ALKALI SILICA REACTION IN AGGREGATES DERIVED FROM THE VALORISATION OF WASTES FROM THE AGATE MINING

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Abstract
The state of Rio Grande do Sul is the third producer of precious stones in Brazil, which also elucidates a significant volume of wastes generated along the production of agate products. It is well known that agate is constituted mainly by quartz, which might shows susceptibility for alkali-silica reaction, if these materials are used as aggregates in concrete/mortar mixtures. Thus the objective of this study is to assess the potential development of alkali-silica reaction in mortars based on different blends agate waste. For this purpose, accelerated tests with mortar bars were performed according to NBR 15577-4 standard. The reactivity was evaluated using the standard cement indicated by NBR 15577-1 and with white Portland cement. The studies indicate that agate waste with a particle size distribution between 150 um a 4.8 mm is highly reactive. However, the inclusion of powdered agate waste reduces the deleterious effect of alkali-silica reaction and expansions higher than 0.19% were not identified.

Keywords: agate; mining waste; alkali-aggregate reaction;

1 INTRODUCTION

The alkali-silica reaction is a chemical phenomenon that involves the alkaline hydroxides released during the hydration of cement and some minerals present in the aggregates. In presence of water, the silica-rich gel formed during the chemical reaction is highly expansive with the subsequent development of cracks in the concrete.

According to Priszulnik [1], the first Brazilian report related to alkali silica reaction in concrete was published two decades later of the first known case in U.S.. Two researchers in 1963 identified the presence of reactive aggregates used in the concrete during the construction of the Jupiá dam, located between states of São Paulo and Mato Grosso do Sul in Brazil.

According to Cândido *et al* [2] prevention is the best alternative to mitigate this pathological degradation. In this sense, non-reactive aggregates, cements with low content of alkalis, mineral and/or chemical admixtures and/or admixtures based on Litio can be used.

The use powdered materials for the reduction of the alkali silica reaction has been reported by different researches, including Andriolo [3], Hasparyk [4], Sabbag [5] and Andriolo[6]. The improvements were achieved with the inclusion of up to 40% of finer particles or even the use reactive aggregate previously crushed to obtain a finer powder. However, there exist few reports related to the use of reactive powdered materials to mitigate this deleterious reaction.

Andriolo[3] assessed the use fine powder obtained from crushed rocks incorporated with a basaltic sand as a method for reducing the alkali-silica reaction. The use fine particles (or fillers) derived from the same reactive aggregate seems to block the expansive reactions as it is also observed with the pozzolanic admixtures. Hasparyk [4] highlighted that the use powdered and reactive aggregates has to be assessed in more detail, as well as the benefits related to its use for the reduction of the expansions. Castro *et al apud* Sabbag [5] identified that the partial substitution of crushing sand by pulverized arenite as fine aggregate was also effective for the reduction of the expansive reactions.

The State of Rio Grande do Sul (RS) is one of the largest exporters of Brazil gems, where the Úmbu agate is the most abundant with the 71% of the registered stockpil [7]. Hartman and Tonezer [8] reported an average production of agate and ametiste in RS of 418 t/month, where 130 t/month

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are transformed in Soledade for the production of more than 6000 finished pieces. During this processing 150 t/month of solid wastes are generated, which represents 30-40% of the mineral treated.

During the different mechanicals processing applied, three types of residues are generated, being all of them light-colored. The residue can be categorized through its particle size distribution as a powdered material, fine and coarser particles with an elongated shape. Therefore, the residues are considered an environmental issue within this mining industry. Currently, the most common disposal method is landfill.

Taking into account its light color, the sieved agate waste can be potentially used as aggregate in white Portland concrete. According to Passuelo [9] the use white cement, in white concrete, will not necessarily satisfy the requirements of color, chromaticity of the mixture of cementitious matrix depends on all of the fine materials (fine aggregates, additions and cements) involved in the process.

However, the residue generated from the agate mining and processing can exhibits a potential reactivity when is used as aggregate due the presence of strained quartz with crypto-crystalline structure [10]. Then, the use of these residues as aggregates in white Portland systems should be assessed in order to verify its technical feasibility.

