021811-COUT

CHEMICAL AND MINERALOGICAL BEHAVIOR OF BRAZILIANAGGREGATES IN EXPANSIVE ASR

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Abstract

Brazilian aggregates are siliceous in their majority. Those of a metamorphic nature include mylonites, gneisses and quartzites while volcanic aggregates are mostly granites and basalts. The reactive potential of several Brazilian rocks are well documented due to the large number of cases of ASR in concrete structures found in hydraulic power plants, dams, building foundations as well as bridges.

This paper presents and discusses the results of experimental research carried out in Furnas ELETROBRAS, which focused on assessing 22 different types of rocks, among them six from ASR-affected structures. The main mineralogical and textural characteristics of rocks were investigated according to ASTM C295 in order to detect the potential minerals in ASR. The chemical method was performed following ASTM C-289 procedures for all rocks. With a view of correlating mineralogical and chemical behaviors, aggregates from rocks underwent the ASTM C-1260 accelerated test method as well as ASTM C-1567, with the use of pozzolanic cement.

The 22 results were modeled while considering dissolved silica, alkalinity reduction and expansion values. A good correlation was seen and a new abacus graph was proposed for the chemical method. In addition, this abacus was compared with 91 other results from siliceous Brazilian rocks tested previously by the chemical method. It was verified that there exists compatibility among test results and the nature of the rocks. Also, pozzolanic cement proved effective in mitigating ASR for all tested Brazilian rocks.

Keywords: Chemical method, alkali-silica reaction, dissolved silica, alkalinity, expansion.

1 INTRODUCTION

Since the discovery of the Alkali-Aggregate Reaction (AAR) phenomenon by Stanton, there has been great progress in understanding this pathological manifestation. Yet, there is no consensus in the technical environment regarding an efficient and cost-effective solution to AAR.

Therefore, prevention is seen as the main means to combat AAR in an efficient and cost-effective manner. To that end, researchers have been performing an ever greater number of tests with time responses that are more efficient, faster and precise in the identification of the reactive potential of aggregates.

One of the first quick methods to assess the potential alkali-reactivity of aggregates was presented by Richard Mielenz in the late 1940s, and called the Chemical Method. It was used in several countries until the 1980s, when its results began to be questioned by the development of methods considered of greater reliability, such as the AMBT (accelerated mortar bar test), initially developed by the NBRI (National Building

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Research Institute). Since then, chemical method results started being used with reservations and solely for comparison purposes, so little was done to improve it.

This study aims to bring the chemical method to the front once again, as it attempts to model the data obtained through this method so as to correlate with accelerated expansion results in mortar bars, involving the study of 22 rock samples of varied lithotypes subsequently compared with a vast survey of 91 results of national rocks found in the literature.

2 EXPERIMENTAL PROGRAM

This experimental program is part of a broader study [1] encompassing other tests and analyses not covered in this paper.

In carrying out this study, seven samples were collected from reactive aggregates found in Brazilian construction works, mostly hydraulic structures. Yet, due to the vast impact of AAR cases in the foundations of buildings in the Metropolitan Region of Recife, Northeastern Brazil, a field innocuous aggregate from that region was also included in the study. In addition to these, a further 15 samples of aggregates were also studied, due to their potential use in each region of the Brazilian state of Goiás, where they were found already crushed in quarry storage yards. Therefore, it was not possible to set a standard for the exact location in the quarry from which the samples were collected, nor was it possible to establish the actual location and date of collection of each supplier. Table 1 shows the origin of each sample.

In order to compare the results of the Chemical Method [2], the potential alkali-reactivity of the aggregates was measured by the AMBT method [3], in addition to the mitigation of the reaction by the specific method for this case [4]. For the mortar tests, two cements available in the market of Goiânia (Brazil) were chosen: Cement A, without pozzolanic admixture and Cement B, with pozzolanic admixture of clay at 30% of content. Their characteristics are described in Table 2.

