EXPANSION TESTS FOR ALKALI-REACTIVITY OF AGGREGATES – A COMPARISON BASED ON A KINETICS APPROACH

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Abstract. *The reactivity of aggregates regarding the alkali-silica reaction (ASR) has been measured by different properties affected by the reaction. One among those properties is the expansion measured by linear dilatation of mortar bars or concrete prisms.*

Several test-methods are used to determine the aggregate reactivity by this property. They differ in procedure for measuring, for accelerating the reaction, as well as in implementing conditions and criteria. Criteria were proposed usually by comparing with performance records of aggregates in field structures.

The determination of reactivity, essentially a kinetic parameter, when measured by the same property, yields by different test-methods data that should be inter related, if converted by the effect of the varied parameters, to pre-fixed reference conditions.

This paper tries to present such a kinetic inter relationship between standards NF P 18-590, ASTM C 1260, and ASTM C 129. Globally, these standards cover a temperature range from 38 to 127 ºC, and different alkalinities. The relationship found shows consistency also for several aggregates, tested for NF P 18-590, ASTM C 1260, and ASTM C 227.

To convert results of tests in standard conditions to a reference, common basis for comparison, at pre-fixed conditions, some assumptions were taken from the literature, to estimate the effect of alkalinity (given directly from the hydroxyl content or estimated from the alkalis content in the cement).

Aspects related to the different experimental conditions on the test-methods and their effects are discussed.

The methodology used in this work was based on the criteria comparison for aggregates with reactivity close to the critical one, for which some standards suggest a nearly linear expansion versus time.

The proposed conclusion is that both the standards and the aggregate results, at the given conditions, are not inconsistent under the kinetic point of view. Some suggestions are made for improvements of accuracy of the relationship obtained.

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1 INTRODUCTION

The alkali-silica reaction (ASR), or in general, the alkali aggregate reaction (AAR), is an expansive, complex cluster of physical and chemical transformations, that occur inside concrete, involving the cement pore solution, normally strongly alkaline, some silica forms contained in the aggregates, and portlandite $(Ca(OH)_2)$ derived from cement hydration. Beginning slowly, it may accelerate until exhausting the expansion potential, usually by reducing the solution alkalinity. The expansion, occurring within concrete, is difficult to control on the basis of the present knowledge.

Discovered in the 1930´s, its main factors were soon identified as:

- aggregate reactivity, which depends on the nature of silica and the alkali minerals present,
- alkalinity, mainly originated from sodium (Na^+) and potassium (K^+) content in cement, aggregate types, admixtures, water or external sources (e.g., saline environment, anti freezers in roads and bridges, sewers),
- humidity, resulting mainly from micro environmental conditions, with relative humidity (RH) higher then 80%,
- temperature, also depending on micro environmental conditions, and
- presence of calcium ions (Ca^{2+}), always occurring in concrete environment, by portlandite dissociation.

The aggregate reactivity is defined as its susceptibility to ASR. It expresses the influence, in all aspects, of the presence of the alkali reactive phases, in what could be designated as the "factor aggregate". As a global property it includes the effect of several sub-factors, such as the content, size and nature of the solid reactive phases (e.g., opal and chalcedony, crystobalite, tridymite, strained quartz, microcrystalline quartz, volcanic glasses), its thermodynamic stability in alkaline environment and crystallinity, existence of activation sites like lattice deformations or displacements, specific surface, degree of hydroxylation/hydration of the surface, porosity/permeability.

The reactivity varies also with the source location, i.e., geological history, in a not fully understood way. For example, flints are reported as non reactive in Ireland , but as reactive in England and North of France [1]. Rayment [2, 3] has shown that flints reactivity depend on an external light colored shell designated by cortex, apparently resulting from weathering, and found it is thinner in glacier gravels which are less reactive. In granitic rocks, a slight metamorphization or weathering can change its reactivity, e.g. by straining quartz grains [4] . In other situations, limestones and rocks non reactive by themselves became reactive due to silica inclusions inside the grains or by matrix impregnation, almost invisible to the naked eye [4]. Wigum 95 [5] underlines that variation of mineral composition and mechanical deformation influences these regional variations.

In Portugal, the more common reactive rocks are granitic or gneisses, quartzites, greywackes and limestones with flint nodules [6].

This notion of reactivity towards ASR has been formulated in many different ways, in reference to several properties inherent to the materials or affected by the reaction. Some of the properties referred to are linear or volume expansion, expansion pressure in a confined space, rate or extension of dissolution in basic environment, the quantity of gel formed or alkalis consumed, rate of expansion or equivalent parameter in a kinetic model, threshold alkalinity required by the aggregate to be reactive, and various mineralogical and petrographical indexes, namely the disorder coefficient (Cd), yielded by Infrared spectroscopy, and quartz crystallinity index (QCI), obtained by X-ray diffraction [7].

Among these properties, one that better expresses the expansive effect is the linear

expansion of mortar or concrete bars.

The reactive behaviour, expressed by its expansive effect, is not, *strictu sensu*, a property due exclusively to the components of an aggregate, but relates rather to the behaviour of the entire system, influenced by all other factors present, such as the alkalinity, humidity and temperature. To simplify, certain conditions of the system are pre-fixed and the global behaviour, expressed by one parameter, is assigned to a single factor. Thus, the reactivity may be formulated by different ways in different reference tests, each defining specific test conditions, reading procedures and allowed limit of expansion.

This formulation, joining several effects, may lead to some ambiguity. For instance some flint containing aggregates may be reactive for flint contents below a certain level and non reactive for the same flint in contents above such level. Also, in some cases, the expansion of the same aggregates may rise with alkalinity below a pessimum level, but lowers with alkalinity increase above such pessimum.

The classification of an aggregate as reactive is ideally defined by its service record. However that can be done only when records exist for structures with the same aggregate for a long time [8], what only happens in large constructions, built several decades ago, and using aggregates certified as similar to the ones under characterization. Thomas et al. [8] refer that long duration, open air tests with concrete cubes are the best second comparison basis. Even so, these latter tests are very long, more than ten years, and more expeditious criteria and easier to implement in a shorter run were needed, and were developed, leading to the different tests or criteria presently in use, after checking their criteria with the available results for aggregates with field record.

