Application of the kinetic analysis in the accelerated test of alkali-silica reaction in aggregates for concrete

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Abstract: The kinetic analysis of the expansion according to RILEM AAR-2 in the accelerated mortar bar test (AMBT) is presented up to 14 days of immersion in the aggressive solution NaOH for the evaluation of the alkali-silica reaction potential of the aggregates for concrete.

The kinetic parameters L_{nk} and M were good indicators of the magnitude and evolution of the expansion with the test age. Therefore, the interpretation of the test AMBT is improved with the use of both parameters.

The model allows the expansion estimation at ages older than 14 days, in this case at 21 and 28 days of immersion. However, the error in the estimation should be considered.

Keywords: Alkali-Silica Reaction. Accelerated Mortar Bar Test. Kinetic Analysis.

1. Introduction

The alkali-silica reaction (RAS) is an internal reaction in concrete that occurs between certain minerals of aggregates (opal, chalcedony, quartz, tridymite, cristobalite, chert and volcanic glass) considered “reactive” and the alkalis (sodium and potassium ions) provided mainly from Portland cement. An alkaline medium is necessary for the reaction to be developed, which is commonly found in the solution in concrete porosity. A consequence of this and in presence of moisture, the reaction products expand, causing cracking and reducing significantly the service life of the affected structure. In addition, the reaction products can cause leaching stains on concrete surface [1].

For this reason, great efforts have been made to develop test methods to evaluate the aggregate reactivity and the deleterious degree of the reaction. Nowadays there are several internationally recognized standardized tests, such as the accelerated mortar bar test [2] [3] [4] [5], the semi-accelerated concrete prism test [6] [1] and long-term concrete prism test (with a duration of one year or more) [7] [6]. The criteria to define the reactivity of the aggregate arises from the expansion obtained after the mortar or concrete bars have been submitted in an aggressive environment for a predetermined period of time.

Although the accelerated mortar bar test (AMBT) has the advantage that the results are obtained in a short term (16 days after the bars are fabricated), it has some limitations. On one hand, an aggregate which was considered reactive in the accelerated test, it could not be reactive in service. On the other hand, in the case of certain types of aggregates that are considered of “slow reaction”, the interpretation of the expansion test - after 14 days of immersion in the aggressive solution – has been questioned. From the existing tests, the long-term concrete prism test is the one that best represents the behaviour of the aggregate in service [8]. However, due to the time that takes the accelerated mortar bar test, it is still largely used for characterizing aggregates in terms of their potential reactivity.

Recently, the RILEM Technical Committee 219-ACS worked on the development of different laboratory test methods for the evaluation of RAS and on the specifications to minimize the damage caused in hydraulic concrete structures. The recommendations included a new method for the interpretation of the result of the AMBT based on the kinetic analysis of the expansion evolution within the test time [1]. Johnston y Fournier [9] were the first to introduce this interpretation method, applying the mathematical model known as Kolmogorov-Avrami-Mehl-Johnson (abbreviated Model KAMJ).

The expansion presents a sigmoid behaviour function called “s-shaped curve” that depends on the test moment. At the beginning there is a significant increase of the expansion in a short time, but after passing through an inflexion point, it decreases progressively towards an asymptotic value [10]. The mathematical model of KAMJ describes the nucleation and the reaction growth kinetics and the transformation phase in the asymptotic stage of the reaction. In this model the percentage of expansion E_t is exponentially related with time t (in days) as shown in the Eq.1:

$$E_t (\%) = 1 + E_{t1} (\%) - e^{-k(t-t_1)^M} \quad (1)$$

Where E_{t1} is the degree of reaction in time t_1 (in days) when the nucleation and growth become dominant and k a constant associated with the reaction rate that combines the effects of nucleation, multidimensional growth, reaction products geometry and diffusion. M is an exponential term related with the growth and shape of the nucleation. This model can be applied to the development of the expansion both in mortar bars and in concrete prisms [9] [10] [11].

From the expansion results up to 14 days of immersion in the AMBT and considering the kinetic criterion for the interpretation of the results indicated by the RILEM recommendation, the $\ln k$ and M coefficients were calculated for 21 aggregate samples. These coefficients allow to define the criteria of reactivity in future works.

For the aggregates presenting an intermediate expansion after 14 days of immersion in the AMBT, the test standard indicates to continue up to 28 days. The aim of the work was to evaluate the accuracy of the model to predict the expansion at 21 and 28 days adopting the coefficients of the kinetic model calculated up to 14 days of immersion. To do this, the prediction results of the model were compared with the experimental data of expansion obtained at both ages. The error of the estimation was calculated.

