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ZEOLITE CRYSTALLIZATION IN PORTLAND CEMENT CONCRETE DUE TO ALKALI-AGGREGATE REACTION

Marfil S. A.[1,2] and Maiza P. J.[1,3]

(1) Dpto. de Geología. Universidad Nacional del Sur. Bahía Blanca. Argentina.
(2) CIC. Comisión de Investigaciones Científicas de la Prov. de Buenos Aires.
(3) CONICET. Consejo Nacional de Investigaciones Científicas y Técnicas.

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ABSTRACT

Concrete used in works and altered by alkali-aggregate reaction was studied in order to identify the reaction products. For this purpose, the methods of petrographic microscopy, XRD and SEM were employed.

The crystalline forms observed by SEM were later determined through the petrographic microscope, as being zeolites on the basis of their optical properties and confirmed by XRD. In order to obtain a minimum amount (10 mg) of the reaction product, many thin sections were prepared. The product was isolated under the microscope for XRD analysis, through which it was identified as being a zeolite (heulandite-clinoptilolite group).

With the aim of determining the minimum limits capable of being registered by XRD, tests with the addition of 1, 5 and 10 % of a similar natural zeolite (clinoptilolite) were also performed on a concrete sample, showing that 5 % is about the minimum.

Introduction

The difficulty in the identification of the alkali-aggregate reaction products is mainly due to the poor crystallinity they display and to the low proportion in which they occur, resulting in a very difficult isolation for the subsequent XRD analysis. The preparation of thin sections of altered concretes used in works and of mortar bars has allowed us, on the basis of their optical properties, to identify the reaction products as zeolites (1). Those products occur filling voids or within fissures, with a random distribution of the crystals in the former case and perpendicular to the trend of the fissures in the latter.

In the current research, XRD was used with the purpose of achieving a clear-cut identification of the reaction products. The problem with that technique

is to isolate enough pure material so as to obtain a good diffractogram. In general, zeolite reflections results are masked by other minerals that are present in larger proportions, such as quartz and feldspar (belonging to the aggregate) and calcite (which always occurs at the surface of concrete).

Methods

The samples were observed with a petrographic microscope, the neo-formation product was identified and the areas of higher concentration were located for their subsequent extraction, placing special care on purity. The reaction products were analysed by XRD, using a Rigaku Denki diffractometer, Geigerflex D-max IIIC, with Cu(Kα) radiation and Ni filter at 45 Kv, 20 mA. Additionally, the products were observed in a JEOL JSM 35 CF SEM in order to determine the crystalline forms.

Results

Ten thin sections were prepared from a concrete altered by alkali-aggregate reaction with the purpose of achieving a sufficient concentration of material so as to be analysed by XRD. The samples are highly fissured. The microfissures, as well as the voids, are filled with a mineral that was identified as a zeolite on the basis of its optical properties (low birefringence, positive elongation, and very low refractive indices, between 1.47 and 1.48). Those zeolites that replace the reactive clasts, are randomly distributed in voids (Photomicrograph N° 1) and grow perpendicularly to the fractures (Photomicrograph N° 2). The edges of the quartz clasts with undulatory extinction are zeolitized (Photomicrograph N° 3).

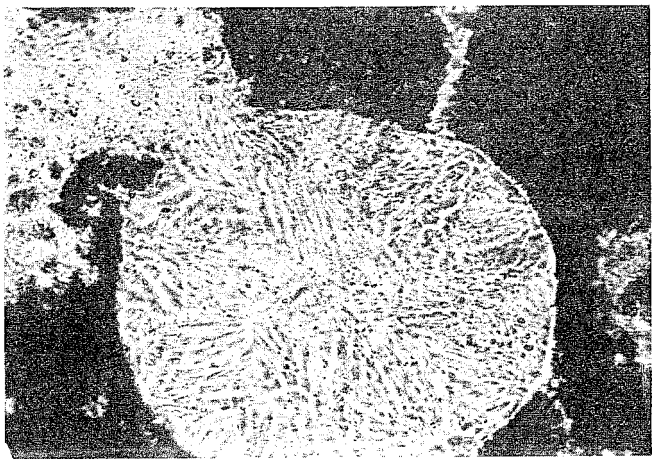
Two reaction zones may clearly be noticed in photomicrograph N° 4: an external one, where the zeolite crystals are perfectly defined, and an internal zone, which still remains amorphous.