The 22 aggregates selected for this study underwent petrographic analyses [5]. These were performed on thin sections, using an optical transmitted light microscope in order to establish their constituent minerals, texture, grain size, structure and other mineralogical properties, as well as traces of minerals potentially reactive to the alkalis.

The chemical method assesses the reactive potential of a previously prepared aggregate, of a large enough size to pass through the 0.30-mm sieve and be retained in the 0.15-mm sieve. Subsequently, 25 g of this material was set aside and placed in a stainlles steel container along with 25 ml of NaOH at a concentration of 1 N for a period of 24 hours and a temperature of 80ºC. After this phase, the solution was filtered and the amount of dissolved silica (DSi) was determined as well as the alkalinity reduction (AR) of the sodium hydroxide, which was measured by titration with HCl, using phenolphthalein as an indicator.

Finally, the result was plotted on a graph featuring three areas which, following the previously set parameters, classified the aggregate as being innocuous, potentially reactive or deleterious (Figure 1).

3 RESULTS AND DISCUSSION

3.1 Chemical Method

The resulting averages (from the triplicates) of the dissolved silica (DSi) and of alkalinity reduction (AR) obtained by the chemical method for the different aggregates tested are shown in Figure 1. After the tests were performed, only samples QZ.1 and QZ.2 were considered deleterious for their reactivity to alkalis through this method. The remaining samples were classified as innocuous.

It must be highlighted that there was a visible separation in the different groups of rocks. Basalts, in general, feature high values of dissolved silica and of alkalinity reduction in relation to the others, due to the great availability of silica (mostly amorphous from glass) or of chloropheite/clay minerals in the interstitial material. At the other end of the spectrum appear the granitic rocks and the quartz schists, which stand out for presenting lower values of both dissolved silica and alkalinity reduction. The quartzites produced alkalinity reduction values of the same magnitude of the granitic rocks and the quartz schists, although dissolved silica values were higher, closer to that of the basalts. This behavior is due to their mineralogy, since quartzites contain 90% quartz as well as a high percentage of silica.

These groups of rocks are in line with the nature of minerals and their transformations in the formation of rocks. In basalts, the silica structure is generally disorganized due to its rapid solidification caused by the outpouring of magma, which explains the high dissolved silica values. However, when the solidification of magma occurs slowly, silica organizes structurally to form an atomic structure network, as in the case of granites, leading to lower dissolved silica values when compared to the basalts. And, finally, when sand sediments comprising silica minerals undergo the process of regional metamorphism, generating quartz-schist type rocks, these have silica materials that are generally more complex than those of a granitic nature, explaining the lower values of dissolved silica in all the groups. Yet, due to the subjectivity of the petrographic analysis, no direct relationship has been found between mineralogical factors that may differentiate these samples within their groups.

Figure 2 shows the average values of the results obtained for the lithotypes, along with an analysis of the variance (ANOVA) to confirm the significance of the groups observed, and Duncan's test, to sort the groups through the multiple comparison of averages. According to the analyses, the values of dissolved silica from the basalt and quartzite samples were statistically the same, as well as for the granitic rocks and the quartz-schists. As for alkalinity reduction values, the basalts appeared isolated in one group, and the granitic rocks, the quartz-schists and the quartzites in another.

3.2 AMBT

For the AMBT study with cement A (without admixture), it was considered the threshold of 0.10% for an innocuous behavior and 0.20% for reactive behavior at 16 days, anyway the behavior along 30 days was also checked; in the case of expansions between 0.10% and 0.20% at 16 days (indicating potentially reactive behavior) due to the slow reactivity of some Brazilian rocks, the limit of 0.20% at 30 days was used for a reactive behavior. For the study with pozzolanic cement (B), the limit was 0.10% at 16 days. Anyway, all tests were performed up to 30 days. Considering cement type A in Figure 3(a), for the basaltic aggregates, there is a rapid evolution in the expansions of sample BA.4, which as early as 16 days presented a highly deleterious behavior (0.62%), reaching an expansion of 0.72% at day 30 of the test. Having more modest rates of evolution, samples BA.5 and BA.7 showed expansions at 16 days between 0.10% and 0.20%, and at 30 days sample BA.7 was classified as reactive (0.28%) and BA.5 only potentially reactive (0.18%). Finally, samples BA.1, BA.2, BA.3 and BA.6 showed expansions below 0.10% at 16 days, and were thus classified as innocuous.