2. Materials and Methodology

2.1 Materials

A Normal Portland Cement - identified as CPN by the standard UNIT 20 [13] - was used to produce the mortars. This cement is for general use in concrete and contains only clinker as the main component, without additions. The samples used have an equivalent alkali content ($\text{Na}_2\text{O}_{\text{eq}}$) between 1.16% to 1.29%, an average autoclave expansion of 0.11% and a specific surface (Blaine) of 330 m^2/kg .

Different types of aggregates were used on this study, all of them considered suitable for concrete according to standard UNIT 1050 [12]. A total of 21 samples were tested: 13 coarse aggregates and 8 fine aggregates. Table 1 shows the identification of each sample, origin, summary description, and reactivity according the AMBT test [3].

Except the samples N° 8, N° 9 and N° 10, the coarse aggregate considered were crushed stone – material that proceeds from a crushing process carried out in the extraction place to obtain a particle size suitable for concrete - and all sands were from natural origins except samples N° 14 and N° 15.

The criterion for defining “coarse sand” and “fine sand” arises from its particle distribution. Coarse sands present large particle size, in Uruguay generally the highest proportion in these is retained in the sieves of greater aperture (between 2.36 mm and 0.30 mm). The fine sands usually present particle size between 0.30 mm and 0.15mm. Both types of fine aggregates must be mixed to form a particle distribution suitable to be used in concrete.

Table 1: Characteristics of the aggregates used for the analysis.

Sample N°	Sample Id.	Type of aggregate	Origin	Summary description	Expansion at 14 days (IRAM 1674)
1	2PPM 2	Coarse aggregate	Minas, Laballeja	Crushed stone. Quartzite	0.4252
2	2PPM 1	Coarse aggregate	Ruta 5 Km 480, Tacuarembó	Crushed stone. Volcanic rocks	0.3581
3	2PPD 3	Coarse aggregate			0.2992
4	MCHA 1	Coarse aggregate			0.2748
5	MCHA 2	Coarse aggregate	Minas de Corrales, Rivera.	Crushed stone. Gabbro rock	0.3079
6	NHA 1	Coarse aggregate			0.0629
7	NHA 3	Coarse aggregate			0.0901
8	1PR48 1	Coarse aggregate	Melilla, Canelones	Natural stone. Granite rock	0.0239
9	1PR48 2	Coarse aggregate			0.0269
10	2PR48 1	Coarse aggregate			0.0292
11	1PPCP 1	Coarse aggregate	Cerro Méndez, Treinta y Tres	Crushed stone. Limestone rock	0.0169
12	CMG 1	Coarse aggregate			0.0852
13	CMG 2	Coarse aggregate	Carrasco, Montevideo.	Crushed stone. Granite rock	0.0757
14	CMF 1	Fine aggregate.			0.0743
15	CMF 2	Fine aggregate.			0.1004
16	2AGC 1	Fine aggregate (Coarse sand)	Aguas Corrientes, Canelones.	Natural sand. Quartz-Feldspatic sand	0.1335
17	2AGC 2	Fine aggregate (Coarse sand)			0.1228
18	1AGPP 1	Fine aggregate (Fine sand)	Paso Pache, Canelones.	Natural sand. Quartz sand.	0.1489
19	1AGPP 2	Fine aggregate (Fine sand)			0.1453
20	3AFT 1	Fine aggregate (Fine sand)	Delta del Tigre, San José	Natural sand. Quartz-Feldspatic sand.	0.0677
21	AFT 1	Fine aggregate (Fine sand)			0.0639

For the AMBT test the coarse aggregate had to be crushed to obtain the required standard sizes [2] and the fine aggregate was used in their natural size. In all cases, a size smaller than 4.75 mm was used and the particles passing the sieve 0.15 were discarded. The size distribution for each type of aggregate is shown in Table 2.

Table 2: Aggregate size distribution for the AMBT test.

Type of aggregate	Sieve (mm)				
	2.36	1.18	0.60	0.30	0.15
Coarse	10 %	25 %	25 %	25 %	15 %
Coarse Sand	10 %	25 %	25 %	40 %	-
Fine Sand	-	-	-	85 %	15 %

For the record of the bars length a vertical comparator of 15mm of maximum displacement and a 300 mm reference bar were used. All the bars were from 25x25x285 (mm x mm x mm) with nominal length of 250 mm. Three bars were casted for each mortar.

