IDENTIFICATION OF ZEOLITES IN CONCRETES AFFECTED BY ASR. EFFECT OF DIFFERENT AGGREGATES.

Maiza, P., Marfil, S. and Batic, O.
Geology Department, UNS. LEMIT-CIC.
CONICET. CIC. Argentina.

Three concretes from structures damaged by alkali aggregate reaction were studied. They were prepared with different aggregates: sandstone, granite (in both of them grains of quartz showed signs of deformation) and the third one mainly constituted by vulcanites. Thin cuts from concretes were analyzed with the petrographic microscope. Zeolites were identified as the main reaction product. They present the same optical characteristics in the three cases. Zeolites correspond to the group of clinoptilolite - heulandite (by XRD). They were also observed at SEM and analyzed by EDAX.

INTRODUCTION

Many authors have studied the products of the alkali - aggregate reaction. Bérubé (1), defines them as siliceous - alkaline gels present in pores and fractures of concrete. Taulow (2), studying thin cuts of concretes damaged by this reaction, mentions the presence of silica - alkali gels in the interior of air entrained voids. Durand et al (3) realized analysis by EDAX of several deteriorated concretes in the area of Quebec, obtaining in all of them a chemical composition almost constant. Davies et al (4), studied the alkali - silica reaction products in samples after NBRI accelerated test were performed. They group the reaction products in: a) a surface gel (amorphous material and tobermorite gel) and b) a white reaction product generated inside concrete.

The objective of this program is to determine the alkali - aggregate reaction products from affected structures, placed in different zones of Argentina.

Samples from concretes prepared with aggregates of different petrographic types were studied.

Concrete N 1, obtained from an airport runway, was made with quartzitic sandstone (coarse aggregate). This material was studied in previous works (5) where the method of picking, employed to separate the reaction product by means of the use of a petrographic microscope, is described. The material obtained in this way was analyzed and identified by XRD.

Concrete N 2, from a pavement, was prepared with a granitic aggregate. Both in aggregates from Concretes N 1 and N 2, the principal reactive mineral was stressed quartz (UEA > 18° and small grain size < 0.080 mm).

Concrete N 3, corresponds to a dam. Aggregates are constituted by vulcanites (andesites, rhyolites, basalts, etc), being the principal reactive mineral the fresh volcanic glass.

In the present work the products of the deleterious reaction obtained from concretes from affected structures were analyzed by means of petrographic examination, XRD, SEM and EDAX.

METHODS AND EQUIPMENTS

To study concretes and the reaction products into concrete, and also to extract them, it was used a petrographic microscope Leitz SM POL, an X-Ray Diffractometer Rigaku Denki geigerflex, a computerized D-max IIIC with radiation Cu Kα, a Scanning Electron Microscope JEOL JSM 35 CF and a Philips SEM equipped with a sound EDAX PV 9900.

RESULTS

Petrographic examination.

Thin cuts were studied to determine the characteristics of the paste, the grade of microcracking, the aggregates, the contact zone between the paste and the grains, the presence of borders of reaction, products of reaction, etc.

Concrete N 1. Grains of aggregates from concrete are constitute principally by quartz (q), cemented with polycrystalline silica, with undulatory extinction, in some of them there are zeolites (z) at their external part, (Micrograph 1. x300). Others present borders of reaction (b) and contact of "caries" with portland cement. There are many fissures in the paste. In air voids (c), the same as in part of the paste (p), there are zeolites as it can be seen in Micrograph 2 (x125).

In this concrete there were identified strained quartz as the reactive mineral and zeolites as the reaction product (AAR).

Concrete N 2. The same as in Concrete N 1, aggregate has strained quartz, then it is considered potentially reactive. There also are small amounts of feldspars. Cement portland paste has many fissures. These microcracks can also be seen at the contact zone between grains and cement. Air voids are filled with a material identified, based on its optical properties, as zeolite (z). In some cases, zeolites cover the whole void, as it can be seen in Micrograph 3 (x125), meanwhile in other cases they grow only at the borders (Micrograph 4, x125), presenting calcite in their external part. Calcite also appears in the interior of the microfissures together with the zeolites.

Concrete N 3. The rocks have in their paste much fresh vitreous material considered as potentially reactive.

Cement paste presents many fissures, with the microcracks filled with zeolites. There also are zeolites at the air voids (c) and at the borders of some grains of quartz (q), subordinated constituent of the aggregate as it can be seen in Micrographs 5 (x125) and 6 (x300).

It must be mentioned there were no fresh gels in none of the three studied concretes. In all cases there were observed crystalline substances, probably due to the old age of concrete and the low percentage of humidity.

This reaction products were identified as zeolites, with similar optical characteristics: low birrefringency, positive elongation, very low refraction index (between 1474 and 1480) and a small extinction angle.

X-Ray Diffractometry (XRD).

To identify the reaction products observed with the petrographic microscope, 10 thin cuts from each concrete were prepared. The reaction product was separated with the help of the microscope, by the picking method. Near 10 mg of zeolite, with the maximum purity that possible, were obtained to be analyzed by XRD. Table 1 shows the results corresponding to Concretes 1, 2 and 3. In the three cases the zeolite is accompanied by the quartz of the aggregate and calcite from the reaction in concrete.

