MONTMORILLONITE INCLUDED IN SOME AGGREGATES A PRINCIPAL FACTOR OF A.A.R.

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This study was realized to determine the principal reasons of deleterious reaction in some aggregates. Two basaltic aggregates (olivinic and tholehitic) and a dolomitic limestone were used. Reactivity was studied using NBRI method together with thin cuts, XRD and TEM. The limestone and the tholehitic basalt had montmorillonite. Mortars with these two aggregates presented signs of reaction. The studies showed that montmorillonite supplies silica and alkali that participate of the ASR forming aluminosilicates (zeolites) as expansive reaction products, and this is the principal cause of ASR.

INTRODUCTION

Available bibliography on the chemical reaction of aggregates, continuously informs about new circumstances or effects that start up the development of the deleterious reactions. Some factors may determine that rocks of the same origin behave in different ways. Some examples are the porosity, deformations in rocks produced by stresses, residual stresses (strained quartz), different temperatures during formation, crystal size, contamination with other minerals (smectites), etc. For these reasons some quarries may present different properties along their extent that must be considered before exploitation.

In this way it was found that there were two important groups of aggregates, usually considered innocuous, that when they were used in concrete under certain conditions of humidity and temperature they produced premature deterioration. These aggregates were a tholehitic basalt from Mesopotamia (northeast of Argentina) and a dolomitic aggregate (carbonatic rock) from Patagonia (south of Argentina).

After analyzing laboratory evaluations, it was found as presumable cause of reaction the presence of smectites disseminated into the mass of the rock.

The studies of these aggregates were made at different periods: it was started with basaltic aggregates, taking two samples of aggregates from different quarries.

One of them was a tholehitic basalt with montmorillonite, and the other one, an olivinic basalt without montmorillonite, innocuous, that was used as blank. Both aggregates were of good quality, suitable to be used in concrete. The usual studies to determine ASR were performed on the samples. The use of different basalts was very helpful to understand test results, specially the comparison of the thin cuts.

The other aggregate studied, was a dolomitic rock, contaminated with smectites. ASR studies complemented with additional tests to determine alkali - carbonate reaction were done.

DESCRIPTION OF MATERIALS

Aggregates

Samples of aggregates were taken from the stock piles of operating quarries (that provide the materials to concrete manufacture plants) being careful that they were representative.

Tholehitic basalt. Northeast zone. Yaciretá, Corrientes Province. Laths of plagioclase have little signs of alteration, they are very abundant and involve phenocrystals of clinopyroxenes. Intergranular spaces are filled with alteration minerals. The most abundant is montmorillonite, with subordinated quantities of chlorites and zeolites. Celadonite is observed in sporadic way, and, as an accessory mineral, apatite appears. The alteration minerals, the pyroxenes, the plagioclase (labradorite) and some interstitial opaque minerals can clearly be seen in Photograph 1. Large amounts of montmorillonite, irregular crystals of zeolites and tubular forms of apatite clearly appear. It calls the attention the absence of signs of alteration in feldspars. The mass of opaque mineral partially covers the montmorillonite making difficult to observe its optical properties. Oxidation, as a consequence of the degradation of glass and pyroxene of the original rock, is principally observed. It can be seen a small amount of volcanic glass, irregularly distributed between the mentioned minerals, partially devitrified; at microscope it is brown-yellow, isotropic, and corresponds to palagonite.

Olivinic basalt. South zone. Piedra del Aguila, Río Negro Province. The rock is composed by laths of calcic plagioclase (labradorite), phenocrystals of olivine and abundant opaque minerals distributed in the intergranular spaces. The rock presents slight signs of alteration, specially noticed in olivines and alteration of the opaque material. Photograph 2 shows a view of the rock with parallel light. Texture varies from intergranular - subophitic to intersectal.

Dolomite. South zone. Valcheta, Río Negro Province. The rock presents a texture formed by grains which can reach 5 cm (usual size: 0.5 cm) cemented with irregular little veins. The cementing material is also dolomite, it does not fill completely the voids, resulting a porous rock. The grains are formed by crystalline aggregation of very fine dolomite, here crystals do not exceed 4 µm; this grains are more than 80 % of the volume. They present variable amounts of montmorillonite and sepiolite which make them rather opaque. There also are small amounts of little pieces of rhyolitic volcanic rocks (Photograph 3). The chemical analysis shows an insoluble residue of 10 % attributed to the sum of clay and litic material. It can be seen accumulations of montmorillonite almost pure into the pores of the rock. The dolomite that cements the grains presents greater development of crystals, 40 µm, they are clean, equigranular and no associated minerals are identified.

The studies made by XRD on the rock are unsuitable to identify the presence of calcite. The studies made on the insoluble residue clearly show that there are montmorillonite and sepiolite. These minerals were confirmed by the use of TEM and treating them with ethileneglycol. The last procedure made possible to determine the expansion of the cell of montmorillonite.

Cements and Alkali Contents.

Two ASTM Type I cements were used. Cement n°1 with high alkali content (1.14 % expressed in Na_2O), and cement n°2 with low alkali content (0.22 % expressed in Na_2O).

Mixing Water.

