CHEMICAL METHOD AND VARIATIONS IN THE TEST FOR SILICEOUS ROCKS

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Abstract

The standard chemical method (ASTM C289) has advantages and disadvantages that need to be studied and improved. This paper reports on chemical tests carried out with rocks that take part in the alkali-aggregate reaction, such as granites, basalts, mica schists, quartzites as well as one mylonite. To assess the method's parameters, variations on the exposure time of the rocks were proposed for the test, from 1 to 3 and 7 days, as well as an increase in rock sieve fraction to 0.30mm-1.18mm. In order to compare the experiments, other tests were also carried out: petrographic analysis and accelerated mortar bar testing. It was observed, among other things, that behaviors like alkali release in solution might be assessed by the chemical attack of rocks. Additionally, the testing period, extended to 7 days, showed results that appear closer to mortar expansion.

Keywords: chemical method, exposure time, sieve fraction.

1 INTRODUCTION

Due to the broad diversity of rocks and their differing texture and mineral properties, it is highly unlikely that one method alone can reliably assess the potential that different aggregates have for developing the alkali-aggreate reaction (AAR)[1]. However, laboratory tests contribute to a clear understanding of the factors related to AAR development. One such example is the provision of alkalis to the concrete pore solution by certain phases occurring in rocks [2,3] and the pessimum amount of some aggregate constituents, such as volcanic glass, among others [4].

What one expects of a method that assesses the potential of rocks against the AAR is that it be quick and reliable [5]. Among the existing possibilities is the simple chemical method, developed by Mielenz *et. al* [6], and which has the advantage of being performed in up to 3 days, depending on the laboratory operator's experience.

This method, standardized by ASTM C 289 [7], has been widely and effectively used in determining the potential rocks have to react with the alkaline solution of concrete pores to form the calcium-alkali-silicate gel responsible for the expansions seen in structures affected by the AAR [1,5].

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It has fallen out of use currently for not producing reliable results for rocks that take part in the slower, alkali-silicate[1] type reaction, since the method was designed for rocks containing opal, tridymite and cristobalite, which participate in reactions known to be faster [4,8].

Due to this problem, it is useful to undertake a study on the applicability of the chemical method with rocks that react more slowly as far as the alkali-silicate reaction (ASR) is concerned. A study was thus conducted to assess the behavior of rocks undergoing a simple chemical attack and with an aggregate exposure time extended to 3 and 7 days. Another variation on the method was also performed, and while the test age was kept at 1 day, the material's grain size was increased to 0.30mm-1.18mm. For comparison purposes, petrography and accelerated expansion in mortar bars tests were also conducted.

These results can broaden the range of correlations between rocks and laboratory tests, enabling greater possibilities in the provision of more reliable diagnoses in the application of rocks for civil engineering purposes.

2 MATERIALS AND METHODS

2.1 General

Nine rocks were selected, processed by a jaw crusher and sieved to meet the fraction specified in the ASTM C 289 standard, between 0.15 and 0.30 mm, and also in a modified fraction, between 0.300mm and 1.18mm. The washing of the samples was done with the use of distilled water to avoid possible contamination of the samples by potential chemical residues in the water provided by the local public utility. The HCl used to obtain parameter R_c appeared normal at 0.049N. The NaOH solution used to attack the samples had its normality determined at 1.000N. The determination of S_c was conducted by gravimetry and the use of a precision scale of 0.0001g. The determination of R_c, by titration was ensured by the use of a grade burette with 0.01ml precision, while the indicators used were phenolphthalein and bromocresol green. All tests were conducted in the laboratory of the FURNAS Civil Engineering Technology Center.

2.2 Materials and mixture proportions

Nine aggregates were selected: 2 granites, 2 basalts, 2 mica schists, 2 quartzites and 1 mylonite. These materials originated from various Brazilian regions, and were donated for the purposes of this reactivity study.

The Portland cement used in the mortar bar accelerated expansion test was CP I, in conformity with ASTM, with no addition of any type. The materials' characterization results are shown in Tables 1 and 2. Preparation of the materials followed the standard recommended by NBR 15577-4 [9, 12]. The cement analyses results are presented in Tables 1 and 2.