According to Figure 3 (b), showing the reactive potential of the granitic group of rocks, only sample ML.1 was considered reactive, and while reaching an expansion of only 0.19% at 16 days, it hits 0.28% at day 30 of the test. As for GR.2, expansions reached 0.11% and 0.19% at 16 and 30 days of the test, respectively, and were only classified as potentially reactive. The remaining samples in this group, namely GR.1, GR.3, GR.4, GR.5 and GD.1 were classified as innocuous.

Figure 3 (c) shows that all the samples of the quartz schist group featured expansions above 0.10% at 16 days, but only sample QX.2 was classified as potentially reactive for having an expansion of 0.17% at 30 days. Samples QX.1, QX.3, QX.4, QX.5 and QX.6 were classified as reactive, since their expansions at 30 days were higher than 0.20%.

Finally, the two quartzite rocks tested, QZ.1 and QZ.2, were classified as reactive, with expansion values of 0.26% and 0.37% at 16 days and 0.36% and 0.43% at 30 days, respectively, as seen in Figure 3 (d).

Grouping all the expansion results by lithotypes tested with cement A, without addition, as seen in the Figure 4, quartzites generally had higher average expansion values both for ages 16 and 30 days, followed by the basalts, the quartz-schists and the granitic rocks. However, the basalts had higher amplitudes in their standard deviations when compared to the other rocks, showing that basalts vary widely in their expansive behaviors in the AMBT. At the other end there are the quartz-schists, which showed close expansion values within the rocks comprising their respective groups, with relatively low standard deviation values.

Figures 3 (e) to (h) display the average results of the same aggregates tested with the pozzolanic cement B in order to promote the mitigation of the expansive reactions of the aggregates. It can be noted that all the aggregates have expansions significantly below 0.10% at 16 days. Cement B is, therefore, capable of mitigating the expansive reaction at levels accepted by the standard test [4].

Similarly to the analysis conducted with cement A, in the general expansion results of mortar bars incorporating the cement B, the quartz-schists were the aggregates showing the highest expansion values both for the age of 16 days as well as for that of 30 days, followed by the quartzites and granitic rocks, which had virtually the same averages, with basalts appearing last. Just like with cement A, the quartz-schists were the lithotypes with the lowest expansion amplitudes for both ages tested, unlike the others. Figure 5 records these considerations.

It was noted that pozzolanic cement (B) tested in combination with the basalts generally had a better performance than when it was combined to the other lithotypes. It is believed that a part of the available alkalis in the test had already been consumed by pozzolanic reactions due to the percentage of mineral additions in cement B, the remainder had reacted early on with the aggregate's amorphous silica, where the conditions were in place for the cementitious matrix to absorb the expansive deformations. This happens as a result of the process of formation of volcanic rocks, which takes place through the sudden crystallization of the minerals, generating a mostly amorphous vitreous matrix. Yet, it was not possible to find a quantitative correlation of the percentages solely by means of the methods employed in this study, since the degree of amorphicity of the matrix cannot be established with precision.

As for the quartz-schists, in the presence of cement B, they proved to belong to another isolated group, with relatively lower efficiency when compared to the others, nonetheless effective in fighting AAR, probably because of the presence of high percentages of strained quartz identified by petrography. By generating reactions involving silicates, which have atom structures that are more complex than those of amorphous silica (the vitreous matrix of the basalts), the reactions happen at a slower pace.