This study assesses the reactivity of agate powder in alkali-aggregate reaction, for future use in white concrete. Two different residues with different particle size distribution were used in mortars produced with white and Standardized Portland cement and analyzed its potential reactivity.

2 MATERIALS AND METHODS

2.1 General

In order to achieve the objectives of this study, an experimental program focused in assessment of agate wastes as recycled aggregates in white Portland concretes was developed.

2.2 Materials and mix designs

Binders

White Portland cement (WPC) and a standardized Portland cement (SPC) from the Brazilian Association of Portland cement (ABCP) were used. The chemical compositions and the main physical properties are listed in the Table 1.

The NBR-15577-6 [11] suggests the use of a reference Portland cement with fineness of 4.600 ± 200 cm²/g, equivalent alkali content of Na_2Oeq= 0.9 ± 0.1%, and autoclave expansion of 0.20%.

Aggregates

The agate aggregates used in this study were generated in different mechanical treatments from a company located in Rio Grande do Sul State. Two residues with different particle size distribution (as is showed in Figure 1) were selected and categorized as 1. Fine agate aggregate, and 2. Agate powder. The chemical composition of the residues is based on silica (Table 2).

The Figure 3 shows that the particle size distribution of the fine agate aggregate is not adjusted according to the technical recommendations suggested by NM 248 [12]. On the other hand, the agate powder has a higher content of finer particles after the sieve of 150 μm.

Water

Deionized water was used for the production of the mortars.

Mix design

In order to assess the reactivity degree of the aggregates a standardized Portland cement (according to NBR 15577-4[13] was used. Likewise, a white Portland cement was also used due to the interest to use these aggregates in the production of white concrete.

The agate powder as replacement (0%, 15% and 30%) of the agate fine aggregate was use.

2.3 Methods for assessment and analysis

X-ray fluorescence and X-ray powder diffraction test were carried out in the residues previously sieved through # 200 mesh size.

X-ray fluorescence (XRF)

The chemical composition of the raw materials was determined by X-ray florescence using a spectrometer Shimadzu model XRF1800 from Laboratory of Ceramics Materials at the Federal University of Rio Grande do Sul (UFRGS).

X-ray powder diffraction (XRD)

The analysis was carried out in a diffractometer Philips X`Pert MPD with a ceramic tube PW 3373/00, detector model PW 3011/10 and a cathodic tube o Cu CuKa (l = 1.5418 Å) with a step size of 0.05º. The crystalline phases were identified through the software X´Pert High Score, comparing the location of the main peaks observed and the database of the Powder Diffraction Files (PDF).

Granulometry.

The particle size distribution of the fine aggregates was determined manually following the procedure suggested by the NBR NM 248 [12] and using the standard series of sieves.

Pozzolanic activity index

To be considered a pozzolan, the material has to present chemical and physical reaction as required by the NBR 12653[14].

To check if the agata powder presents any pozzolanic activity, tests recommended by NBR 5751[15], and NBR 5752 [16]were conducted. They are based on the strength activity index. In test method proposed by NBR 5751[15], the 7 d compressive strengths of a mortar prepared with a lime:pozzolan:aggregate of 1:2:9 (mass basis) are compared to those of a control mortar. While the control mortar is prepared with a slump of 225± 5mm.

In test method proposed by NBR 5752 [16], the 28 d compressive strengths of a mortar prepared with a 25% agate substitution for cement, on a mass basis are compared to those of a control mortar. While the control mortar is prepared with a water-to-cement ratio by mass (w/c) of 0.48, the additive content of the test mixture is adjusted to provide an equivalent flow to that measured for the control.