2.3 Methods for assessment and analysis

General

The petrographic analyses [10,11], the mortar bar expansions [9,12] and the simple chemical test [7] were performed in conformity with the standardized methodologies. Regarding the variations to the chemical test, aggregate exposure time in the alkaline solution, set at 24 hours in the simple test, was increased to 3 and 7 days; aggregate size, set between 0.15mm and 0.30mm, was increased to the fraction between 0.30mm and 1.18mm. Apart from these changes, the rest of the procedure went by the book, as recommended by ASTM C 289 [7] for all the tests.

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[1] Reaction between alkalis and some kind of silicates presents in certain rocks as strained quartz, by tectonic process, and the filossilicates founded in slates, phylites, schists, gneiss, quartzites, among others. Generally this kind of reaction occurs slower than the alkali-sílica reaction.

Petrographic analysis

The samples were macroscopically assessed and were classified as particle´s size, as well as identified in their color and type of apparent structure. The physical-chemical properties were also characterized as very coherent, coherent, not very coherent and friable. Finally, the petrographic blade test (30µm in thickness), under a Leitz transmitted light optical microscope (Ortholux 2 – Pol BK model), was performed to classify the rock in texture, grain size, mineral composition, presence of deleterious phases, estimate of microgranular quartz content and quantity, occurrence of textures in the feldspar and of microcracking, and state of alteration.

Accelerated expansion in mortar bars

Four mortar bars measuring 25 mm x 25 mm x 285 mm were cast, to the proportion 1:2.25 (cement:aggregate) and w/c equal to 0.47. After demolding, a first reading of the length was conducted and the mortar bars were placed in water at 80°C for another 24 hours. After that, a further reference reading was performed and the bars were stored in a container with a NaOH 1N solution at 80°C, with daily readings of the bar length up to the age of 30 days.

Simple chemical method and variations

Three 25g samples with grain sizes ranging from 0.15mm to 0.30mm were each placed in a stainless steel container, to which 25ml of NaOH 1N were added. The same was done to the samples tested at 3 and 7 days of exposure to the solution. For larger grain size samples, three 25g portions were set aside, each ranging from 0.30mm to 1.18mm. A fourth stainless steel container was used as a blank test to which were added only 25ml of the same solution used in the rock samples. After sealing, the containers were immersed in a water bath at the temperature of 80°C for 24 hours (except the samples tested for 3 and 7 days, which were immersed for 72 and 168 hours, respectively). At the end of the times set, the solution in the containers was filtered and sent for R_c and S_c analyses. Great care was taken in keeping filtration time strictly the same for all the samples. R_c was determined by titration and S_c by gravimetry. The results were plotted on the graphs in Figures 1, 2 and 3, in order to define their reactive character.

3 RESULTS

Petrography

GR.1 has a solid/massive structure while in GR.2 it is foliated. Both rocks also feature strained quartz with an undulatory extinction angle higher than 30° (assessed by Dollar-Mantuani method [13]), but in GR.1 that deformation is seen in few grains (less than 5%) while in GR.2 it appears in an amount below 5% of microgranular quartz. Regarding alteration, GR.1 is slightly altered while GR.2 can be classified as a fresh rock. By the Brazilian petrographic criteria [10], GR.1 is classified as potentially innocuous, while GR.2 is potentially reactive. The general mineral composition of the two rocks is shown in Table 3.

What stands out in basalts is the intergrowth of quartz and K-feldspar in BA.7 (2%), which 15% to 30% is on microgranular form. This rock is considered slightly altered, while BA.5 was classified as fresh rock. The mineral composition of these rocks is shown in Table 4.

In the mica schists, what was noted was strained quartz with an undulatory extinction angle above 30° in QX.3 and below 15° in QX.5, which also has microgranular quartz below 5% and some carbonates throughout its foliation surface. Both rocks were classified as potentially reactive by the Brazilian criteria, and their mineral compositions are shown in Table 5.