Diffractograms corresponding to Concretes N 1, N 2 and N 3 are shown in Fig.1 a, b and c respectively, identifying in all cases a zeolite of the group of the heulandite - clinoptilolite.

Scanning Electron Microscope (SEM).

The material analyzed by XRD was lately studied with SEM. It can be seen for Concretes N 1, N 2 and N 3 (Micrographs 7, 8 and 9 respectively), that the crystalline forms correspond to structures of the framework type, attributable to zeolites of the group clinoptilolite - heulandite.

Chemical Composition of the Reaction Products.

Concrete N 2 (granitic aggregate) was the most affected by the alkali - aggregate reaction. There are zones where the reaction products are well developed, reaching the crystals up to 20 μm. Some of these fragments were extracted under the petrographic microscope and then prepared to be analyzed by EDAX.

Results are shown in Table 2. Values obtained on natural heulandite are also informed. It can be seen that both results are similar.

Compared with the chemical composition of the clinoptilolite (Deer et al (6)), the studied samples have higher calcium and lower potassium contents.

These comparisons show that the zeolites found belong to the extreme heulandite of the series clinoptilolite - heulandite.

CONCLUSIONS

Based on the studies realized on samples of three concretes affected by alkali - aggregate reaction, prepared with aggregates of different origin, the following conclusions were obtained:

- The products of the deleterious reaction placed at the aggregate - paste interface, fissures and air voids of the studied concretes have similar optical characteristics and chemical composition.

- Results obtained by means of the study of optical properties, XRD and EDAX indicate that the reaction product is a zeolite from the group of the heulandite.

- The homogeneous calcium content found in the reaction products of the three concretes can be compared to the calcium content of natural heulandite content, and it is high referred to the clinoptilolite's. This is caused by the abundance of calcium during the development of the reactions in concrete.

REFERENCES

1. Bérubé, M. et Fourier, B., 1986, Canadian Mineralogist Vol.24, 271.

2. Thaulow, N., 1983, "Alkali - Silica Reaction in the Itezhitezhi Dam Project", 6th Int. Conf. Tech. Univ. of Denmark., Copenhagen.

3. Durand, B. and Berard, J., 1987, Materials and Structures, 20, 39.

4. Davies, G. and Oberholster, E., 1988, C.C.R. Vol.18, 621.

5. Marfil, S. and Maiza, P., sent to C.C.R.

6. Deer, W., Howie, R. and Zussman, J., 1965, "Rock-forming minerals". Vol.4. Framework Silicates. Ed. Longman. London. England.

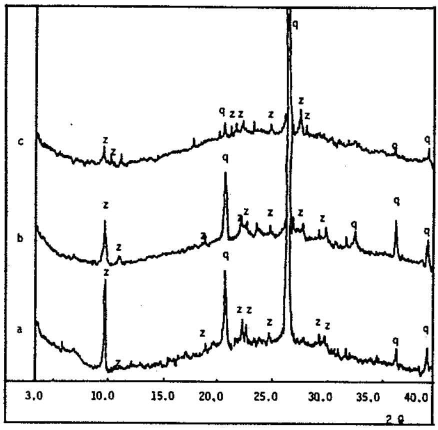
TABLE 1 - X-Ray Diffractometry.

Clinoptilolite JCPDS 39 - 1383			Zeolite Concrete N 1		Zeolite Concrete N 2		Zeolite Concrete N 3	
d Å	I/Io	hkl	d Å	I/I_1	d Å	I/I_1	d Å	I/I_1
8.95	100	020	9.03	29	9.02	16	9.05	39
7.93	13	200	7.92	9	7.95	9	7.84	31
6.78	9	201	6.78	9	-	-	-	-
5.12	12	111	5.14	12	-	-	-	-
4.65	19	131	4.66	13	4.65	13	4.63	53
4.35	5	401	4.266	30 Q	6.26	29 Q	4.267	59 Q
3.976	61	131	3.966	19	3.973	18	3.980	61
3.905	48	240	3.917	17	3.911	17	-	-
3.738	9	312	-	-	3.742	14	3.773	60
3.554	9	312	3.577	16	3.565	14	3.570	57
3.392	12	402	3.350	100+Q	3.348Q	100+Q	3.353	100+Q
3.316	6	002	-	-	3.300	18	3.305	58
3.170	16	422	-	-	3.189	16	3.200	68
3.120	15	441	-	-	-	-	3.140	56
2.998	18	351	3.034c	15	3.036c	15	3.036c	55
2.971	47	151	2.983	15	2.974	15	2.984	54
2.795	16	530	2.801	12	2.796	13	-	-
2.730	16	261	-	2	2.735	14	2.730	47
2.458	3	641	2.457	11 Q	2.457	17 Q	2.457Q	40

* : Isolated by picking under the microscope
Q : Quartz
+Q: Quartz + Zeolite
c : Calcite

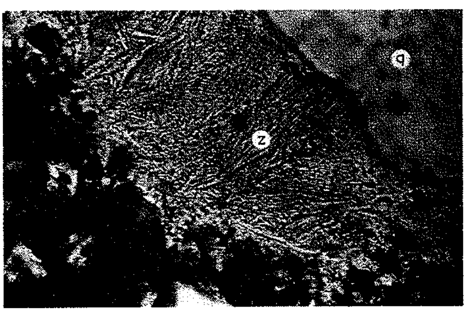
TABLE 2 - Chemical Composition of the Reaction Products in percentage. EDAX.

