. These specimens, 20 mm in diameter and 50 mm high, were kept in a 1 N sodium hydroxide solution at 60°C. At the start and after 4, 5, and 7 months' preservation, chemical analyses were performed. The results, processed in accordance with the protocol described above, were used to monitor the kinetics of mobilization of the silica of the aggregates (Fig. 2).

At the end of 7 months, nearly 5 % (referred to the mass of the mortar) of silica from the quartzite had participated in the alkali-aggregate reaction. Even with the calcareous mortar, all of the included silica (0.4 %) was mobilized before 4 months, whereas on structures, after several years, no excess could be detected in concretes made with these calcareous aggregates. This shows that the treatment of the specimens leads to a considerable amplification of the dissolution of the silica. Furthermore, these tests confirm that with the proposed analytical protocol it is possible to monitor quantitatively the kinetics of mobilization of silica in the alkali-aggregate reaction while taking account of the inevitable variations of cement content in the production of the specimens.

Application to bridges affected to various degrees

The normative calculation was repeated on 39 cores of concrete, already surveyed, of which the CO_2 of carbonation was precisely determined by thermogravimetry. This study concerned 18 bridges exhibiting signs of degradation. The statistical results given in figure 3 show that the excesses of silica range from 0.2 % to 1 % with respect to the total mass of concrete. Two domains are apparent; the first, in which the mobilized silica is less than 0.5 %, concerns 11 cores in which the concrete is relatively little affected by the alkali-aggregate reaction. The corresponding structures are merely monitored.

The second domain, involving 20 concretes in which the excess silica ranges from 0.5 % to 1 %, corresponds to severe cases, in which some of the values are close to the "per cent", corresponding to approximately 1.3 % of the mass of the aggregates. There were, moreover, a few very severe cases in which the structures concerned had to be replaced.

In the silico-calcareous concretes, the excess silica is almost always accompanied by alumina and a little ferric oxide. The statistical study of the ratio of silica to alumina and/or excess ferric oxide merits special attention. In effect, many concretes studied to the LCPC in the last five years, exhibiting pathological signs, were made with calcareous aggregates from the Avesnes or Tournai areas, containing pyrites. In all of the samples in question, the $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ ratio by weight is close to 2, or approximately 4 in molar terms (Fig. 4). This is in line with the hypothesis according to which clays and sulphur (oxidized pyrites) are involved in the process of formation of the silico-calco-potassic gel observed by scanning microscopy, which is very often associated with ettringite (Deloye and Louam (9)). Finally, in all of these studies, the oxides from the aggregates used that are soluble under acid attack (SiO_2 , Al_2O_3 , Fe_2O_3 , etc.) are counted so as not to overestimate solubilization by the set of binder-aggregate reactions. In this connection, it should be noted that aggregates tending to contain soluble silica are certainly sensitive to the alkali-aggregate reaction.

* Thesis of Ms. Catherine LARIVE, in progress

CONCLUSIONS

The purpose of this work was to establish a calculation protocol making it possible to quantify the alkali-aggregate reaction from chemical analyses. Precise allowance for the carbonation of the binder, using the derivative curve in thermogravimetry, makes it possible to use lime as the pilot oxide for the calculation of the cement content and therefore to determine the silica of the aggregates mobilized by the phenomenon.

This protocol, developed and validated on sound concretes and mortars made in the laboratory, has been used on affected structures. This revealed: on the one hand, the size of the quantity of silica involved in the reaction (1 % with respect to the total mass of concrete in the most severe cases), and on the other, the practically systematic accompaniment of this silica by alumina and ferric oxide in some silico-calcareous concretes. This accompaniment suggests that clays and pyrites may play a significant role in the development of binder-aggregates reactions.