Tests conducted

Alkali aggregate reaction (AAR) was assessed in mortars bars following the protocol suggested by the NBR 15577-4 [13]. The mortars were produced with a cement:aggregate ratio of 1:2.25 and water/cement ratio of 0.47. The workability of the fresh mortars was adjusted through the use a superplasticizer in order to achieve a slump of 210±10 mm. Prismatic samples of 25x25x280 mm were produced as is shown in Figure 4. The samples were demolded after 24 h and the first measurement was immediately registered and used as a reference value. Subsequently the samples were immersed in an alkaline solution of sodium hydroxide at 80 ºC during 30 days (Figure 4). After 16 and 30 days the samples were extracted from the alkaline solution, immersed in water during 24 h and three measurements were registered. Over this period six intermediate measurements were also registered in the mortar samples according to the recommendations suggested by NBR 15577-4 [13].

The AAR is a reaction that can not be contained after it started. It is necessary to use measures to prevent their onset. The NBR 15577-5 [17] provides mitigation options to minimize the risk of expansion. To verify the reactive potential of an aggregate, the standard classifies the reactivity on 4 levels and each level proposes mitigation measures (Table 3).

3 RESULTS AND DISCUSSION

Table 4 shows the results obtained in the pozzolanic index tests of the agate powder with lime and also with Portland cement. In the first test 3 specimens (cp's) were tested and for the second test 4 cp's were tested. The mortars tested were in absence and in presence of the agate powder replacement. To be considered a pozzolan, the material, has to present chemical and physical reaction as required by the NBR 12653[14]. This standard establishes that a pozzolanic material shall has pozzolanic activity index with lime at 7 days when presenting strength ≥ 6 MPa, and a strength index of performance with Portland cement at 28 days, relative to ≥ 90% of the strength of the control sample. Table 4 shows that the average strength obtained was 5.10 MPa, and the pozzolanic index was 83% of the strength of the control sample, classifying the material as not pozzolanic. However, one must take into consideration, the results obtained in the two tests were very close to the minimum set by these NBR. Also it is noteworthy that the NBR 12653[14] was recently updated and the pozzolanicity index requirements have changed, comparing the result with what was required by the

NBR 12653:2012[14], the pozzolanic activity index was at least 75%, then the agate powder would be considered a pozzolanic material.

Figure 5 shows that mortars produced with the fine agate aggregate elucidates a reactivity categorized as 2nd degree according to the NBR 15577, which requires a moderate prevention. These results are aligned with the reports made by Dal Bello *et al* [18] and Chiaro *et al* [10]. In mortars with substitutions of 15 and 30% of fine agate aggregate (AA) by agate powder (AP), the expansions after the immersions were highly reduced. In mortars with a 15% and 30% of AP, the expansions identified were reduced up to ~66% and 92%, respectively. These results were not expected due to the higher content of a reactive material with higher specific surface (as is identified for AP). Finer materials should show a more extended formation of rich-silica gel and large expansions. The reduction of the expansions derived from the alkali silica reaction is characteristics when a pozzolanic admixture is used.

The Figure 6 shows that the fine agate aggregate in the white Portland mortars can be considered as a 3rd degree of reactive, which requires special assessment in order to reduce its susceptibility and to be used without restrictions. In the work reported by Dal Bello *et al* [18], reactivity of the fine agate aggregate was also observed. However, Chiaro et al [10] identified that the use fine agate aggregate with white Portland cement was categorized with a reactivity degree of 1. This difference between the results can be attributed to the differences between the batches of white Portland cement, mainly to the alkalis content, as well as its finer particle size distribution when compared to the reference cement from ABCP. Therefore, the white Portland cement is more reactive and also can be attributed to the milling process used here for the aggregate, which has a strong effect in the results. On the other hand, the difference between the present work and the study developed by Chiaro *et al* [10] can also be attributed to the difference in the particle size distribution of the agate aggregates incorporated in the mortars. Chiaro *et al* [10] produced mortars using an agate aggregate with a defined granulometry based on the Brazilian standards related to particle size distribution. However, the aggregates used here were used in its natural state for the production of the mortars in order to verify the real influence of the agate residue.