Finally, for the granitic and quartzite rock groups, the performance of cement B in fighting expansive reactions is in an intermediate position between the basalts and the quartz-schists. For the granitic rocks, this behavior can also be explained by the nature of the formation of the rocks, since these are plutonic igneous rocks (with the exception of mylonite, which is metamorphic), in which the crystallization of the minerals took place more slowly, allowing time for the total or partial formation of crystalline products. Another factor is related to the intensity of grain deformation, which was not as intense as the metamorphic process of formation of the schists, reported earlier. With regard to the quartzites, while formed by complex silica structures featuring higher quantities of strained and microgranular quartz when compared to the vitreous mass of the basalts, they are less complex than the quartz-schists.

3.3 Chemical Method x AMBT

Several papers have long been pointing out the incompatibility between the accelerated method in mortar bars and the chemical method. This study was no different. The chemical method interpreted many results as being false negatives when compared to the results produced by the AMBT.

While the chemical method has been widely used through the years in many countries, the results obtained are not always satisfactory, since the values of dissolved silica and alkalinity reduction can be affected by a number of mineralogical factors [6]. For instance, quartz solubility increases as its grain size is reduced, so that material finer than 300 μm may unduly increase the value of dissolved silica [7]. In addition to the compounds cited earlier, gypsum, clay minerals, magnesium silicates, iron oxides and organic matter will all somehow have a strong influence on the chemical results [7]. Another strong influence in the results is linked to the phenolphthalein used as indicator in titration, producing false results in the presence of carbonate ions as well as by the amount of silica in solution [8]. The reduction in alkalinity, in turn, may be underestimated due to the reactions involving the ions of certain minerals that contain sodium and potassium [7], which normally occur in many of the rocks tested.

Although the limits between the methods analyzed were discrepant, the results showed strong correlation as can be seen in Figure 6, in which test results are compared. In this figure, axis Z shows expansion values at 30 days into the test through the accelerated method of mortar bars; axis Y shows the reduction in alkalinity; finally, axis X shows the values of dissolved silica. This graph was obtained by means of a random mathematical model, in which all the terms are statistically significant and also correlate well. Figure 7 shows an abacus which is the projection of a surface curve obtained by Figure 6, so as to provide an idea of the expansion value at 30 days of any aggregate tested with the cement in this study, considering the values of dissolved silica and alkalinity reduction.

As part of this study, 91 results were collected from chemical and mortar-bar expansion tests performed with samples of Brazilian rocks [9, 10, 11, 12, 13, 14], with a view of checking the same correlation between the two tests assessed. Unfortunately, the same mathematical model did not yield a satisfactory correlation coefficient, due to the variability of the physical and chemical characteristics of the cement types used in the different studies. This situation is illustrated in the Figure 8, in which the red-circled dots were classified as potentially reactive by the interpretation of AMBT [3] at 30 days of age, and the green triangles as potentially innocuous.

However, it was noted that when a 45°[1] straight line was drawn between axis X and Y, corresponding, respectively, to the values of dissolved silica and alkalinity reduction, the results below this line with dissolved silica values below or equal to 20 mmols/l are considered potentially innocuous by the AMBT [3]. Also values below the line, but with dissolved silica results above 20 mmols/l, were considered potentially reactive. As for values above this line, nothing can be made of them, as other tests are needed to prove their reactive potential. Figure 9 shows this setting, and although this second analysis had shown a good correlation of results, the first analysis (Figure 7) presents more reliable results since the tests were performed with an ordinary Portland cement with the same clinker, and this information is not available for the other tests used in the second analysis.

4 CONCLUSIONS

The results obtained through the chemical method did not correspond to the results found through petrography and the tests conducted in mortar bars through the accelerated method; therefore, the results

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[1] It can be noted in Figure 9 that, due to the logarithmic scale in axis X, the 45°-line develops a curvature that is also logarithmic.

from the former need to be considered with caution, requiring a reassessment of test conditions so as to make it more reliable and with greater applicability.