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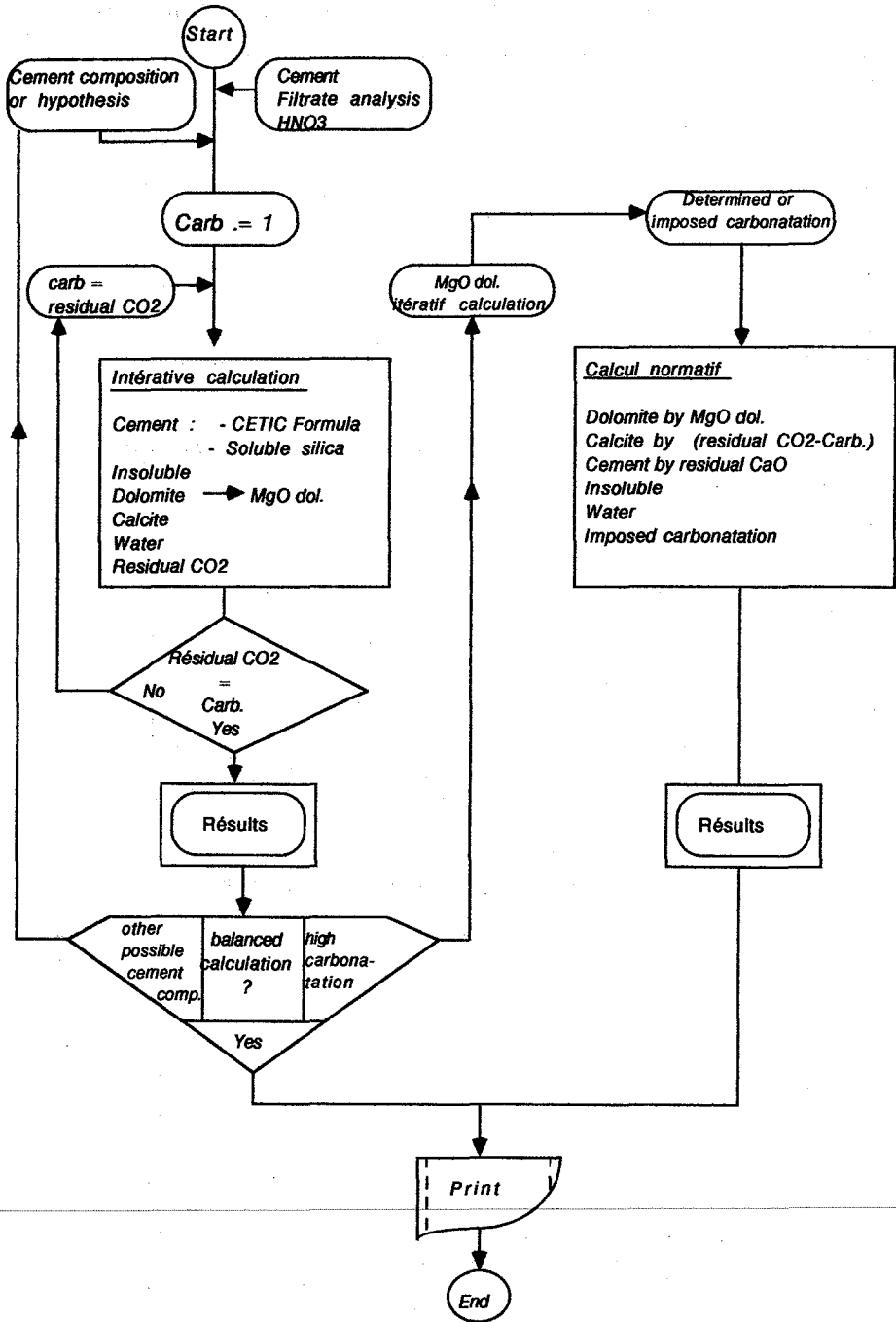


FIGURE 1 : FLOW CHART OF MINERALOGICAL CALCULATION

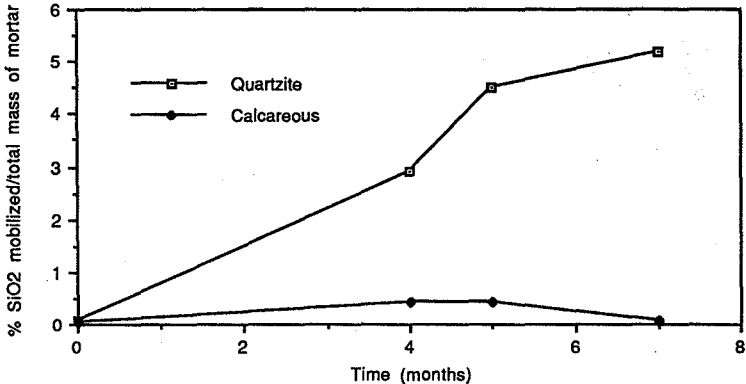


Figure 2 : kinetics of alkali-aggregate reaction in mortar

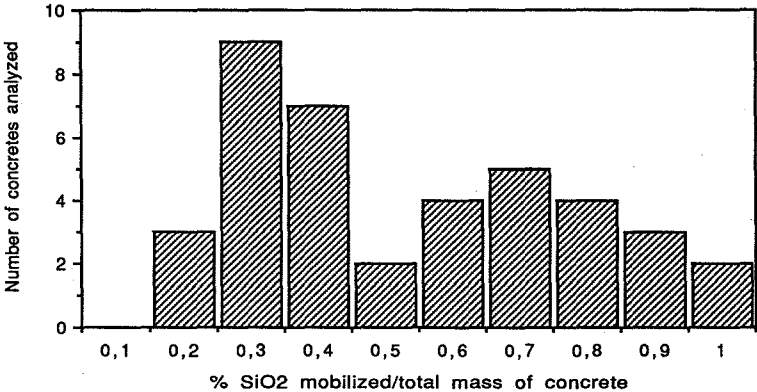


Figure 3 : Alkali-aggregate in structure

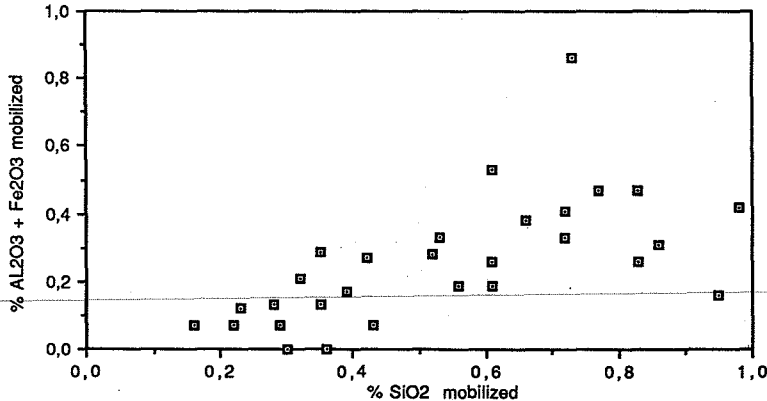


Figure 4 : Alkali-reaction in silico-calcareous concrete structure