The Figure 6 also elucidates that the use agate powder as partial substitution of fine agate aggregate reduces the expansions and the inclusion of this powdered material can be considered as an effective option for reducing the alkali-silica reaction of this residue. The use of 15% of AP reduced the expansions in 69% and smaller expansions (83%) were identified at higher contents of AP (30%). Andriolo [3] verified a similar behavior in mixtures with crushed basaltic sand and the use of a finer filler made from the same basaltic source. The higher the content of finer reactive material, the lower is the expansion attributed to the reaction. Andriolo [6] referenced articles related to the use finer reactive aggregates (as a powdered material) as a reducer of the expansive reactions whit a similar performance than the pozzolanic materials. According to this author, the use of fine particles (or fillers) derived from the same source of reactive aggregates can be considered as a solution to mitigate the expansive reactions.

However another point has to be discussed. Test methods such as the accelerated mortar bar test using 80ºC, as proposed in the standard tested here, are generally not suitable for performance testing. The elevated temperature might cause false results; one reason for this is that materials not being pozzolanic at lower temperatures may become pozzolanic at such high temperatures. In this study agate powder seems to have a mitigating effect. However, it will only be possible to assure when it will be tested under more realistic conditions, for example using a concrete prism test with 38ºC (NBR 15577-6[19]).

Should also be argued that the proposed method NBR 5751 is not appropriate for evaluating the highly reactive pozzolans because of the exhaustion of the alkalinity during the test period [20]. Another factor that be observed is that the standards for the evaluation of the pozzolanic index are not comprehensive; the vast majority does not consider the physical, chemical and mineralogical characteristics of mineral admixtures [21].

Therefore, a more detailed assessment is required in order to achieve a better understanding of this deleterious process and their mitigation.

4 CONCLUSIONS

The pozzolanicity index test demonstrates that the agate powder was not classified as a Pozzolanic material by the NBR 12653 [14], however the results obtained in the two tests were very close to the minimum set proposed by this NBR.

The fine agate aggregate can be categorized in the 2nd level of reactive materials when is used with standardized cement from ABCP, which requires moderate protocols for the reduction of the

alkali-silica reactions. The same aggregate when is used with white Portland cement is considered as level 3 of reactivity degree requiring high and more careful protocols for the mitigation.

The use agate powder with a reference Portland cement from ABCP reduced the development of alkali-silica reaction at the proportions used. When this residue is included in white Portland cement systems at 15%, the reaction was reduced and even can be considered negligible. If the content of agate powder is higher (30%) this deleterious effect can be avoided.

Although the fine agate powders were found to be effective in mitigating ASR distress when used as aggregate replacement material, long-term exposure tests at lower temperatures have to be conducted to study whether the mitigation offered by the agate powders in the lab tests conducted in this investigation translates to extended ASR mitigation in field structures. Also is recommended the implementation of other testing methods to confirm whether or not the agate powder has no pozzolanic index activity.

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TABLE 1: Chemical and physical characterization of the cements.

Chemical compositions		**White Portland cement**	**Values suggested by the Standard[1]**	**Standardized cement ABCP**
SiO_2 (%)		22.4	-	19.52
Al_2O_3 (%)		1.68	-	4.80
Fe_2O_3 (%)		0.29	-	2.26
CaO (%)		67.5	-	62.33
MgO (%)		0.27	6.5	1.90
SO_3 (%)		1,62	4	3.64
Na_2O (%)		0.05	-	0.32
K_2O (%)		0.06	-	0.87
CO_2 (%)		2.37	11	2.59
Na_2Oeq[2]		0.09	-	0.89
Fineness – Sieve 75 μm – 200%		0.20	-	0.09
Specific weight (gm/cm³)		3.02	-	3.09
Specific surface (cm²/g)-Blaine		3820	-	4920
Workability (normal consistency) (%)		30	-	29.4
Initial time of setting (h:min)		2:20	≥ 1	3:04
Final time of setting (h:min)		3:05	≤ 10	5:15
Compressive strength (MPa)	1 day	15.3	-	25.4
	3 days	31.4	≥ 15	38.50
	7 days	40.5	≥ 25	42.40
	28 days	52.6	≥ 40	50.70

[1] Values suggested by NBR 12989 (Associação Brasileira de Normas Técnicas, 1993).