The pozzolanic addition in cement B was efficient in mitigating expansions, regardless of the type of rock tested. It was clear that the intensity of mitigation is influenced by each rock's lithotype. Efficacy of the cement B in reducing expansion was the highest with the basalts, followed by the granitic rocks and, finally, the quartz schists, due to the presence of silicates (deformed quartz) in their constitution.

There was a statistical correlation between the values of dissolved silica and alkalinity reduction of the chemical method with the expansion values of the AMBT. However, the mathematical model could not be extended to the data collected in the literature on previous studies, greatly due to the distinct types of cement used in each study.

Nevertheless, changes in the methodology to obtain more reliable chemical method parameters are highly recommended, since several authors have highlighted the misleading effect of the test parameters determined. Subsequently, there should be a correlation with the expansion results of the concrete prism method [15] or even with expansion values obtained through instruments for longer periods in concrete blocks.

Acknowledgments

The authors wish to thank Furnas ELETROBRAS, particularly in regard to ANEEL's R&D Program, for the financial support, as well as CAPES, UFG and the FURNAS Department of Technical Support and Control for having made this research project possible.

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TABLE 1: Location of the aggregate samples analyzed

Sample	*Lithotype*	*Source*
BA.1 to BA.6	Basalt	State of Goiás
BA.7	Basalt	Antônio Moro Quarry – Ponta Grossa, PR
GD.1	Granodiorite	State of Goiás
GR.1 to GR.2	Granite	State of Goiás
GR.3	Granite	Recife, PE (potentially innocuous)
GR.4	Granite	Moxotó Hydroelectric Plant – Paulo Afonso, BA
GR.5	Granite	Compensation Reservoir Pedro Beicht – Cotia, SP
ML.1	Mylonite	Recife, PE (potentially reactive)
QX.1 to QX.6	Quartz schist	State of Goiás
QZ.1	Quartzite	Furnas Hydroelectric Plant – Alpinópolis, MG
QZ.2	Quartzite	Jaguara Hydroelectric Plant – Rifaina, SP

TABLE 2: Chemical and physical characteristics of the cement

Chemical properties						Physical properties		
Determined properties (%)	*Cement A*	*Cement B*	*Determined properties (%)*	*Cement A*	*Cement B*	*Determined properties (%)*	*Cement A*	*Cement B*
Silicon dioxide (SiO_2)	30.61	26.36	Free calcium oxide (CaO)	1.5	1.4	Specific gravity (g/cm³)	3.02	2.96
Aluminium oxide (Al_2O_3)	6.81	13.24	Loss of ignition	2.85	3.17	Blaine fineness (cm²/g)	4,820	6,290
Iron oxide (Fe_2O_3)	3.04	2.43	Insoluble residue	20.50	25.99	Residue on sieve #200 – 75 µm (%)	0.9	1.8
Calcium oxide (CaO)	47.74	44.84	Sodium oxide (Na_2O) - totals	0.41	0.62	Residue on sieve #325 – 45 µm (%)	5.5	9.0
Magnesium oxide (MgO)	4.64	4.16	Potassium oxide (K_2O) - totals	1.00	1.04	Average size of the grains (µm)	10.58	11.64
Sulphur trioxide (SO_3)	2.37	3.01	Alkaline equivalent (Na_2O_{eq})* - totals	1.06	1.30	Autoclave expansion (%)	0.1	0.1

* Na_2O_{eq} = %Na_2O + 0.658 . %K_2O

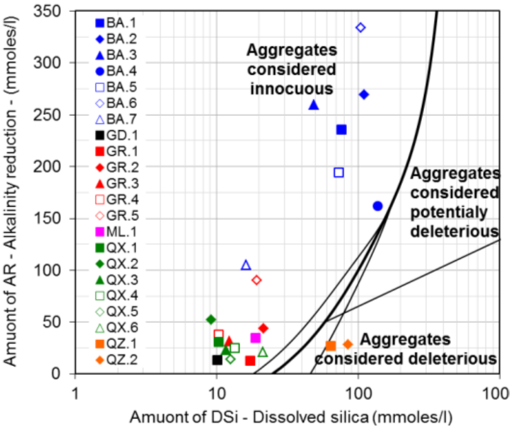

Figure 1 – Average results obtained in the chemical method.