Resulting from different procedures, the pre-fixed conditions differently affect the rate of reaction allow accelerating the tests, against a certain setting apart from the conditions of actual use of the aggregates. Even when expressed by properties other than the rate of reaction, reactivity is an essentially kinetic property and the modeling of its kinetics and respective factors should allow to inter-relate results obtained in different test conditions. As the kinetics refers to a cluster of transformations, this modeling should be simpler when the controlling processes are the same within the range of situations to consider, a situation found often in heterogeneous reaction kinetics studies, as is the case for ASR.

This paper tries to analyze this inter-relation, and the existing information, having selected the standardized reference tests NF P18 -590 [9], ASTM C 1260 [10] and ASTM C 1293 [11] for a first comparison, widened to a few other tests. The same correlation was also carried for the first two tests and the ASTM C 227 [12] test, using already available data [13] for several types of aggregates.

2   COMPARATIVE DESCRIPTION OF THE SELECTED TEST-METHODS FOR AGGREGATES ALKALI-REACTIVITY EVALUATION.

The reference methods used are all based on the measurement of length change as described in test ASTM C 490 [14], and are of two types.

In ASTM C 227 and ASTM C 1293 test-methods the specimens (3 by test) are kept in saturated atmosphere over a water bath in a closed container, in a temperature controlled chamber, set to 38 ºC $\pm$ 2 ºC. The specimens with dimensions 25 x 25 x 285 mm and 75 x 75 x 250, respectively, prepared by different ways, have their expansions measured at certain ages.

The ASTM C 227 test specifies a cement rich in alkalis but indicates no fixed composition. Expansions are measured at several ages up to 12 months and, if necessary, after that with an interval of 6 months. The conditions and result interpretations report to an annex of the standard ASTM C 33 [15], that indicates for a cement with minimum of 0.8% Na_2O_{eq}, a critical expansion above 0.05% at 3 months or 0.10 % at 6 months, the last limit prevailing

in case of divergence. This standard refers that these limits may not be conservative for slow reacting aggregates, but it is not recommended for these cases, suggesting instead the ASTM C 1260 or ASTM C 1293 test-methods.

The ASTM C 227 was reviewed critically by several authors considering it, in general, on the conservative side, as it may yield false negatives, i.e., fail to identify reactive aggregates. Also, the alkali content of the cement is not fixed, and the duration is too long. Thus, Grattan-Bellew [16, 17] proposed to reduce the allowable expansion, to 0.05% at 6 months, first, and later to 0.05% at 12 months. Santos Silva [13] quotes Bérubé and Fournier [18] as reporting that the test result depends on alkali content and water/cement (w/c) ratio, and also on storing conditions of the specimens, leading to the adoption, in Canada and France, of an increase of Na_2O_{eq} to 1.25%, cement basis, by addition of NaOH to the mix, of a w/c = 0.5 and eliminating the absorbent wicks lining the inside surface of the containers.

In ASTM C 1293, Concrete Prism Test (CPT), were tested 3 specimens with dimensions 75 x 75 x 285 mm. The cement must have a value of at least 0.8% Na_2O_{eq}, and NaOH is added to the mixing water, so that the Na_2O_{eq} content, cement basis, is raised to 1.25%. Expansion is read in the beginning and at 7, 28 and 56 days, and 3, 6, 9 and 12 months, if necessary being extended with readings at a 6 month interval. The aggregate is considered reactive if expansion is higher than 0.04% at 12 months. The test is recommended when others are not satisfactory (e.g., ASTM C 227 and ASTM C 1260).

In ASTM C 1260, 3 mortar bars with dimensions 25 x 25 x 285 mm are immersed in a solution 1N NaOH, in a container inside a oven at 80ºC ± 2º C. The bars are prepared with aggregate/cement ratio of 2.24, and w/c ratio of 0.47. This standard refers that the cement alkali contents has not a significant influence on the results (ASTM C 1260, Note 3 [10]).

In NF P 18-590, 3 bars with dimensions of 40 x 40 x 160 mm, are prepared using a w/c ratio of 0.5, and using a cement with Na_2O_{eq} > 0.75%, later corrected to 4% on cement basis, by addition of NaOH. After 24 h of curing, in environment with RH>95%, the bars are immersed in water for another 24 h, and after placed in water in an autoclave where they are stored at 127±2 ºC and 0.15MPa for a period of 5h ± 10 minutes. After autoclaving, steam vent is opened, and the bars are placed in water and the length is measured. If the expansion thus measured is more than 0.15%, the aggregate is considered to be reactive.

Different reference tests may not lead to a same classification of all aggregates. A balance of the ASTM tests in what concerns results for different types of North American aggregates is presented in ASTM C 33. Some cases are referred to in an annex of ASTM C 1260.

Comparisons between tests for different aggregates are commonly found in the literature, some of which are referred. Grattan-Bellew and co-authors [16, 17] have them analyzed critically these and other standard tests. Wigum revised critically in 1995 [19] similar tests defined as standards in several countries (ASTM C 227, C 289, C 1260 and C 1293, the last at that time only in the Canadian version) [5, 19] and in a more systematized work revised in 2006 [20], the standards of many European countries. In some countries, criteria of reactivity had to be slightly adapted to local aggregates to reduce the number of aggregates not matching the original criteria. Chak and Chan 2004 [21] revised the standards in several countries for alkali reactivity and formulation of concrete to withstand ASR. Bauer et al 2006 [22] revise and summarize also comments to these tests.

In general terms, the ASTM C 227, as defined originally, is considered too permissive, with false negatives reported, and the duration is too long.

The ASTM C 1260, with much shorter duration, is considered very practical and useful, but on the tight side, with false positives reported in one of the most significant evaluations. Wigum [19] cites Berubé et al [23] as having tested 142 Canadian aggregates where it has failed to identify only one aggregate with reactive field record, but classifying as reactive

several aggregates without field problems. The Canadian version of this test (CSA, test A23.2-25A) sets a limit of 0.15% at 14 days [19], or of 0.1% for limestones and a few other aggregates [21].