2.1 Methodology

The initial length (L_{t0}), the length at intermediate test times L_{ti} and the length at the end of the immersion period were recorded for each bar during 28 days of immersion in the aggressive solution of 1N NaOH at 80°C (AMBT methodology test in the IRAM 1674 standard) [3].

The expansion of each bar to certain immersion age E_t was calculated as the difference between length at that age L_{ti} and the initial length L_{t0} . This was referred to the nominal length of the bar L_n (250mm) in percentage according to Eq.2.

$$E_t (\%) = 100 * (L_{ti} - L_{t0}) / L_n \quad (2)$$

The result of an aggregate sample expansion is calculated as the average expansion of three bars tested. The coefficient of variation per sample was calculated to verify the accuracy of measurements of the different bars, according to the limits indicated by the ASTM C1260 [2].

To analyze the reaction evolution depending on the immersion time t , the growth curve of the expansion relative to the expansion E_{14} (%) and the kinetic analysis were determined applying the mathematical model, according the RILEM recommendations [1]. Doing a variable change by applying the double natural logarithm on both sides of the Eq.1, a lineal behavior model in the variables y and x was obtained according to Eq.4 and Eq.5.

$$y = M * x + \ln k \quad (3)$$

Where:

$$y = \ln\left(\ln\left(\frac{1}{1+E_{t1}-E_t}\right)\right) \quad (4)$$

$$x = \ln(t - t_1) \quad (5)$$

A linear adjustment of the model to the experimental data was carried out and the kinetic parameter M and $\ln k$ of the Eq.3 were obtained. For the coefficients calculation the expansion up to 14 days was adopted (the coefficients were identified as M_{14} and $\ln k_{14}$).

The induction time t_1 was adopted as the first intermediate recording (3 days) taken during the 28 days of immersion.

The kinetic model error was calculated at 21 days and 28 days. This was estimated as the absolute relative difference (in percentage) between the calculated expansion ($E_{ti\text{ cal}}$) and the experimental expansion at 21 and 28 days according to the Eq.6.

$$errorE(ti) = \frac{abs(E_{ti\text{ cal}} - E_{ti\text{ exp}})}{E_{ti\text{ exp}}} \times 100 \quad (6)$$

Where $errorE(ti)$ is the estimated error, ($E_{ti\text{ cal}}$) the percentage referred to experimental expansion ($E_{ti\text{ exp}}$). ti is the time at 21 days and 28 days.

3. Results

3.1 Expansion evolution

The average of the expansion of three bars immersed in the aggressive solution was calculated (according to Eq.2). Figure 3.1 shows the results for 28 days of immersion. For a better visualization of the results, the tests graphics were identified with colors according to the standard reactivity criterion (IRAM 1674) for the expansion at 14 days of immersion E_{14} ($E_{14} > 0.2\%$: red; $0.1\% < E_{14} < 0.2\%$: orange, $E_{14} < 0.1\%$: green).

Figure 3.1: Expansion graphs up to 28 days of immersion in NaOH.

The evolution of the expansion E14 is represented on graphics of Figure 3.2.

Figure 3.2: Expansion evolution graphics relative to E14.

The samples with $E_{14} > 0.2\%$ presented an expansion between 20% and 90% greater at 28 days than at 14 days. A different evolution of the expansion was observed among them: 2PPD3 presented a faster growth than the rest of the samples (after 14 days and up to 28 days there was an increase of only 20%), the 2PPM1, 2PPM2 and MCHA1 presented the slower growth and less asymptotic behavior (after 14 days and up to 28 days there was an increase between 66 % y 90%).

The samples with E_{14} between 0.1 % and 0.2 % presented similar behavior of the expansion. After 14 days there was a growth of approximately 60% for all the samples. The samples with $E_{14} < 0.1\%$ for 28 days presented an expansion from 55% and up to 154% higher than the expansion at 14 days.

3.2 Application of the kinetic model

The kinetic model coefficients (Lnk and M according Eq.3) determined by the change of variables y and x (Eq.4 and Eq.5) were adjusted by the least square technique to the experimental data (graph in Figure 3.3). The calculation of the coefficients - identified as Lnk14d and M14d - was made with the expansion up to 14 days.

Figure 3.3. Model kinetic graph for the samples with expansion up to 14 days.