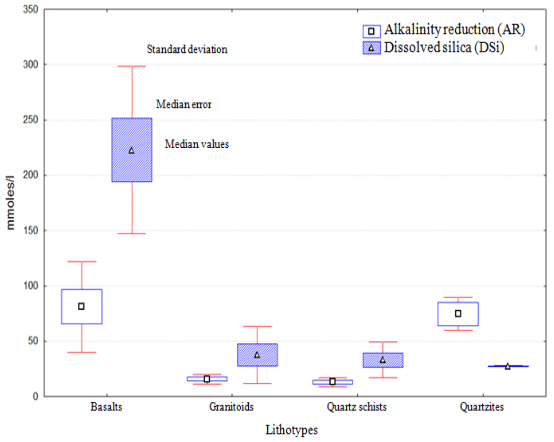

Figure 2 – Average results obtained in the chemical method according to lithotypes.

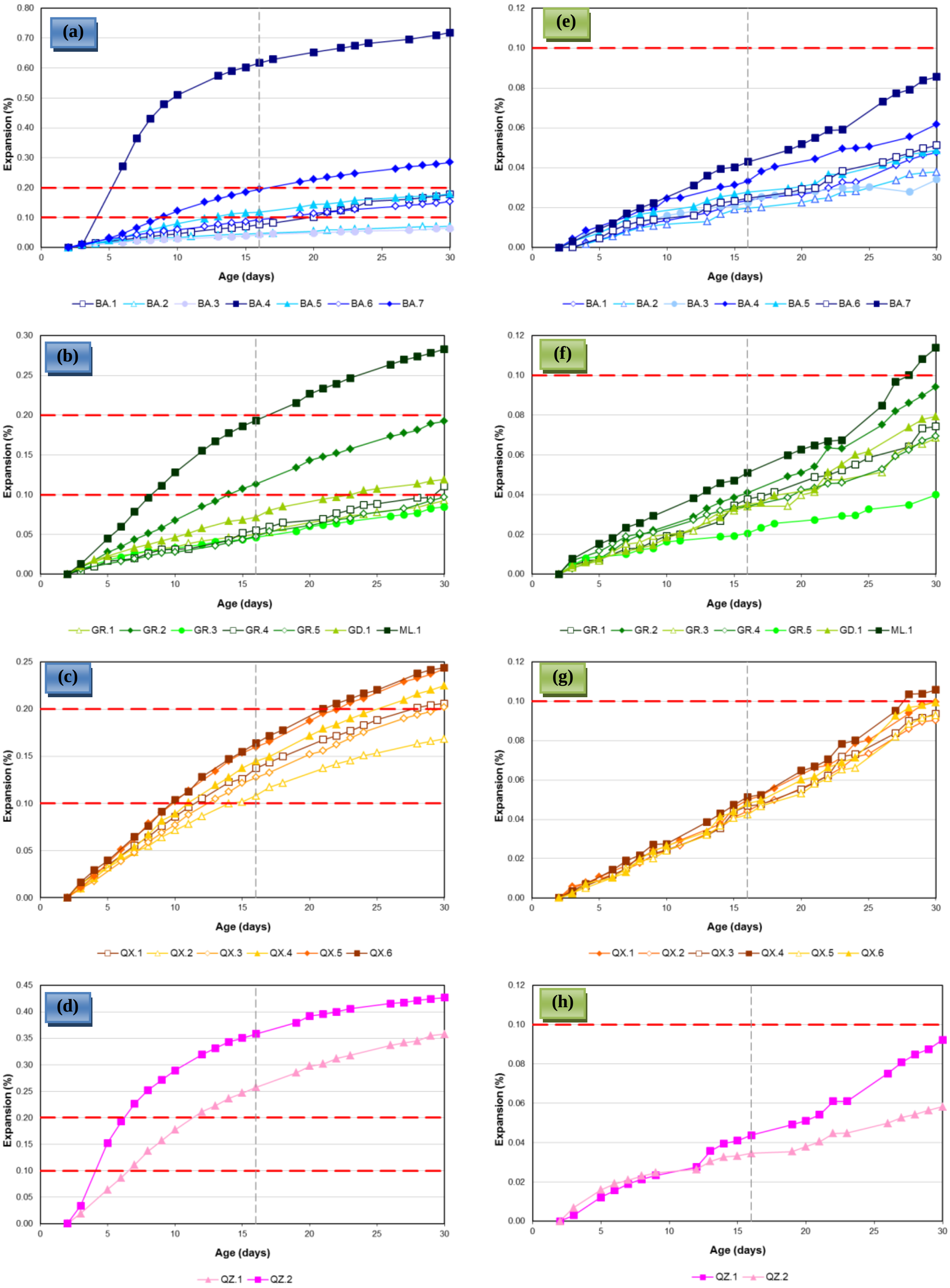

Figure 3 – Average expansions of aggregates in mortar bars: a), b), c), d) Cement A, without addition; e), f), g) h) Cement B, Pozzolanic

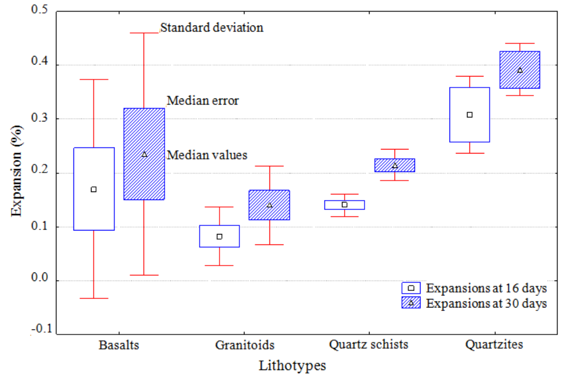