For the XRD analysis, it was possible to isolate, by picking under the microscope, 10 mg of the reaction product from the ten available thin sections. The material was dispersed with acetone on a glass slide. Table I shows the reflections obtained where, besides the quartz ones, those corresponding to clinoptilolite can be observed.
They are compared with card JCPDS 39-1389, with a structural formula similar to $KNa_2Ca_2(Si_{29}Al_{17})O_{72}.32H_2O$, of the monoclinic system. The corresponding diffractogram is shown in figure A.

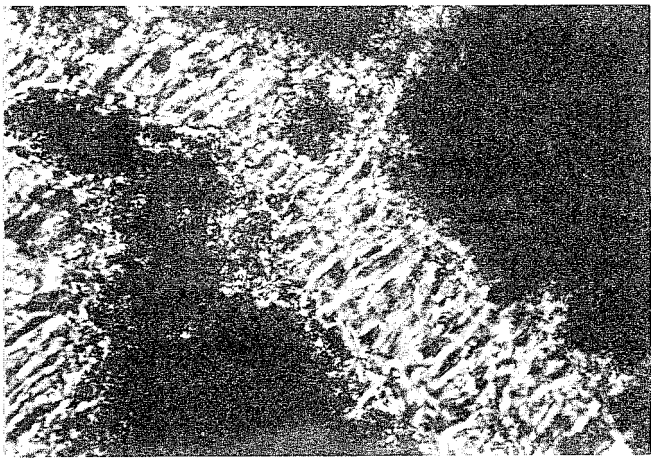
The material was examined by SEM (photomicrographs N° 5 and N° 6) where the most common crystalline forms, resembling the monoclinic system, can be seen.

With the purpose of defining the minimum detection limits for zeolite by XRD, a concrete sample was worked with the addition of 1 %, 5 %, and 10 % of a natural zeolite of similar composition. Clinoptilolite was used in this case, which was identified by XRD (JCPDS 39-1389). (Table N° II). The results with the addition of 1 %, 5 % and 10 % zeolites are shown in Table N° II and figure B.

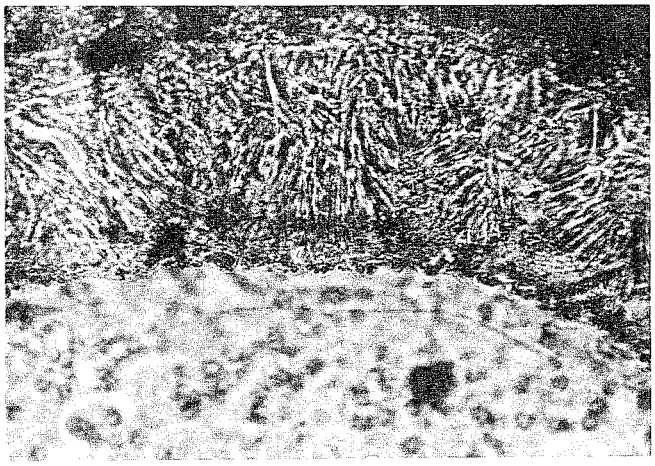
With the addition of 1 % zeolite (Figure B1), the large reflection (8.95 Å, 2θ = 9.88°) is very small, while the remainder corresponds to quartz and feldspar. With 5 % addition (Figure B2), other reflections, besides those of intensity 100, also appear. And with 10 % (Figure B3), zeolite is clearly identified. The diffractogram of the zeolite isolated under the microscope corresponds to that obtained by adding 10 % clinoptilolite to a concrete sample, although differences in crystallinity must be taken into account.