Quartzites are very similar in their mineral properties -- fresh rocks with microgranular quartz above 15% and undulatory extinction angle above 30°. They differ in structure -- QZ.1 has a foliated structure and

QZ.2 a schist-like one. They are classified by petrography as potentially reactive, and their mineral composition appears in Table 6.

The mylonite features quartz with high levels of microgranular quartz and higher than 30° undulatory extinction angle. Intense fragmentation can be seen in the quartz and feldspar grains, and it was classified as potentially reactive. The mineral composition of this rock is shown in Table 7.

Simple chemical method and variations

Figures 1, 2, and 3 show the graphs of the chemical method with variations for each specific group of rocks: granites, basalts, mica schists, quartzites and mylonite. In view of the result in R_c for GR.1 being negative at 3 days, a change in the graph scale was required to enable the observation of the point representing the aggregate. As well, the test was double-checked and confirmed the negative result but, it would be interesting re-test this sample.

Accelerated mortar bar expansion

Figure 5 shows the results obtained through this method at the age of 30 days. The rocks classified as potentially reactive reached expansions above 0.19% at this age, which is the threshold set by the Brazilian standard [9]. Among the samples analyzed, only GR.1 was characterized as potentially innocuous.

4 DISCUSSION

The standard chemical method was not effective in identifying the reactivity of the rocks in this study, as the literature has pointed out [5, 14], with the exception of quartzites, which have been classified as deleterious. Nor did the variation in the diameter of the samples indicate results close to those obtained by the mortar bar expansion test, taken as a reference. It is noted that when ML.1 is tested with the larger fraction, it draws closer to the reactivity curve, which may be related to the inhibited dissolution of Ca^{++} type ions [14]. The reduction on particle size increase the dissolution potential of minerals, that might either enhance the quantity of Ca^{++} ions, released by some minerals in this rock, on the solution. Therefore, the conventional method could support a higher presence of Ca^{++} ions in solution, supporting either the C-S-H formation (which interfere the dissolved silica determination [14]). Whether, the increase on size particles inhibit, in certain way, the dissolution of Ca^{++} ions then, might occurs, that some S_c "non determinate" by conventional methodology (due its C-S-H precipitation) now could be considered on gravimetric results, approaching the representing point of this rock to the reactivity curve on graphic.

Generally, increased aggregate exposure time has brought results obtained from the chemical method closer to those of the accelerated mortar bar test [15]. The present study also witnessed such behavior: the aggregates came close to the reactivity region at 3 and 7 days of exposure, which is enough to determine the reactive nature of the 2 tested mica schists and of BA.5 by day 7 of the attack.

Staying with the increased time of aggregate exposure, by day 3 of the attack, GR.1 displayed a unique behavior – a reduction in R_c, lowering this variable to negative values. Researchers such as Lu *et al.* [2] have mentioned that aggregates containing the mineral K-feldspar may be contributing to an increase in alkaline ions in an already alkaline solution. By examining Table 3, one notes that GR.1 has lower content of that mineral, but with a diameter smaller than that of GR.2, which could be promote the more pronounced behavior in the GR.1 samples. It is weird considering that extending the test to 7 days this behavior has not been observed, what need to be investigated individually.

Another interesting fact is that BA.5 – which displayed the highest silica dissolution in the standard tests, and diameter variation and exposure in 7 days – was also the rock that yielded the highest expansions in the accelerated mortar bar test, when compared to BA.7. Comparing the two samples in the basalt group, the former is also the rock with the highest amount of volcanic glass (around 10%), at a proportion known for promoting the pessimum effect [4].

Rocks of the same group also showed a similar behavior, in different regions of the graph. The basalts feature high R_c and S_c; the granites, in turn, keep to a lower values of the two parameters; the mica schists stay close to the mylonite, and the quartzites display high silica dissolution even in the early ages of the test. This grouping behavior was either observed by [16] when studying the effects of clay minerals in the chemical method.