The ASTM C 1293 test results (similar to the RILEM AAR3) are considered more representative of the concrete field performance [annex, standard ASTM C 33]. Thomas [8] refers that no divergence between field record and reactivity classification by this test was known to him. However, the test has the inconvenient of its long duration.

In some aggregates, the behaviour can be more complex and differ from this general pattern. In particular, aggregates with siliceous inclusions as grains, nodules, veins, intergranular or matrix siliceous cement, and aggregates that liberate alkali ions slowly, like the granites, do not always fit well in these expansion tests.

In the present approach, based on common features, the variations are supposed to be due to factors that are specific of those aggregates, e.g., the liberation of alkali ions, and might be included in one single model, to develop in future work. However, each case must be considered in separate.

3   ASSUMPTIONS ON THE EFFECT OF THE FACTORS CONSIDERED

Modelling the effect of the main factors is one of the essential aspects of the formulation issue. For that, a review and study for each factor, on published information was carried out and the respective models were adopted as the best fitting the present approach.

3.1 Reactivity

The marginal or quasi reactivity designates for each test corresponds to the critical expansion for one or two reaction times, or ages. Such critical levels, if more than one, are proportional to the reaction time. The ASTM C 1260 and ASTM C 227 tests suggest for such condition of reactivity an expansion nearly proportional to time, i.e, an aggregate with nearly critical reactivity, would have, in these tests, a constant rate of expansion.
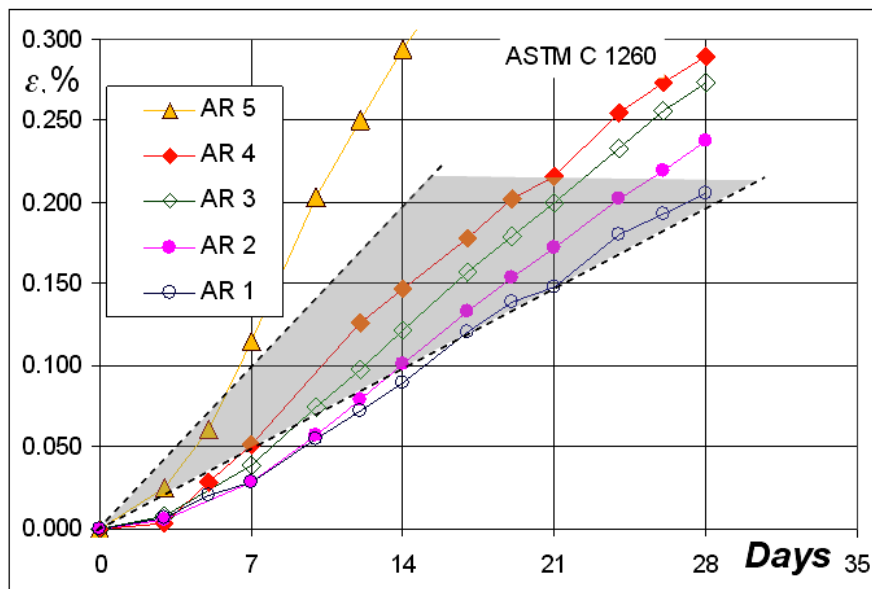

Figure 1: Results of ASTM C 1260 for sand aggregate samples – inside the shaded area the reactivity range, between dashed limits - AR 5 is reactive, AR1 is non reactive, although very close to the limit.

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Assuming that reactivity is a property of the material, the same extends to other tests, with only one critical limit. In the case of ASTM C 1260, the critical reactivity is defined by an upper limit, above which the aggregate is clearly reactive, and a lower limit, below which the aggregate is clearly non reactive. In the region between these, the aggregate is classified as potentially reactive.

This assumption of a nearly proportional expansion was checked by experiments with aggregates with reactivity near critical, as depicted in figure 1. Other tests on other aggregates yielded similar results. As shown, a proportional expansion was observed in the expansion 0.125-0.30 for AR4 sample. A linear expansion is observed in many cases for marginally reactive aggregates, but after an expansion of *ca* 0.02%, i.e, near proportional. Sample AR5, on the reactive field, is already not linear at all.

In case of proportionality, the critical conditions for reactivity can be defined not by the expansion, but by the rate of expansion, a parameter more conventional and akin to a kinetic perspective. In the present case a linear expansion after a short period is equivalent and validates the current assumption.

As a matter of fact, many authors refer to reactivity as expressed by the rate of reaction with alkalis, namely the rate of dissolution of silica in alkaline solution. A reference test for reactivity, ASTM C 289 [24], tried to assess reactivity by this way.

Johnston et al [25] used expansion data from ASTM C 1260 (even non linear) for fitting parameters of the nucleating and growth model (Avrami):

$$\alpha = 1 + \alpha_o - e^{-k(t-t_o)^M} \tag{1}$$

where α is the conversion (between 0 and 1), α_o the initial expansion at t_o , 4th day of cure, k is the kinetic constant and M the exponent.

They found that the rate constant of this model had a critical value for reactivity for the aggregates teste, given by *ln (k) = - 6* .

Note that the equation is applied directly to the expansion readings. The fact it uses expansion, not conversion or extension as given by the number of transformed moles, assumes proportionality or a linear dependence between extension of reaction and the resulting expansion. This assumption, although fitting in the general character of the present approach, reduces the relation precision.

The correspondence or even equivalence between expansion and extension of reaction is however a result or an assumption of many studies and models, namely the Larive work [26] where it is assumed explicitly in the development of her model. Ben Haha [27, 28] has measured both separately and found in several aggregates that they are proportional in the beginning [29], but later although following a trend similar for the aggregates tested, is no longer proportional. Lu et al [30] refer however the possible non proportionality between expansion and extent of reaction, indicating that some aggregates, e.g., greywackes, have significant expansion without similar evidence of reaction products.