The variable “ y ” values are negative. It is observed that “ y ” increased with the test age. For each sample only three results were used for the adjustment (at 7 days, 10 days and 14 days) (in all the cases the model presented an $R^2 > 0,92$). The value at 3 days was the induction time (t_1).

For the test age t a greater expansion result corresponds to a greater difference $E_{t1} - E_t$ and consequently a greater value of the variable y . This is the reason why the lineal regression model “moves towards the axis of the abscissa” when the expansion is greater.

Figure 3.4 shows the scattergram and summarizes the statistical parameters of the coefficient M14 and Lnk14. The coefficient M presented values closed to 1. Samples with $E_{14} > 0.2\%$ and $0.1\% < E_{14} < 0.2\%$ presented M values with a smaller scatter than samples with $E_{14} < 0.1\%$ (range of 0.245, 0.200 and 0.650). This shows the greatest variation in the growth of the expansion presented up to 28 days of immersion in the samples with $E_{14} < 0.1\%$ (Figure 3.2).

Lnk presented values between -6.783 and -3.022 (Figure 3.4). The samples with $E_{14} > 0.2\%$ presented the highest values, the samples with $0.1\% < E_{14} < 0.2\%$ and some of the samples with $E_{14} < 0.1\%$ presented intermediate values. The samples with $E_{14} < 0.1\%$ showed the highest scatter (a range of 2.547 against 0.891 and 1.305 for the other two cases).

Figure 3.4: Scattergram and statistical parameters of the coefficients M14 and Lnk14.

Analyzing together the evolution of the reaction and the parameter arising from the application of the kinetic model it could be observed that the M coefficient is associated with the growth of the reaction. The aggregates with the fastest reaction growth presented a lower value of M.

The Lnk coefficient (interception of the line with the ordinate axis) not only depends on the relative growth of the expansion at different test times, but also on the magnitude of the expansion.

Previous researchers [11] [14] concluded that higher values of Lnk and lower values of M indicated high reactivity aggregates. Higher values of Lnk are associated with high expansion values and therefore considered expansive. However, for lower values of Lnk the aggregate reactivity degree will depend on the parameter M. Lower values of Lnk together with lower values of M (more asymptotic behavior) indicate a better aggregate behavior.

Both kinetic parameters (M vs Lnk) were graphed allowing a better visualization of their behavior (Figure 3.5). On the same graph coefficients from the literature are presented identifying reactivity zones according to field experience [11] [14]. As a general trend it could be observed that the coefficients that arise from the experimental data showed similar values to some of those reported in the literature which allowed to reinforce (or extend) the field experience analysis reported.

Figure 3.5: Graph M_{14} vs $\ln k_{14}$. Experimental and literature data.

3.3 Error of the expansion estimation at 21 and 28 days

The expansions at 21 and 28 days were calculated adopting the kinetic model. Then the error in the estimation (errorEti) at 21 and 28 days was calculated according to Eq.6. In Figure 3.4 it can be observed the scattergram and the summary of the statistical parameters of the error.

Summary of error E21d				Summary of error E28d			
error E21d	E14>0,2 %	0,1%>E14>0,2%	E14<0,1%	error E28d	E14>0,2%	0,1%>E14>0,2%	E14<0,1%
Sample size	5	5	11	Sample size	5	5	11
Minimum	6,295	7,936	0,036	Minimum	12,391	8,878	2,264
Maximum	19,944	12,554	15,874	Maximum	35,051	24,649	30,764
Range	13,649	4,619	15,838	Range	22,660	15,771	28,500
Median	10,436	10,101	9,228	Median	16,045	15,377	17,514
Mean	11,843	10,047	8,156	Mean	19,080	16,334	16,887
3rd Quartile	14,163	11,521	11,710	3rd Quartile	17,466	17,389	22,625

Figure 3.4. Scattergram and statistical parameters of the error E21d and error E28d.

The average estimation error at 21 days was close to 10%. The samples with $0.1\% < E_{14} < 0.2\%$ presented the lowest scatter (a range of 4.619 against 13.649 for the samples with $E > 0.2\%$ and 15.838 for the samples with $E_{14} < 0.1\%$).

The average estimation error at 28 days was close to 17%. The samples with $0.1\% < E_{14} < 0.2\%$ presented the lowest scatter (a range of 15.771 against 22.660 for the samples with $E > 0.2\%$ and 28.500 for the samples with $E_{14} < 0.1\%$).