5 CONCLUSIONS

The standard chemical method did not prove satisfactory in assessing the reactive behavior of all slow-reactive aggregates tested, but it offers useful results that help to interpret the behavior of rocks in an alkaline environment. However it is not recommended using a test which did not provide reliable results in assessment of alkali-silica/silicate reaction. For example, according table 8, only two rocks had their equal potential on different tests. Still, studies of a greater number of aggregates belonging to the same type of rock are essential for the creation of specific graphs for each group, so that this methodology can continue to be used in reactivity studies that provide different curves for different types of rocks.

Among the variations tested, the increase in rock exposure time to 7 days was the one that came closer to the result obtained in the accelerated method, but further testing needs to be performed, including the concrete prism test.

Aggregates containing alkaline minerals, like K-feldspar, may contribute to increasing the alkalinity of the solution, leading to the formation of the gel responsible for concrete expansions.

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TABLE 1: Chemical characterization of the cement.

Tests	Test methods	Results (%) in mass	Limits of NBR 5733/91
Loss to ignition	NBR NM 18/04	2.86	≤ 4.5%
SiO_2	NBR NM 11-2/04	19.58	***
Al_2O_3	NBR NM 11-2/04	4.42	***
Fe_2O_3	NBR NM 11-2/04	2.41	***
CaO	NBR NM 11-2/04	61.34	≤ 6.5%
MgO	NBR NM 11-2/04	1.78	≤ 4.5%
SO_3	NBR NM 16/04	4.04	***
Na_2O (total)	NBR NM 17/04	0.21	***
K_2O (total)	NBR NM 17/04	1.01	***
Na_2O (soluble)	ASTM C 114/06	0.25	***
K_2O (soluble)	ASTM C 114/06	1.00	***
CO_2	NBR NM 20/04	2.15	≤ 3.0%
Insoluble residue	NBR NM 15/04	0.20	≤ 1.0%
Alkaline Eq. Na_2O (total) (0.658 x K_2O% + Na_2O%)		0.88	***
Alkaline Eq Na_2O (soluble) (0.658 x K_2O% + Na_2O%)		0.91	***

Source: ABCP – Brazilian Association of Portland Cement.

TABLE 2: Physical-chemical characterization of the cement.

Tests	Test methods	Results (%) in mass	Limits of NBR 5733/91
Fineness – residue in 75 um sieve (%)	NBR 11579/91	0.20	≤ 6.0%
Specific gravity (g/cm³)	NBR NM 23/01	3.09	***
Specific area (cm²/g)	NBR NM 76/98	4860	≥ 300 m²/Kg
Normal consistence water paste (%)	NBR NM 43/03	30.20	***
Start of setting (h:min)	NBR NM 65/03	0:10	≥ 1h
End of setting (h:min)	NBR NM 65/03	0:18	≤ 10h
Le Chatelier expansion - hot (mm)	NBR 11582/91	0.00	≤ 5 mm
Autoclave expansion (%)	ASTM C 151/05	0.02	***

Compressive strength (MPa) - (NBR 7215/96)

Age (days)	Test specimen no.				Average	Maximum relative deviation (%)	Limits of NBR 5733/91
	1	2	3	4			
1	26.4	27.9	26.3	26.2	26.7	4.5	≥ 14.0 MPa
3	38.6	39.3	36.6	38.8	38.3	4.4	≥ 24.0 MPa
7	42.7	40.8	43.5	43.2	42.6	4.2	≥ 34.0 MPa

Source: ABCP – Brazilian Association of Portland Cement

TABLE 3: Granite´s mineral properties.

Mineral	GR.1		GR.2	
	Quantity (%)	Size (mm)	Quantity (%)	Size (mm)
K-feldspar	40	1.2	55	2.5
plagioclase	10	1	15	0.8
quartz	30	0.3 - 1.2	25	0.2 - 2.5
biotite	10	1.5	2	0.7
muscovite	7	1.5	1	0.5
opaques	1	-	-	-
epidote and titanite	2	-	-	-
garnet, epidote, apatite, zircon	-	-	2	-

TABLE 4: Basalt´s mineral properties.