3.2 Alkalinity

Diamond and Penko [31] cites Longuet et al [32] as having pioneered the expression and analysis of the pore solution in concrete, finding alkali hydroxides hundred times higher than calcium's, and pH values well above 12.6, maximum value explained by dissolution of $Ca(OH)_2$ present in concrete in excess, and formed in OPC hydration.

In OPC hydration the alkali ions are released and go to interact with other cement phases, present or just formed by hydration, in special with aluminates and $Ca(OH)_2$ leading , i.e., to the capture of anions and corresponding Ca^{2+} cations, which is equivalent globally to anions

exchange by hydroxyl ions (Dron & Brivot [33], Diamond & Penko [31]). This process may explain the rise of pH close to 14.

In these conditions of high pH, the concentration of OH$^-$ is nearly the sum of Na$^+$ and K$^+$ concentrations. As most (but not all) soluble alkalis were formed from cement phases, cement composition yields a good alkalinity estimation of the concrete pore solution.

The initial alkalinity, resulting globally from these processes was empirically modeled by Helmut el al 1993 [34], obtaining

$$[OH^-] , mol/L = 0.339 \, Na_2O_{eq} \, \% \, / \, (w/c) + 0.022 \pm 0.06 \qquad (2)$$

where w/c = water/cement ratio.

Alkalinity also depends on the interaction with portlandite, which start to dissolve when Ca^{2+} concentration lowers, or due to its release from some aggregates, e.g, feldspars.

The initial alkalinity thus estimated may vary with the reaction progress, with humidity and leaching. With ASR progress it lowers as measured experimentally by several authors (Kawamura 1997[35], Owsiak 2005[36], Rivard 2007[37]), being one of the parameters used in ASTM C 289 test, and was the basis of a topochemical model (Furusawa et al. 1994 [38]).

In ASTM C 1260 test, however, the contribution of the immersion solution is dominant, and alkalinity variations are not considered within the test (note 3 in the test-method).

In the expansion tests done in saturated environment (ASTM C 227 or ASTM C 1293) the alkalis leaching is significant and affects the overall expansion [8, 39-41].

3.3 Humidity

The water content in concrete is an ubiquous factor, with effects at multiple levels, from the participation in hydration to the direct expansion of aggregate, cement paste and ASR gel formed, the volume of pore solution and degree of filling of pores.

Absolute humidity is a measure of the chemical activity of water in equilibrium with the atmosphere, and Relative Humidity (RH) conditions, in the long range, the amount of water in concrete in equilibrium with the environment. Variations in the short run are apparently accommodated by water redistribution inside concrete.

The activity of water in concentrated solutions is lower than one, the value corresponding to HR of 100%, i.e, in equilibrium with pure water. Thus, in tests under saturating conditions, condensation is continuous and forms a leaching stream that reduces alkalinity, as was shown experimentally by Rivard et al 2003 [41].

As it is expected from its multiple interactions, its effects are not easy to model in detail. There is a wide consensus that ASR stops at humidity's lower than ca 70% (value that varies with temperature), accelerating fast above 80-85%. Poole, in Swamy 1992 [42], represented graphically this dependence, and Capra [43] modeled as proportional to the eighth power of HR. Hou et al 2005 [44] present a similarly shaped experimental curve for sorption measured on a exudation gel from Furnas, Brazil.

The model by a factor of (HR)[8] was adopted in the present paper, with the caveat that its application at very high values, above 90-95% may imply extensive leaching, and consequent loss of alkalinity and reduced expansion. Thomas et al 2006 [8] and Wigum 2006 [20] cite papers that point to a maximum of expansion at ca 95%.

The humidity was considered to be saturated in all tests in analysis.

Leaching is particularly significant for ASTM C227 and C 1293 tests. Rogers and Hooton [39, 40] have shown for the former a strong variation in expansion due to internal lining of the containers with absorbent material, referring differences of 400% for the whole set of experiments and, for the same type of container, having found variations by a factor of 2 just by removing the lining. The same authors refer that this effect is, however, of opposite sign

for tests using Pyrex as aggregate, indicating as cause the liberation of alkalis, aspect that must be kept in mind when interpreting test results of aggregates known as liberating alkalis.

3.3.1 Model of leaching dynamics

Without more detailed information, the available data was tentatively used to model the dynamics of leaching, for aggregates without liberation of alkalis.

The model assumes in the bar or prism uniform conditions and pore solution concentrations and that it is place in a closed container with bottom water, in a chamber with temperature control set to 38 ºC. When temperature rises evenly, humidity rises by mass transfer close to the interface air/water, and propagates by natural convection to and through the air until interface with concrete, where it is deposed.

Thus, there is a transport system of water vapor from the water in the bottom to the interface with concrete, where it condenses, diluting locally the pore solution, i.e. increasing its volume. As this process continues, the pore became filled and the solution superficial film slips down and drips to the bottom of the container. Draining superficial ions in solution, mainly alkaline, this continuous flow creates a diffusion flux inside the bars from the bulk to the more diluted outer surface and the overall alkalis in the bars lower.

As the volume of water initially in the bottom of the container is much larger than the one in the pores, the amount of alkalis leached by this process affects more the concentration of the pore solution, rather than the liquid in bottom, where there is an alkali build-up, and the overall process extends for long time, theoretically until both concentrations are the same.

To model this process, let us consider as constant k, global coefficient of mass transfer in the bar, due to the difference between Cas, average concentration of the pore in the bulk of the bars and ca, surface concentration, assumed as uniform throughout the bar.

The variation of alkalis concentration in concrete, by unity of time, equals the quantity of alkalis transferred through the external surface, and washed by the condensate. The model tried to formulate this quantitatively, for one of the simplest situations.