[2] $Na_2O_{eq} = Na_2O + 0.658\ K_2O$

TABLE 2: Chemical characterization of the fine agate aggregate and agate powder.

Chemical composition (%)	**Fine agate aggregate (AA)**	**Agate powder (AP)**
SiO_2	90.87	95.01
Fe_2O_3	3.92	1.24
Al_2O_3	1.46	0.85
CaO	1.19	0.59
SO_3	0.29	0.06
TiO_2	0.26	-
MnO	0.10	0.03
ZrO_2	0.05	-
CO_2	1.82	2.06

TABLE 3: Classification potential reactivity aggregates, according to NBR 15577-5: 2008.

Expansion of mortar bars to 28 days (%)	**Classification of reactive potential of aggregates**	**Mitigation measures due to the intensity of the preventive action**
Less Than 0.19	Potentially innocuous	Unnecessary
Between 0.20 – 0.40	Potentially reactive grade 1	Minimal
Between 0.41 – 0.60	Potentially reactive grade 2	Moderate
Bigger than 0.61	Potentially reactive grade 3	Strong

TABLE 4: Pozzolanicity index with lime to 7 days of agate powder (AP).

	Compressive strength (MPa)
Individual	5.13
	5.02
	5.16
Average	5.10
Deviation standard (MPa)	0.07
Coefficient of variation (%)	1.44

TABLE 5: Pozzolanicity index with Portland cement to 28 days of the agate powder.

Compressive strength (MPa)	**Reference mortar (MPa)**	**Mortar with AP (MPa)**
Individual	46.34	37.96
	45.07	36.47
	42.07	37.64
	45.91	36.21
Average	44.85	37.07
Deviation standard (MPa)	1.93	0.86
Coefficient of variation (%)	4.30	2.31
Performance index with Portland cement (%)	-	83

(a) (b)

FIGURE 1: Visual image of the residues of agate. a) Fine agate aggregate b) Agate powder.

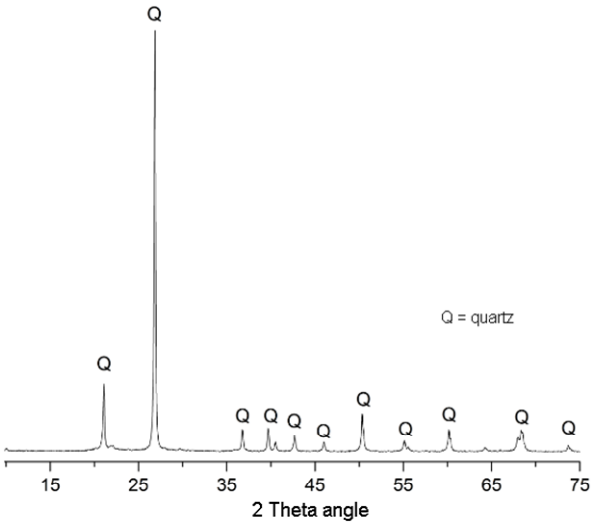


FIGURE 2: X ray diffractometer of the fine agate aggregate.