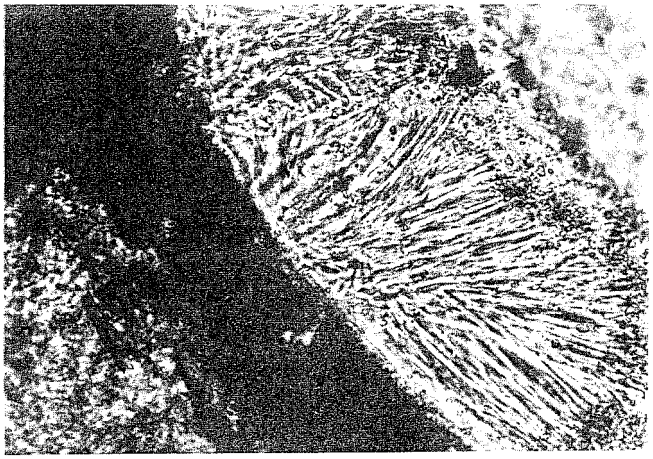
PHOTOMICROGRAPH N° 1



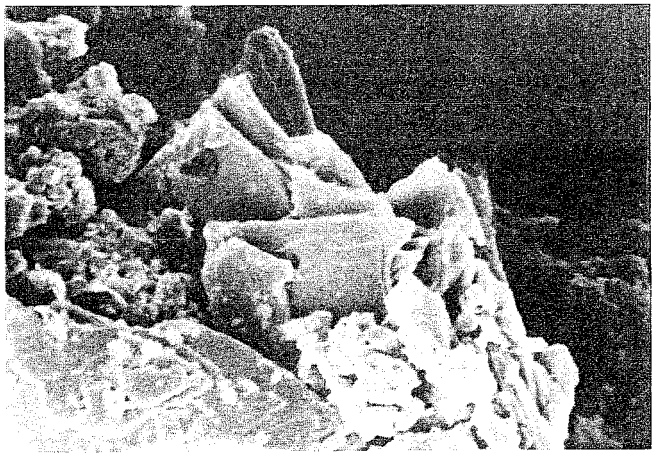
PHOTOMICROGRAPH N° 2



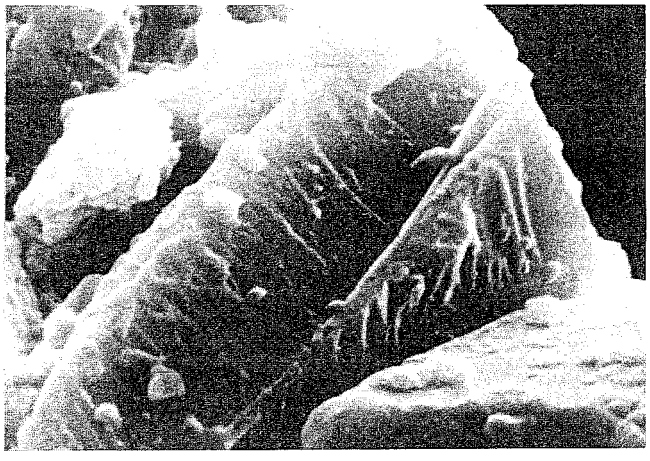
PHOTOMICROGRAPH N° 3



PHOTOMICROGRAPH N° 4



PHOTOMICROGRAPH N° 5



PHOTOMICROGRAPH N° 6

TABLE I

Clinoptilolite JCPDS 39 - 1383			Zeolite concrete *	
d A	I/I_o	hkl	d A	I/I_1
8.95	100	020	9.03	29
7.93	13	200	-	-
6.78	9	201	6.78	9
5.24	10	311	-	-
5.12	12	111	5.14	12
4.65	19	131	4.66	13
4.35	5	401	4.262	30 Q
3.976	61	131	-	-
3.955	63	400	3.959	19
3.905	48	240	3.910	17
3.554	9	312	3.570	16
3.424	18	222	-	-
3.392	12	402	3.343	100 Q
3.170	16	422	-	-
3.120	15	441	-	-
2.998	18	351	-	-
2.971	47	151	2.976	15
2.795	16	530	2.794	12
2.730	16	530	-	-
2.458	3	641	2.450	11 Q
-	-	-	1.982	10 Q
-	-	-	1.820	12 Q

* Isolated by picking under the microscope
Q = Quartz

Conclusions

1. The product of alkali-aggregate reaction of the studied concrete corresponds to a zeolite of the heulandite group: clinoptilolite.

2. The XRD method allows a clear identification of the reaction products, provided a high degree of purity is achieved when isolated from concrete, although the use of the petrographic microscope furnishes excellent results.

3. Isolation by using thin sections is the safer concentration method, the material being contaminated only by the minerals of the aggregate. For the identification of the zeolite, 10 mg of sample proves to be enough.