Thus, let Cas be the concentration of the pore solution in the solid bars, and Vs its volume, S being the external surface area, and L the flow rate of condensing water, displacing the same volume of solution with concentration ca, the following balance holds:

$$Vs\ d\ Cas/dt = -\ kS(Cas-ca) = -\ L\ ca \tag{3}$$

Whilst in the bottom of the container, the liquid, volume V and concentration Caf, the rate of build up of alkalis is given by

$$V\ d\ Caf/dt = L\ ca \tag{4}$$

and thus $ca = (Vs\ d\ Cas\ /dt + kSCas)/\ (kS)$ and $ca\ (L+kS) = kS\ Cas$,

so that $ca = (Vs\ d\ Cas\ /dt + kSCas)/\ (kS)\ =\ (kS/(L+kS)\ )\ Cas$,

$$Vs/kS\ d\ Cas\ /dt + (L/(L+kS)\ )\ Cas = 0 \tag{5}$$

If L is considered constant during a certain period, the equation corresponds to a first order process

$$d\ Cas\ /dt = -\ (kS/Vs\ )\ (L/(L+kS)\ )\ Cas\ ,\ ou\ d\ Cas\ /\ Cas = -\ (kS/Vs\ )\ (L/(L+kS)\ )\ dt$$

$$ln\ Cas = -\ (kS/Vs\ )\ (L/(L+kS)\ )\ t\ +ln\ Co,\ \ Cas = Co\ .\ exp\ (-\ (kS/Vs\ )\ (L/(L+kS)\ )\ t)$$

At beginning, $Cas = Co$,   and at end $t = infinite$, $Cas = 0$

$$Cas = Caso\ .\ exp\ (-\ (kS/Vs\ )\ (L/(L+kS)\ )\ t) \tag{6}$$

If the losses (i.e., *Cas/ Caso*) are known at a certain age, this equation allows estimating the group *(kS/Vs)(L/(L+kS)* as time constant characteristic of the model, and allows to estimate at other ages the concentration *ca* and the average concentration in a time interval

This model of leaching shows, within the limitations of its physical model and assumptions, a possible influence of variations of *L* due to internal lining of the container, as it varies the effective area of evaporation.

In fact, *L* varies also along the leaching process with the difference between concentrations of liquid in the bottom and in the concrete pores, both changing. The weakest assumption, however, is not considering the diffusion inside the bars. But a better model would need a program of experiments, out of the present scope of work.

The model above was used to estimate the average alkalinity for the ASTM C 227 test. Thomas [8] refers loses by leaching at 12 months of 35% of alkalis, what gives to the model a time constant of 0.00118 and, for an initial contents of 1.25% Na_2O_{eq}, an average alkalinity in that period of 1.01% Na_2O_{eq}, and a final value de 0.81%. These changes, determined for only one case, are generalized, until better information is available, so that confirmation and improvements of the data and the model used are recommended, preferably with a program of consistent experiments. These improvements might be essential to understand and model expansion in concretes in open air experiments.

In the case of NF P 18 590 test, although the bars are immersed in water, it was considered that, as the test duration is very short, only interactions inside the concrete would be relevant - there is leaching, but its non quantified extension was taken as null, considering the short test duration, high concrete alkalinity, and quasi reactive aggregates, supposed to lead to slight cracking. These assumptions however should be confirmed whenever possible.

3.4 Temperature

The temperature accelerates all considered transformations. If the controlling transformation is the same and is thermally activated, the relation of Arrhenius should be valid:

$$ln (1/K) = k1. exp (-Ea/RT) \tag{7}$$

where *K* is the kinetic constant of the reaction, *k1* the pre-exponential constant, *Ea* the apparent energy of activation, and *T* the absolute temperature, in degrees Kelvin.

If the controlling reaction or step is not the same, or there is a mixed control, the equation still applies to the partial reactions, if the respective separate kinetic constants can be determined, for instance selecting conditions in which several are sequentially accelerated substantially so that their contribution become negligible in a kinetic treatment.

Several authors advert caution on the application of these relationships for ASR, particularly in wide ranges of temperature, by experience or other reasons. Citing a few, Grattan-Bellew 1983 [16] hints that at higher testing temperatures other reactions not occurring at normal temperatures, namely hydrothermal, may take place and affect expansion results. Cyr and Guisbergues [45] refer measurements of different time scales for early and mature expansions, what may imply reactions or steps with different energy of activation. Lenzner [46] considers that in accelerated tests expansions may start while concrete is not yet fully consolidated, so that a part of the early expansion may be absorbed at higher temperatures. Chatterji [47] comments on the relevance of differences between test and field conditions, e.g. final expansions are higher at lower temperatures and cites authors referring that reaction and expansion are not directly related, an assumption widely accepted as referred above.

Not disregarding these words of caution and good sense, the present work focused in

determining in which extent the information assumed and conditions pre-fixed for reference tests could lead to results that might result in a linear Arrhenius plot, assuming the possibility of such linearity as a criterion of kinetic consistency for the reference tests. Note that this is expected to happen if the same step transformation remains controlling, despite changes in the set of transformations and their rates.

4 OTHER KINETIC ASSUMPTIONS

4.1 Order of reaction

Based on several papers and proposed models, the reaction is assumed as first order relating to the concentration of OH^-, at least in the initial stages. The issue may be more complex, given the interactions of the solution with the several solid phases in presence. The expected variation due to the reaction, in contents of hydroxyls and the corresponding alkali ions, is partially counteracted by the dissolution of portlandite, present in large amount, driven by the precipitation of Ca^{2+} ions restrained by silica dissolution. These processes are linked to the low contents of Ca^{2+} that simultaneously limits the silica content in solution, in addition to alkali substitution that recycle a part of the alkali ions in the alkali gel itself.

4.2 Effect of other factors, not directly considered

The present approach considers the effect of all factors as if only were due to the aggregate reactivity, and for all test conditions, the same controlling step (or, quite unlikely, different steps with same energy of activation). This scenario may be over-simplified.

The possible presence of other transformations has been referred to. Kawamura [35] reviewed the expansive reactions in alkaline solution. Wang et al [48] analyzed the thermodynamic possibility of other reactions of different minerals with alkaline solutions, under the perspective of alkaline ions release.