Figure 4 – Average results obtained in the accelerated method in mortar bars according to lithotypes - Cement A.

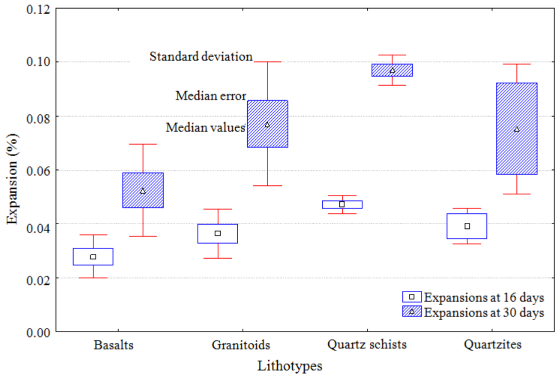

Figure 5– Average results obtained in the accelerated method in mortar bars according to lithotypes - Cement B

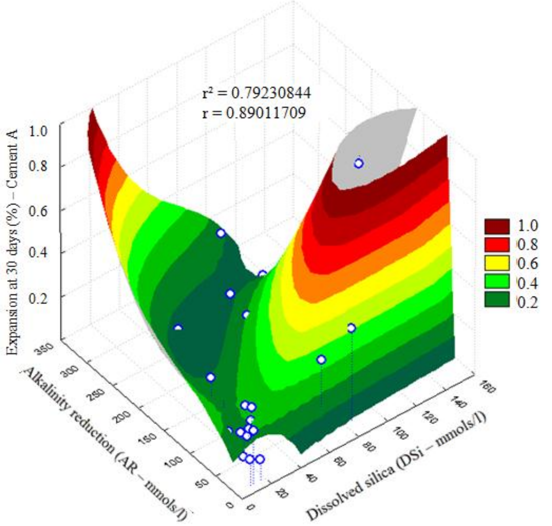

Figure 6 – Surface of correlation between test methods ASTM C-1260 x ASTM C-289 for the 22 rocks analyzed.