Demineralized water, usually employed in laboratories, was used.

TESTS AND RESULTS

The objective of the testing program was to determine which were the causes that produced the premature deterioration of some concrete structures built with these aggregates.

The characterization of basaltic samples was made by petrographic examination complemented with thin cuts, XRD and chemical analysis. To study the reactivity NBRI method without modifications, in accordance with Van Aardt – Visser (1) and Obersholster – Davies (2), was applied. Mortar bars were molded with each basaltic aggregate, using two portland cements, one of them with high alkali content and the other with low alkali content. The usual curing process was followed, at 48 hours old bars were placed into a sodium hydroxide solution 1 N at 80 C. Measurements were continued until the age of 28 days, according to our previous experiences Batic et al (3.4). At this age (28 days) the surface of the bars was observed and thin cuts on internal sections were made to determine the origin or cause of the expansion and fissures. Grains of affected aggregates, the state of the paste and the products of the deleterious reaction were observed.

The studies of the dolomitic aggregate started few months later. This aggregate was studied because the petrographic identification showed that it had smectites disseminated into the mass. The chemical analysis showed that the aggregate had an insoluble residue of 10.68 %. Smectites were found in the insoluble residue by XRD. As it was a dolomitic rock other studies were added to determine if there was alkali - carbonate reaction: tests on rock cylinder ASTM C-586, concrete prisms CSA A-23-2 14A and as a complement the mortar bar ASTM C-227 (Milanesi - Batic (5)).

Results obtained with NBRI method are principally analyzed.

Mortar mixes are identified as follows:

M1a: Basalt from Yaciretá, with high alkali cement
M1b: Basalt from Yaciretá, with low alkali cement
M2a: Basalt from Piedra del Aguila, with high alkali cement
M2b: Basalt from Piedra del Aguila, with low alkali cement
M3: Dolomite from Valcheta, with high alkali cement

NBRI test results are shown in Fig. 1. The aggregates behave in different way according to their origin.

Bars made with mix M1a presented fissures at the surface since day number 13. Thin cuts taken from the interior of the bars made with M1a and M1b showed signs of reactions. The grains of aggregates have the surface corroded, there are deposits of reaction products (zeolites), and it also appears great amounts of fissures into the paste, and some of them pass through the grains (Photographs 4 and 5).

Photograph 6 shows a microfissure filled with crystals of zeolites. They grow normal to the fissure axis; this fact can be indicating that growing in this way crystals produce the expansion.

Observations of the surface of the bars and of thin cuts showed no fissures or alteration of aggregate grains in mixes M2a and M2b.

Surface and thin cuts observations of mortar M3, after the test in the solution of Na(OH) 1 N at 80 C, enabled to detect two principal phenomena attributed to the chemical reaction of the aggregates.

The first one was the dedolomitization, it is the elimination of the magnesium (Mg) from the molecule of dolomite transforming it into calcite. This process leaded to the crystallization of the calcite, clearly identified by XRD.

The second one, the smectites (montmorillonite and perhaps sepiolite) reacted with the alkaline solution breaking their crystalline structure and liberating their component elements: silicon, alkalis, etc.

This second reaction corresponds to ASR. The participation of these clays (montmorillonite and perhaps sepiolite) in the reaction was manifested by the formation of a reaction product (crystallized zeolites) in air voids, in fissures or disseminated in the paste of the rock. It was observed a void filled with clay material where there were clear evidences of reaction, with the formation of amorphous material in the fissures, attributed to ASR. The expansion, in this case was produced by the sum of two reactions, the ACR and the ASR.

ANALYSIS OF RESULTS

The petrographic study showed that the aggregates from Yaciretá have small amounts of volcanic glass partially devitrified disseminated in the mass (which makes it less dangerous), and as a "strange" mineral they have montmorillonite, being very difficult to determine its percentage.

Aggregates from Piedra del Aguila have no reactive minerals, for that reason they can be considered innocuous.

The aggregate from Valcheta is a dolomite, and then ACR can be expected; it also has montmorillonite which leads to ASR.

Results from NBRI test (Fig.1) showed that mortar bars made with M1a and M1b (aggregate from Yaciretá) gave expansions, that in the case of M1a exceeded the maximum values recommended at 14 days (0.11 %) (2).

Bars made with M2 (basalt from Piedra del Aguila) did not have expansion, aggregates are innocuous, in accordance with the expected results.

Although mortar M3 with aggregates from Valcheta, did not reach the limit of expansion at 14 days, and it exceeded the limit at 20 days.

Observations made with petrographic microscope on mortar bars showed that M1a is the most affected mix, followed by M1b. Affected grains, deposits on the aggregates and voids, and a profuse internal microcracking of mortars can easily be seen.

Observations of thin cuts corresponding to M2a and M2b confirmed the behavior mentioned before, in the aggregate from Piedra del Aguila there are neither deleterious signs nor reaction products.

On the contrary studies with microscope made on M3 showed a more complex situation: there were fissures at the surface and two signs of reaction clearly identified in thin cuts: dedolomitization corresponding to ACR and, fissures and some deleterious reaction products corresponding to ASR.