The liberation of alkaline ions in some of these reactions, and even the reaction with silicates (e.g., in granites) and recycled glass, may be related to a significant effect in alkalinity [49], what may be interpreted as other reactions being present, namely DEF.

5 PROPOSED APPROACH

5.1 Assumptions overview

Summarizing, the following assumptions are considered
- extent of reaction is proportional to strain, and measured by it;
- constant rate of reaction, for marginally reactive aggregates;
- reaction rate proportional to the initial concentration of OH^-, defined as the same of the solution of bar immersion for ASTM C 1260 test, and the estimated by equation of Helmut 1993 [34] for ASTM C 1293, ASTM C 227 and NF P 18-590, correcting for the average value during the two first, longer tests, using a leaching model now proposed. For test NF P 18-590, no correction was applied due to its short duration;
- existing kinetic consistency, the dependence on the temperature of the equivalent rates of the same reaction with the other corrections, would be represented by a linear Arrhenius plot. ***The possibility of this linear plot was assumed as a criterion of kinetic consistency***.

The kinetic consistency may refer to a same controlling reaction or reaction step, without specifying it, but does not mean all other transformations are the same if conditions change.

5.2 Rationale of the proposed kinetic approach

For each reactivity test, critical limits of expansion were carefully studied by many researchers and compared with field records. Sharp criteria were thus defined for each set of conditions defined in each reference test (these limits translate/resume so to say the knowledge on behaviour of the aggregates, at least for most of them), so that strains above that are considered an indication of reactive aggregates and the inverse for non-reactive ones.

In the framework of the assumptions presented above, each such criterion corresponds to a rate of strain, equivalent to a rate of reaction. Even if there is no real aggregate exactly with such critical rate of strain, all following considerations are valid assuming it as virtual.

The same aggregates should ideally be classified the same way in different tests, and so would our virtual critical aggregate. Of course this is not exactly true for all aggregates and all tests, but it may be accepted as correct for most, otherwise, the tests would not be in use.

Comparing tests is then comparing criteria, i.e., rates of reaction. As these refer to different conditions, they are converted to common standard conditions, for comparison.

For that, it is used the information and models on the effects of different factors and adapted each criterion, i.e., the critical rate of reaction for each test, to the set of standard conditions. The factor humidity is dealt two fold: the effect on gel expansion is neglected, as all tests run on very high humidity; the effect on leaching due to condensing is considered for tests in saturated container at 38 ºC, based on the leaching effect on alkalinity. The effect of the factor of alkalinity (assumed as first order) is considered, yielding an equivalent-to-standard-alkalinity rate of reaction, one for each test at a particular temperature.

As the tests are carried out at different temperatures, these equivalent rates of reaction obtained for the different tests should give a linear Arrhenius plot if the same reaction, or reaction step, is the controlling step in all tests.

Finally, as reaction rates are assumed constant for marginally reactive aggregates, and rates have a meaning more difficult to grasp, a standard strain is fixed, and rate is expressed as equivalent time for each test, as the time it would take to reach that standard strain if the rate would be constant for sufficient time.

5.3 Rate of reaction equivalent at the standard concentration

For test comparison, relevant rates of reaction are not the given directly from the different tests, but the equivalent rate of reactions estimated for identical, prefixed conditions, assumed as standard, and chosen as 1M alkalinity concentration.

The "experimental" rate of reaction $v_e = \delta_e/t_e$, δ_e being the strain measured after a test time t_e, is assumed for a critically reactive aggregate to have the limit value defined by each reference test and, being proportional to the concentration used for each test, C_e , may be corrected for the effect of concentration, for the standard concentration, C_S :

$$v_s = v_e \, (C_s/C_e) = \delta_e/t_e \, (C_s/C_e). \qquad (8)$$

5.4 Time equivalent to a standard strain

Although Arrhenius plots are referred to reaction rates, these are meaningless parameters for most experimentalists in expansion tests; reference tests mention strains and times at different alkalinities and temperatures what might turn difficult the interpretation of the plot.

Now, reaction rates are assumed constant in the relevant period of the tests, and thus it seemed more adequate a representation of the Arrhenius plot in terms of the time equivalent to reach, if the rate was constant, a standard strain, fixed as 0.1 %.

The equivalent time thus defined is a virtual value, estimated in the present framework,

valid for quasi reactive aggregates. The standard strain of 0.1%, also virtual, doesn't need to correspond to a real strain, which would be absurd when applied to a non reactive aggregate. It is only an artifact to allow expressing reaction rates in times needed to reach a strain.

The correction of the test strain to the standard conditions thus assumes that the rate of reaction is constant, i.e.,

$$v_s = \delta_S/t_S ,$$

δ_S being the standard strain, 0.1%, and t_S the equivalent time at standard conditions, or the inverse of ten fold the equivalent rate of reaction $t_s = 1/(10.v_S)$. From the equivalent rate of reaction equation,

$$\delta_S/t_S = \delta_e/t_e \ (C_s/C_e) ,$$

it is, then

$$t_S = t_e \ (C_e/C_s) \ (\delta_S/ \ \delta_e) \qquad\qquad (9)$$

Table 1   Experimental conditions and calculated equivalent time for each reference test

The subscript "e" stands for test or experimental, and "s" for standard	ASTM C 227 [12]		ASTM C 1293 [11]	ASTM C 1260 [10]	NF P 18 590 [9]
t, ºC	38		36	80	127
δ_e , %	0.1		0.04	0.1-0.2****	0.15
t_e , days or hours	181 d		365 d	14-28d****	5.25 h
C_e , Molar if solution or				1 M	1.786 (estim)
from equation of Helmut et al. 93,	a/c = 0.5		a/c=0.45		a/c=0.5
with Na₂O$_{eq}$,% before leaching	0.89**	1.25**	1.25		4
average in leaching	0.73	1.01	1.01 ***		
Equivalent rate of expansion, %/day	0.00087	0.00064	0.00014	0.00714	0.25
Equivalent time*, days	115	162	714	14 - 7	0.39