4. The minimum percentage detectable by XRD for the reaction products studied is approximately 5 %.

FIGURE A

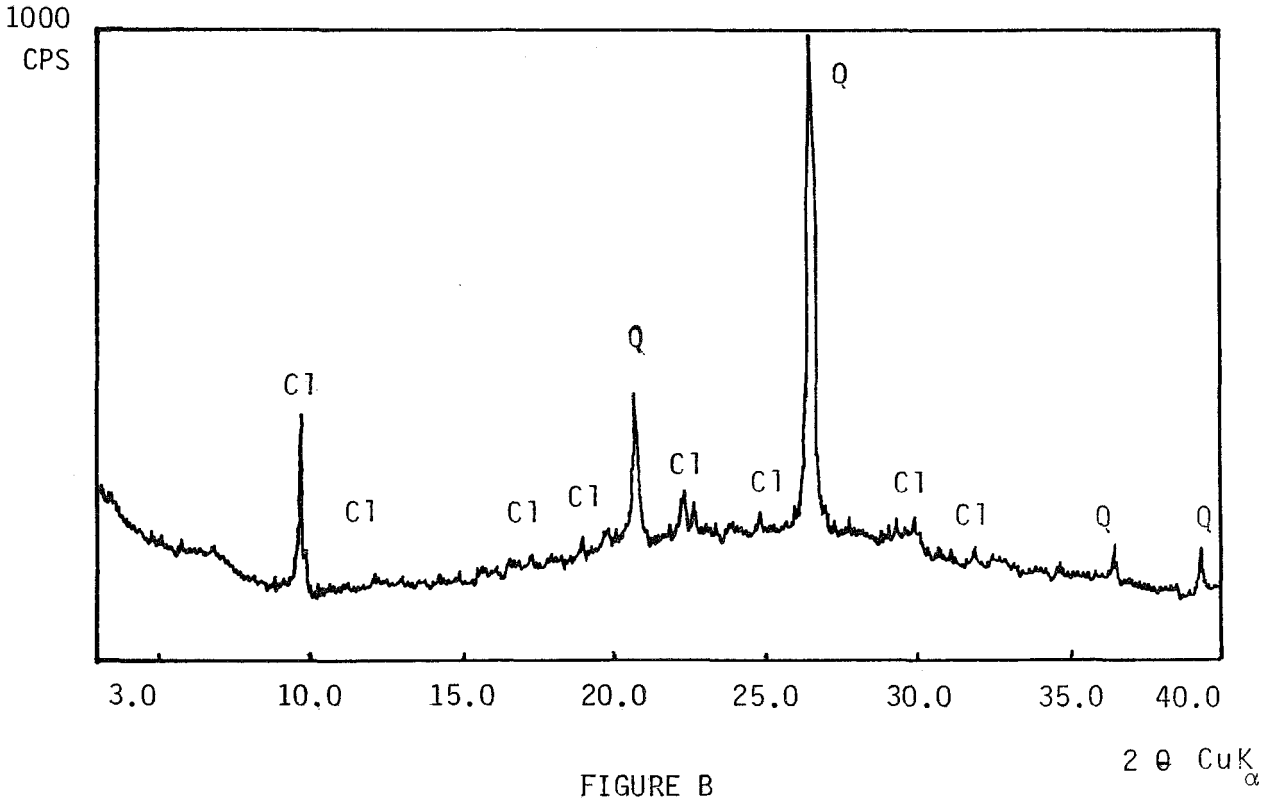
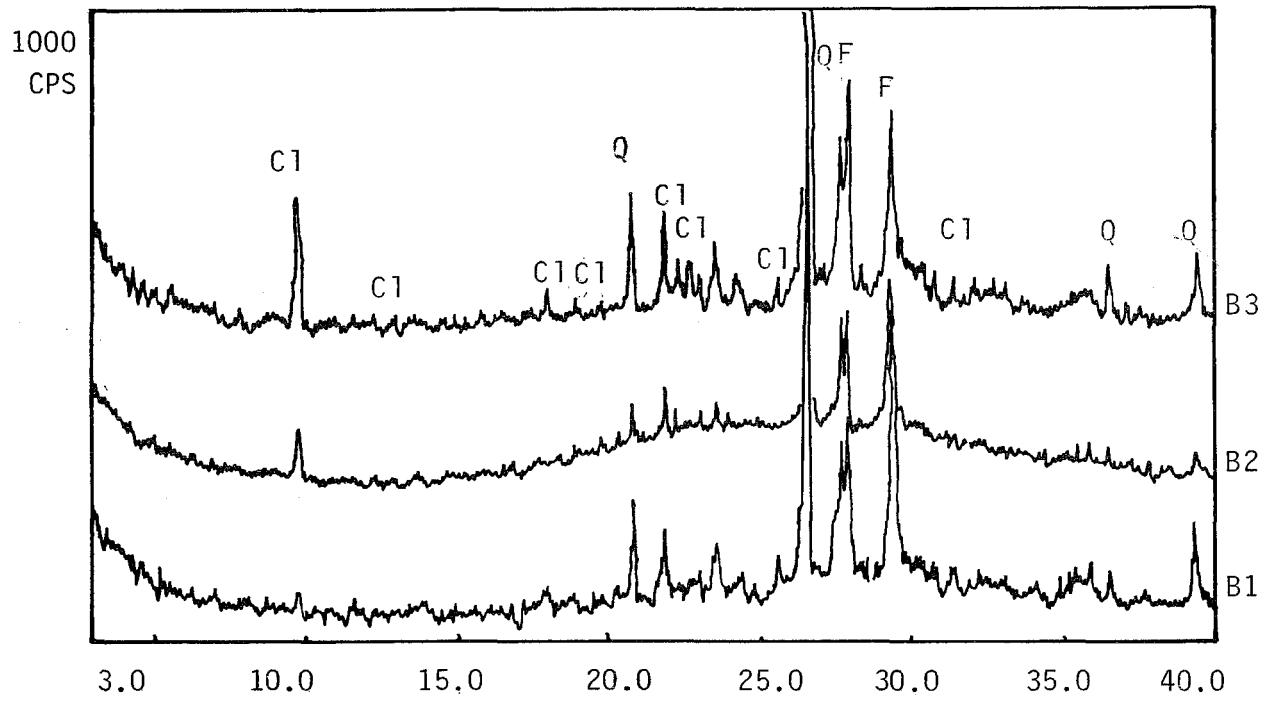