As a consequence of this study it can be inferred that aggregates that have smectites (montmorillonite and perhaps sepiolite) react giving uncontrolled expansions; depending on the state the smectites are into the mass of the rock and on their percentage.

To complete the study of the behavior of the aggregate with montmorillonite, and considering that in their natural state these are materials very avid of water, what could modified dimensional stability due to changes in water content (producing swelling), specific tests (wetting and drying, immersion in ethileneglycol and immersion in water) were performed.

According to the obtained results, swelling by water incorporation must be discarded, and as a consequence the expansion must be attributed to the chemical reaction between the aggregate and the alkali present in concrete pore solution.

CONCLUSIONS

The principal objective of this study was to study the fundamental roll that the montmorillonite present in some aggregates has on ASR produced in concrete.

The most interesting conclusions obtained are:

Aggregates with montmorillonite and in some cases sepiolite (M1 and M3) disseminated in its mass gave clear manifestations of deleterious chemical reaction.

Disintegration of montmorillonite (easily observed with mineralogical microscope) and the presence of reaction products (zeolites) at the interfaces give evidence of their active participation in ASR, by means of the supply of silicon by disgregation of the rock and the supply of alkali by cationic interchange (Na^+ or K^+ by Ca^{++}).

According to the results obtained in this study aggregates with more than 3 % (in weight) of montmorillonite must be considered potentially reactive.

The study of mortar bars prepared with M3 (by means of the specific tests and NBRI method) shows that with this aggregate there also takes place alkali - carbonate reaction, observing manifestations of dedolomitization.

By means of complementary tests it was demonstrated that aggregates with smectites, in this occasion, do not produce swelling by incorporation of water and that expansions shall only be attributed to a chemical reaction of the type ASR.

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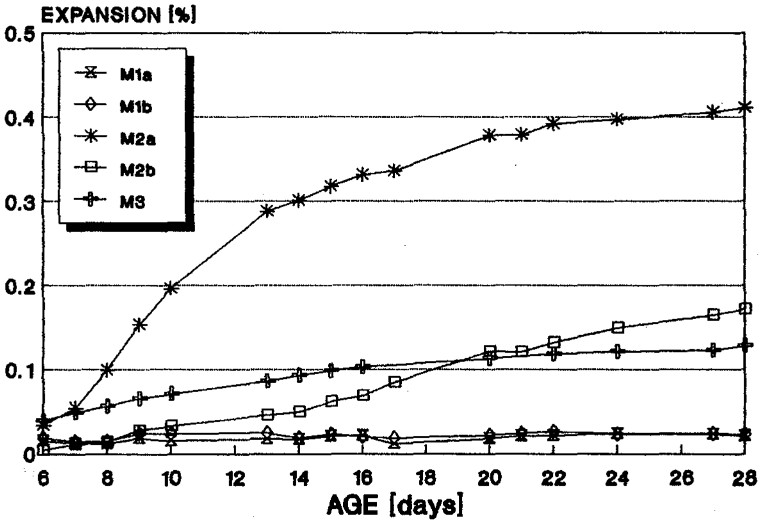
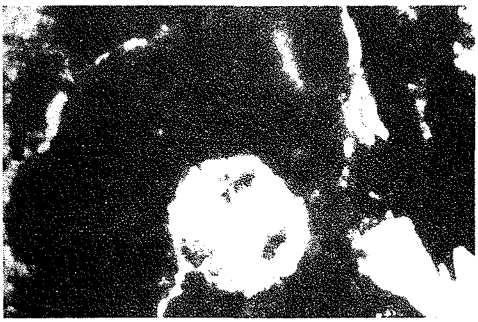


Figure 1 N.B.R.I Tests Results

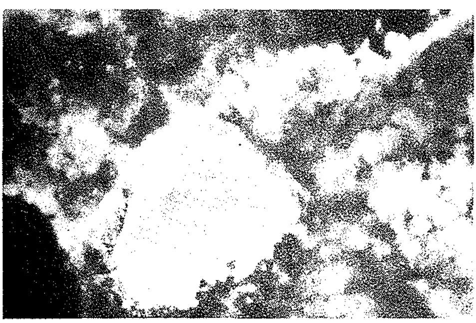
Photograph 1 Tholehitic basalt. Yaciretá.

Photograph 2 Olivinic basalt. Piedra del Aguila.

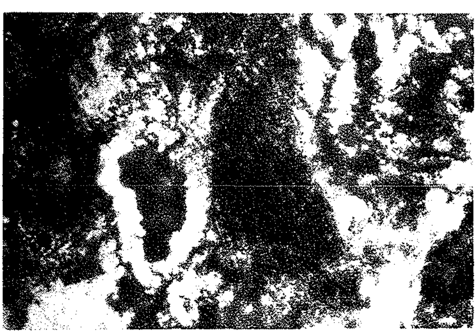
Photograph 3 Dolomite. Valcheta.



Photograph 4 Reaction in grains, fissures and products of reaction. (Parallel light).



Photograph 5 Fissures and borders of crystal with zeolites.
(Parallel light).



Photograph 6 Grain of montmorillonite degraged and parcially replaced by zeolite.
(Crossed Nicoles).