*Equivalent time at 1M and 0.1% standard expansion, given by equations above.
**This standard defines no alkali content for the cement to use; for the present estimation purposes two values are considered, that correspond chronologically to the levels used when improving the test.
***By this standard, to the cement to be used, it must be added NaOH up to 1.25% Na₂O$_{eq}$, cement basis; Thomas 2006 refers ca 35% losses by leaching; with a first order dynamic model, such losses lead to a final value of 0.81 with an average of 1.01%.
**** The definition of non reactive uses the lower limit; the upper is used for reactive; in between may occur both non reactives and reactives, and the test is extended to 28 days; if the strain is >0.2, the aggregate is considered as potentially reactive, and of dubious reactivity if not. This classification is considered too severe and may lead to gales positives. On the other side the original standard alerts that in granites, gneisses and metabasalts expansion may be less than 0.1%, for aggregates with reactive field record. The corresponding Canadian standard uses a single limiting value at 0.15%, and requires confirmation by the Concrete Prism Test similar to ASTM C 1293.

6   RESULTS

6.1 Comparison of limiting values

From the experimental conditions of each reference test, the equivalent times were estimated as presented in table 1.

The equivalent time for each of the three tests considered, *NF P18-590, ASTM C 1260,* and *ASTM C 1293*, were represented in an Arrhenius plot (see figure 2), and are aligned as a straight line with a high correlation coefficient. As these tests refer to rates of reactions in

conditions of critical reactivity, higher rates (plotted above this line) mean reactive rates, i.e., reactive aggregates, so that the line defines the reactive field (above the line) ant the non reactive field (below the line). Equivalent times for the test **ASTM C 227** were also plotted in the same figure, for two levels of cement alkalis, at 0.9 and 1.25% Na_2O_{eq}, assuming a leaching correction factor identical to the discussed for ASTM C 1293, so that the difference is, for the present evaluations, only in the criteria.

These results are close to the comments comparing these tests, under different perspectives, to which this kinetic approach gives a certain unity.

Limit values for expansion of AMBT, at 80 ºC and 1M Na_2O_{eq}, have varied in several standards within the range of 0.08 to 0.15 [19, 23, 50]. The ASTM C 1260 test defined it as 0.1%, a limit referred to by some authors [51, 52] as severe.
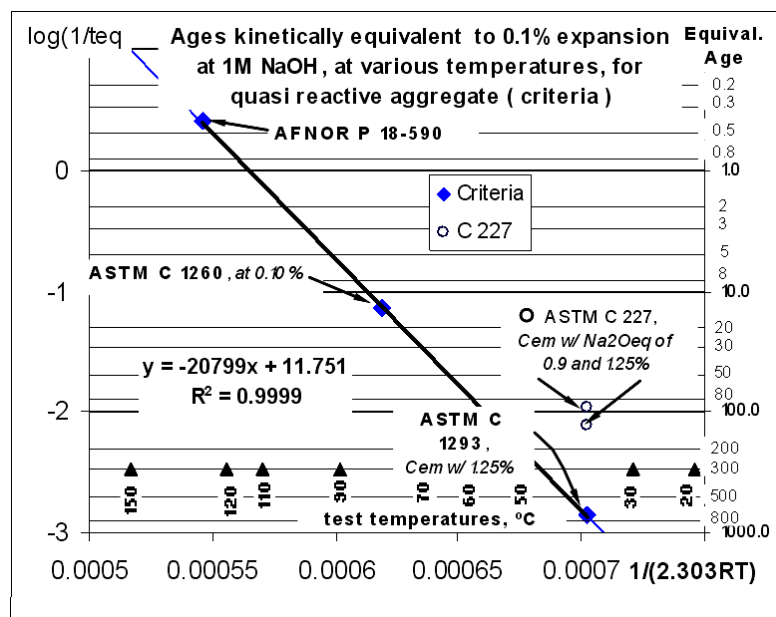

Figure 2: Arrhenius plot relating reference tests ASTM C 1260 [10], ASTM C 1293 [11] and NF P18-590 [9]. The regression line with high correlation, defines two fields: the reactive one, above it (higher rates or lower equivalent times) and the non reactive one, below. The test ASTM C 227 [12] (corrected for leaching) falls in the reactive field, in line with comments referring that it may fail to identify aggregates with reactive record.

In figure 2, the exactly collinear position of this test within the two others, corresponds to 0.11 at 14 days, or 0.1 at 12.7 days. Both values equal the limit for reference AMBT tests, respectively, in Norway and Germany [20]. In Canada the test uses 0.15 as limit (0.1 for limestones and some other aggregates [21]).

The original criterion of ASTM C 227 test plots in figure 2 as conservative, in line with remarks of several authors, namely of Grattan Bellew 83, 97 [16, 17], who proposed to lower the limit in standard ASTM C 33 nearly 4 fold, close to the value in the test ASTM C 1293.

The test comparison procedure displayed in figure 2 doesn´t apply directly to more complex tests, where bars after hardening cure at two temperatures, e.g., the microbar test (AFNOR P18-588 [53]), with an intermediate cure at 100ºC before autoclaving at 150ºC.

Besides a favourable comparison found, the present knowledge only allows approximate estimates, so that results obtained must be considered preliminary, being necessary to include ill or not quantified effects of factors of known relevance like leaching, size distribution and bar size, and to quantify better the effects of the factors considered, alkalinity and humidity.

6.2 Comparison of reference test data with several types of aggregates

Independently of an apparent consistency between rates matching reactivity criteria, *identical behaviour should be observed for the expansion of real aggregates critically or quasi reactive, if determined in the same tests*.

Data were taken from three tests (NF P18-590, ASTM C 1260 and ASTM C 227), already carried out in LNEC [13], and covering types of aggregates with varying reactive properties (5 sands, 5 limestone's, 4 granites, 2 quartzite's and one schist); in test ASTM C 227, a cement with 0.9% Na_2O_{eq} was used, but no other alterations were made to this reference test.