It should be considered that the age of 21 and 28 days are out of the age range used to determine the kinetic model (between 3 and 14 days).

4. Conclusions

The evolution of the expansion up to 14 days of immersion in the accelerated mortar bar test (AMBT) for the study of RAS has been correlated with the mathematical model recommended by the RILEM Technical Committee 219-ACS. The kinetic model determined by least squares adjustment to the expansion experimental data was calculated using ages of 3 to 14 days of bars immersion in the NaOH aggressive solution.

The kinetic parameters L_{nk} and M were good indicators of the magnitude and evolution of the expansion with the test age. Therefore, the interpretation of the test AMBT with the use of both parameters was improved. However, to be able to define a limit value for the coefficients, it is necessary to establish a correlation with the concrete prisms of long duration (1 year or more) or aggregate behavior field experience.

The model allowed the expansion estimation at 21 and 28 days. Therefore, when the kinetic model is applied it will not be necessary to continue the AMBT test beyond the 14 days. The error in the estimation should be considered: close to 10% at 21 days and 17% at 28 days (in the samples tested).

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6. References

- [1] Nixon, P y Sims, I. (2016), RILEM Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures, State-of-the-Art. *Report of the RILEM Technical Committee 219-ACS*.
- [2] ASTM C1260 (2014), Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method), *ASTM International*, West Conshohocken, PA, 2014, www.astm.org.
- [3] IRAM 1674 (1997), Agregados. Determinación de la Reactividad Alcalina Potencial Método Acelerado de la Barra de Mortero, *Instituto Argentino de Normalización y Certificación*, Argentina.
- [4] NBR 15577-4 (2009), Agregados – Reatividade álcali-agregado. Parte 4: Determinação de expansão em barras de argamassa pelo método acelerado. *Associação Brasileira de Normas Técnicas*, Brasil.
- [5] AENOR UNE 146508 EX (1999), Ensayos de áridos. Determinación de la reactividad potencial álcali-sílice y álcali-silicato de los áridos. Método acelerado en probetas de mortero. *Asociación Española de Normalización y Certificación*, España.
- [6] IRAM 1700 (2013), Agregados. Método para la determinación del cambio de largo en prismas de hormigón, debido a la reacción álcali-agregado. *Instituto Argentino de Normalización y Certificación*, Argentina.
- [7] ASTM C1293-08b (2015), Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction, *ASTM International*, West Conshohocken, PA, 2015, www.astm.org.
- [8] Falcone D., Milanesi, C., Método acelerado del prisma de hormigón. Evaluación de la RAS con agregados de diversas regiones de la Argentina, en el *V Congreso Internacional y 19º Reunión Técnica de la AATH*, Bahía Blanca, Argentina, 2012.
- [9] Johnston, D. y Fournier, B., A kinetic-based method for interpreting accelerated mortar bar test (ASTM C1260) data, en Alkali-Aggregate Reaction, *Proceedings of the 11th International Conference*, Québec, Canada, 2000, 355–364.
- [10] Stokes, D., Concerning the Use of Expansion Data from AST Testing, en Marc-Andre Berube Symposium on Alkali-Aggregate Reactivity in Concrete, *ACI International Conference on Recent Advances in Concrete Technology*, Québec, Canada, 2006.

- [11] Johnston, D., Stokes, D., Fournier, B., Surfahl, R. Oy otros (2000), Kinetic characteristics of ASTM C1260 testing and ASR-induced concrete damge, *en 12th International Conference on Alkali-Aggregate Reaction in Concrete*, Beijung, China, 2004.
- [12] UNIT 1050 (2005), Proyecto y ejecución de estructuras de hormigón en masa o armado. *Instituto Uruguayo De Normas Técnicas*, (Montevideo, Uruguay), p. 288.
- [13] UNIT 20 (2017), Cemento pórtland para uso general. Definiciones y requisitos. *Instituto Uruguayo De Normas Técnicas*, (Montevideo, Uruguay), p. 13.
- [14] Bronstein, B., Hocking, D., Bacolod, J. Sirivivatnanon., V. (2015),The use of reaction kinetics in classifying alkali silica reactivity potential of aggregates, *in Proceddings of the concrete 2015 conference: 27th biennial national conference of the concrete institute of Australia in conjunction with the 69th RILEM week conference*, 2015, pp. 704–711. ISBN: 978-1-943847-70-9.