Mineral	BA.5		BA.7	
	Quantity (%)	Size (mm)	Quantity (%)	Size (mm)
plagioclase	50	0.1- 0.2	50	1
pyroxene	40	0.3 - 0.6	45	4
volcanic glass, chlorophyta, opaques	10	-	-	-
opaques	-	-	3	1
quartz and K-feldspar	-	-	2	-
volcanic glass	-	-	traces	-

TABLE 5: Mica schist´s mineral properties.

Mineral	QX.3		QX.5	
	Quantity (%)	Size (mm)	Quantity (%)	Size (mm)
quartz	50	0.1 - 1.5	40	0.01 - 0.8
biotite	25	0.4	15	0.7
garnet	15	0.4	-	-
chlorite	10	3.5	-	-
plagioclase and K-feldspar	traces	0.4	-	-
muscovite	-	-	30	0.4
pyroxene	-	-	10	0.4
opaques	-	-	5	0.4

TABLE 6: Quartzite´s mineral properties.

Mineral	QZ.1		QZ.2	
	Quantity (%)	Size (mm)	Quantity (%)	Size (mm)
quartz	90	0.01 - 0.2	90	0.01 - 0.2
muscovite	10	0.1	10	0.1
opaques	traces	-	traces	-

TABLE 7: Mylonite´s mineral properties.

Mineral	ML.1	
	Quantity (%)	Size (mm)
K-feldspar	39	0.4 - 2
plagioclase	36	0.3 - 1.5
quartz	20	0.01 - 1
biotite and muscovite	3	0.6
opaques, epidote, apatite, carbonate and zircon	2	-

TABLE 8: Summary of results of the tests applied.

Test Method	Aggregates								
	GR.1	GR.2	BA.5	BA.7	QX.3	QX.5	QZ.1	QZ.2	ML.1
Petrography	I	PD	PD	PD	PD	PD	PD	PD	PD
ABMT (ASTM C1260)	I	PD	PD	PD	PD	PD	PD	PD	PD
ASTM C289	I	I	I	I	I	I	D	D	I
Chemical attack (Ø 0,30-1,18 mm)	I	I	I	I	I	I	D	D	I
Chemical attack (3 days)	I	I	I	I	I	D	PD	D	D
Chemical attack (7 days)	I	I	PD	I	D	D	PD	D	PD

I: Innocuous;
PD: Potentially Deleterious;
D: Deleterious.

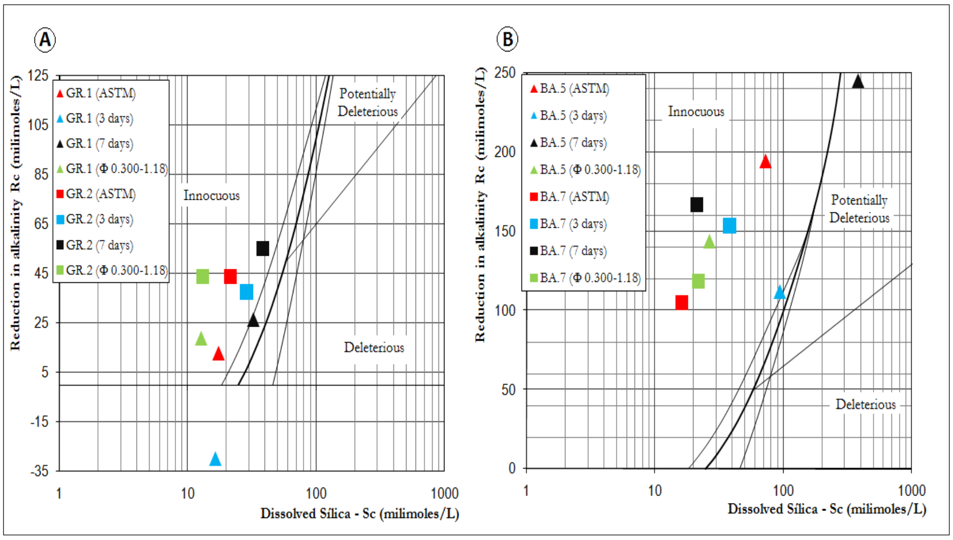

FIGURE 1 – Graphs for the simple chemical method and variations: A) Granites and B) Basalts.