Figure 3 depicts that behaviour for the 5 sands, the same considered in figure 1, being essentially identical to the displayed by the limestones, quartzites and schist tested (two very non reactive limestones had completely misaligned plots, attributed to the larger influence of experimental errors in determining very low rates of reaction). As for granites tested, ASTM C 227 test yields a lower equivalent time than the corresponding to the present model, may be due to the longer duration of the test and consequent heavier leaching effects.
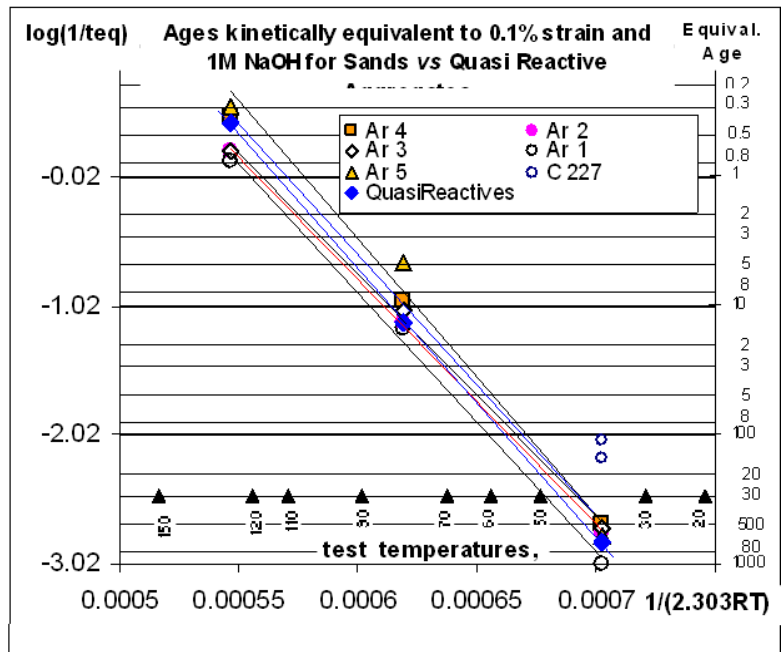

Figure 3: Arrhenius plot of the inverse of equivalent times form data of expansion tests NF P18-590, ASTM C 1260 and ASTM C 227 on sand aggregates of varying reactivity (same as in Figure 1). AR 5 is clearly reactive. Others are quasi reactive, near the threshold line. The regression lines and their correlation coefficients are listed in Table 3.

For easier comparison the line regression and correlation coefficients are listed in table 3

Table 3. Regression lines of Arrhenius plots (figure 3) of the inverse of equivalent times, transformed from data of tests for several types of sands

Data source	Regression line of 1/teq *	R^2
Tests	= -20799x+11.751	0.9999
AR1	= -19974x+11.067	0.9966
AR2	= -18932x+10.541	0.9995
AR3	= -18672x+10.421	0.9978
AR4	= -20223x+11.508	0.9997
AR5	= -21400x+12.34	0.9861

* $x = 1/(2.303\ R\ T)$

It is then possible to conclude that:

- the kinetic relation between the results of the tests *is similar* to the obtained before, for the tests, at least for a range of reactivity *near the quasi reactive* (and in some cases even out of it); in this range the expansion is nearly linear with time, as assumed initially ;

- the alignment obtained are in general almost parallel to the obtained for the criteria (aspect to look in closer detail, and relate to its cause);

- the position in the plot of the results of ASTM C 227 test, modified in contents of alkali as mentioned, coincides with the position foreseen by ASTM C 1293 test, corrected for leaching (expected, as the Arrhenius plot applies to rates of reaction, and is in line with earlier suggestion to reduce the limit of expansion).

7   CONCLUSIONS AND RECOMMENDATIONS

The paper shows that kinetic consistency may exist for the criteria adopted in ASTM C 1293, ASTM C 1260 and NF P 18-590 tests and for aggregates with reactivity near the critical.

The approach in these conditions assumes a constant rate of expansion and represents the effect of main factors (alkalinity, humidity, temperature) by models found in the literature.

The kinetic consistency was observed by a linear Arrhenius plot of the critical rates of expansion defined by the standards for several temperatures, correcting the effect of other factors to the same base of prefixed standard conditions.

A similar alignment in Arrhenius plot was tried for expansion rates with available data [13] using ASTM C 227, ASTM C 1260 and NF P 18-590 reference tests for different types of aggregates: 5 sands, 5 limestones, 2 quartzites and one schist. It was observed a rate of expansion nearly linear for marginally reactive aggregates, particularly if considering only data above 0.02 % de expansion. The regression lines determined for each aggregate yields a slope (apparent energy of activation) similar to the one found for critical rates of expansion defined by the standards. The reason for this similarity is not clear.

Also on the same basis, data of 4 granites [13] were compared. For these, the ASTM C 227 test has an equivalent time slightly misaligned with the other two tests, these displaying the same, general slope. This might result from a longer duration effect of alkali release, known to occur in these aggregates.

For the less reactive limestones, the relative error in measuring strain is too high, and the present procedure has no meaning.

This approach tests somehow the validity of the different equations used and their limits of application, suggesting possible improvements; on the other hand, if assumed as correct, it might be used for comparison with other aggregates, other tests, and suggest critical conditions for tests at other temperatures and conditions.

The proposed, tentative approach has weak points for criteria comparison, mainly a large number of assumptions and their lack of accuracy, that could not be avoided in dealing with a complex transformation with simultaneous action of several factors, based essentially on published data from other papers and very crude, approximated models, e.g., for linearity of expansion, relating alkalinity with content of alkalis and the effect of leaching.

However, the representation of data from experimental expansion tests on aggregates, linear in most cases, lead to slopes practically equal to the obtained in the Arrhenius plot of the critical rates of strain, and they depend in less models and assumptions.

The quality of the assumptions and the models should be improved in many aspects, by

i) extending of the comparison to other reference tests based on linear dilatation, mainly at other temperatures, and data from more aggregates, from other sources and methods,

ii) improvement of all models used, in special those of

variation of alkalinity due to leaching,

variation of alkalinity due to the reactions,

effects of humidity.

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