Principal Element	Zeolites of Concrete with Granitic Aggregate			Natural Heulandite
	1	2	3	
Si	50.99	47.96	49.31	50.98
Al	29.29	34.89	31.12	31.09
Ca	17.27	14.52	16.84	18.19
Na	2.45	1.65	2.29	2.75
K	0.00	0.60	0.23	0.00
S	0.00	0.38	0.20	0.00

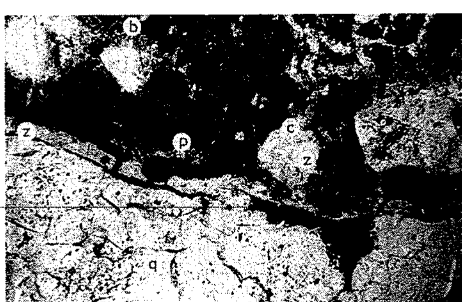


z: zeolite
q: quartz

Figure 1 Diffractograms of the reaction products.
a) Concrete N 1, b) Concrete N 2, c) Concrete N 3

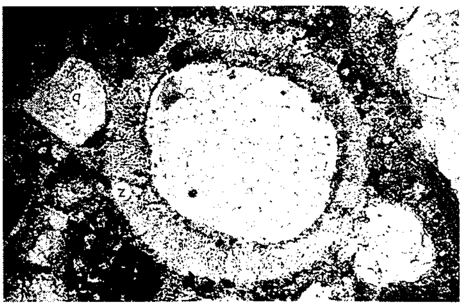


Micrograph 1 Stressed quartz (q) with zeolites (z) at the border. (x300)

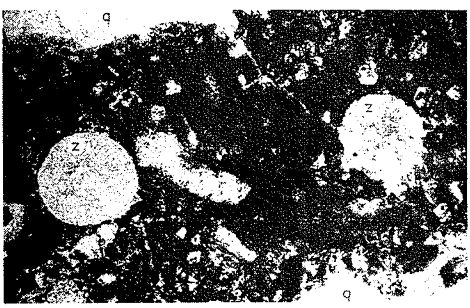


Micrograph 2 Stressed quartz (q) with zeolites (z) at the border, microcracked paste (p) and air voids (c) filled with zeolite (z). (x125).

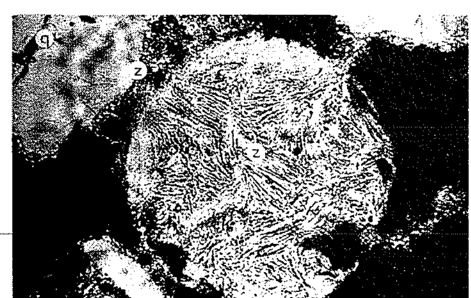
Micrograph 3 Air void (c) completelly filled with zeolite (z). Abundant microcracking in the paste. (x125).



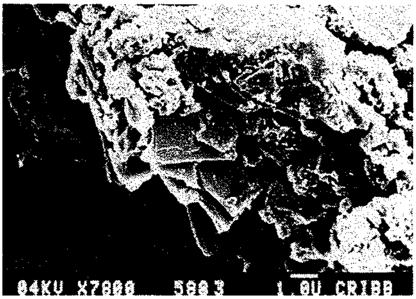
Micrograph 4 Aggregate with zeolites (z) at the external border. Internal zone with amorphous material (a). (x125).



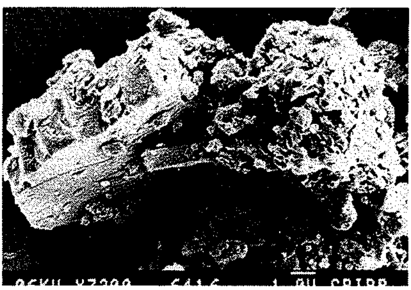
Micrograph 5 Air voids (c) with zeolite (z), and strained quartz with border of reaction (q). (x125).



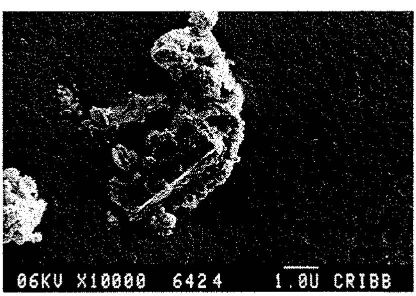
Micrograph 6 Detail of air void (c) with zeolite (z), and strained quartz with border of reaction (q). (x300).



Micrograph 7



Micrograph 8



Micrograph 9