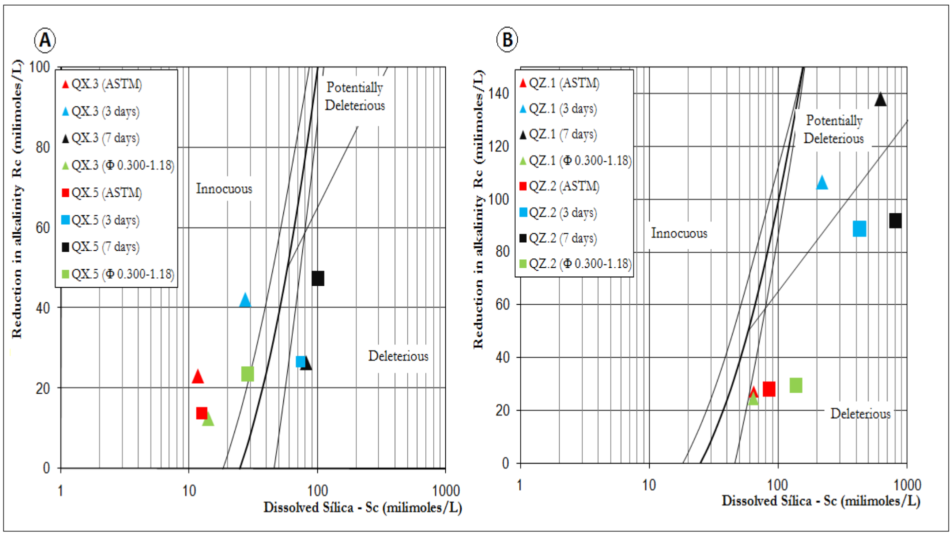

FIGURE 2 – Graphs for the simple chemical method and variations: A) Mica schists and B) Quartzites.

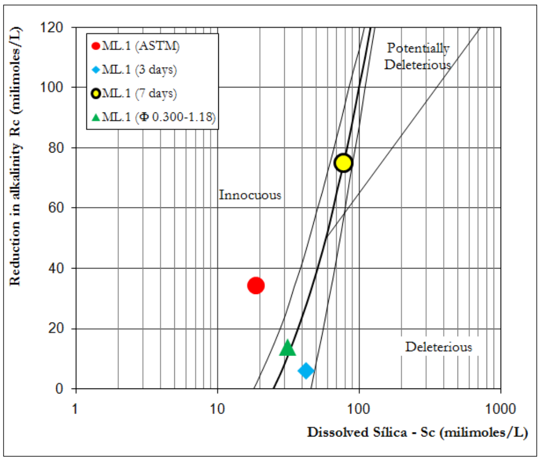

FIGURE 3 – Graph for the simple chemical method and variations for Mylonite.

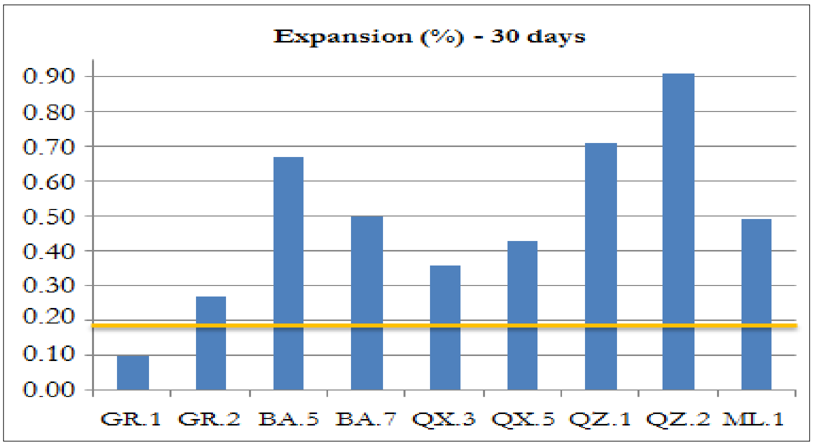

FIGURE 4 – Graph for accelerated mortar bar expansion at 30 days (%).