FIGURE B



Q = Quartz
Cl = Clinoptilolite F = Feldspar

TABLE II

Concrete with the addition of 1 % of zeolite		Concrete with the addition of 5 % of zeolite		Concrete with the addition of 10 % of zeolite		Natural zeolite (Clinoptilolite)	
d A	I/I_1	d A	I/I_1	d A	I/I_1	d A	I/I_1
8.95	11	9.02	18	8.98	23	8.97	100
-	-	-	-	6.77	9	6.80	6
5.24	9	-	-	-	-	5.25	6
-	-	-	-	5.13	10	5.12	9
-	-	4.67	10	-	-	4.66	12
4.26Q	23	4.267Q	21	4.263Q	23	4.358	5
-	-	4.04	15	3.975	14	3.989	27
3.854	14	3.859	13	3.899	15	3.959	24
-	-	-	-	3.860	13	3.912	20
-	-	-	-	3.567	11	3.556	7
-	-	3.477	12	3.517	11	3.427	15
3.346Q	100	3.350Q	100	3.347Q	100	3.395	10
-	-	3.323F	15	3.311F	14	-	-
-	-	3.187F	37	3.189F	37	3.174	12
3.122	14	3.127	13	3.126	14	3.125	9
3.086	14	3.067	15	3.042	30	-	-
-	-	-	-	3.006	18	2.997	14
-	-	-	-	2.968	15	2.979	20
-	-	2.779	12	2.788	13	2.801	13
-	-	2.730	12	2.731	13	2.734	8
2.456	13	2.460	15	2.458	15	2.448	5
-	-	2.099	12	-	-	-	-

F = Feldspar

References

1. S. A. Marfil and P.J. Maiza. Mineralogía de los productos formados en hormigones deteriorados por la reacción álcali-agregado. Primer Congreso Uruguayo de Geología. Tomo I Pp. 149-153. Montevideo. Uruguay.