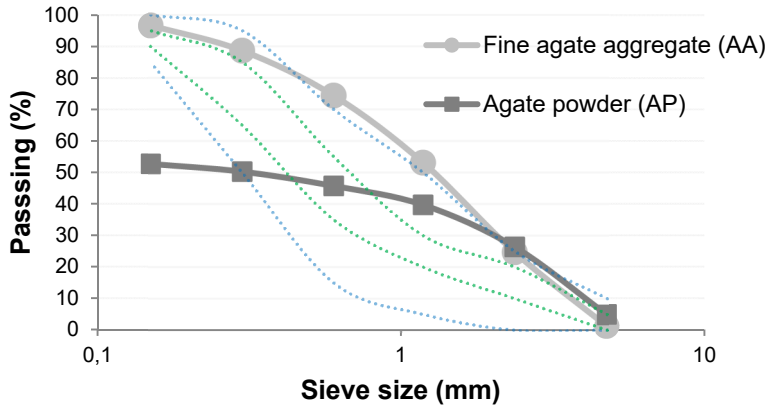
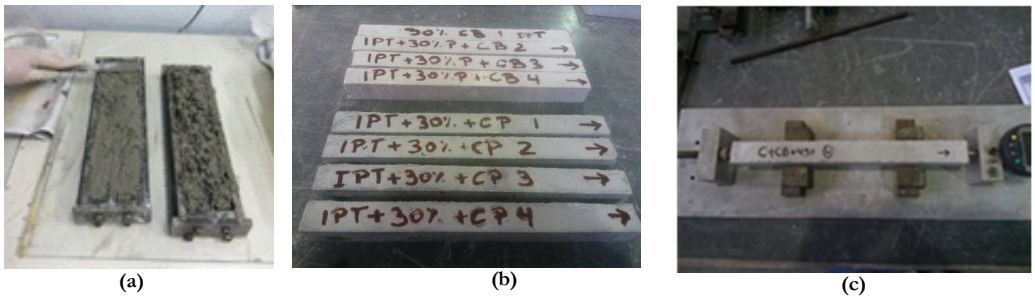


FIGURE 3: Particle size distribution of the fine agate aggregate and agate powder.



(a) (b) (c)

FIGURE 4: Alkali silica reaction test. A) Samples production; B) Samples produced; C) Measurements with the extensometer.

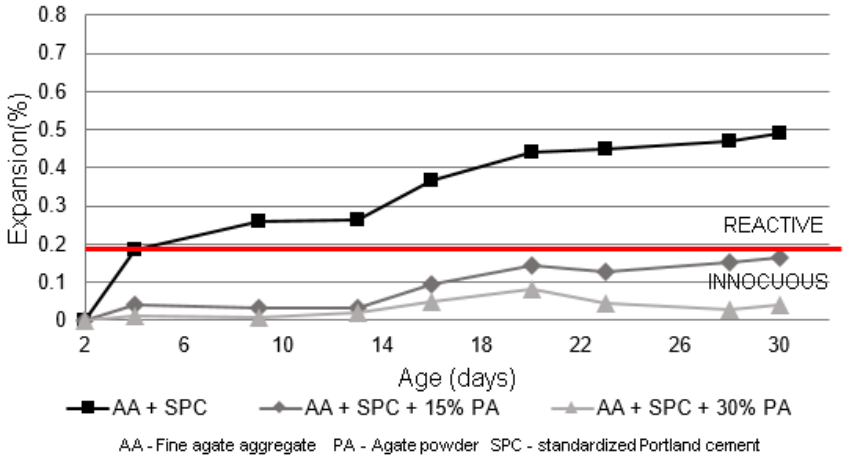


FIGURE 5: Expansions measurements of the samples produced with standardized Portland cement from SPC.

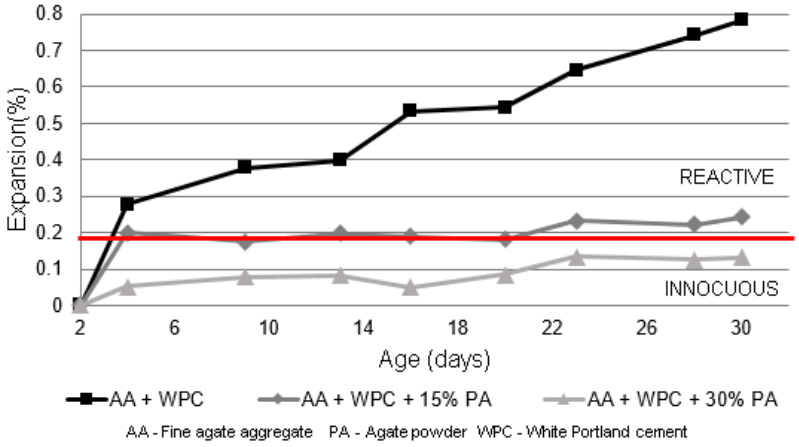


FIGURE 6: Expansions measurements of the samples produced with white Portland cement.