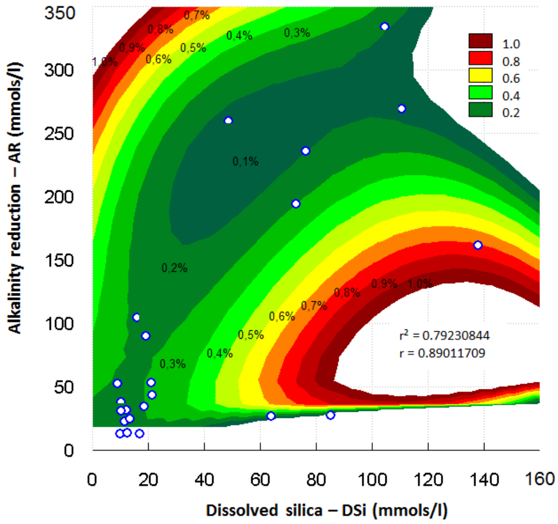

Figure 7 – Projection of correlation between test methods ASTM C-1260 x ASTM C-289 for the 22 rocks analyzed

Model used:

$$Exp(\%) = -1.50 \times 10^{-6} \times DSi^3 + 7.90 \times 10^{-8} \times AR^3 + 3.70 \times 10^{-4} \times DSi^2 - 2.80 \times 10^{-5} \times AR^2 - 0.158 \times (DSi / AR)^2 - 8.30 \times 10^{-5} \times DSi \times AR + 263.401 \times 10^{-3} \times DSi / AR - 7.59 \times 10^{-3} \times DSi + 4.595 \times 10^{-3} \times AR + 53.066 \times 10^{-3}$$

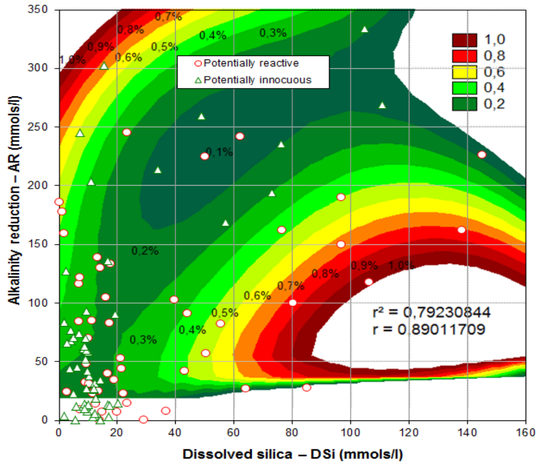

Figure 8 – Correlation between test methods ASTM C-1260 x ASTM C-289 for 91 different rocks.

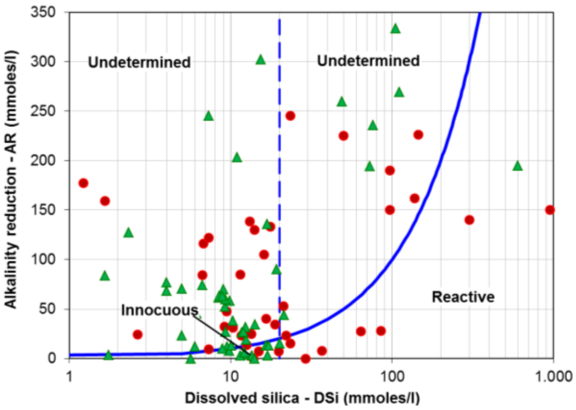

Figure 9 – Correlation between test methods ASTM C-1260 x ASTM C-289 for 91 different rocks.