

ALKALI-AGGREGATE REACTIONS PRODUCTS IDENTIFIED IN CONCRETE AFTER HIGH TEMPERATURE CURE IN ALKALINE SOLUTION AT 150°C.

V.Andrei (1) A.Criaud (2)

(1)CEPROCIM SA-National Institute for Cement, B-dul Preciziei 6, Sector 6,
Bucharest, Romania

(2)TEHNODES SA-Technical Center of the Group Italcementi-Ciments Francais,
Guerville, France

ABSTRACT

The temperature can accelerate the evolution of AAR. The results concerning AAR reaction products were obtained for cement pastes, mortars and concretes with different compositions and cured for 5 weeks at 150°C in water and alkaline solutions. SEM-EDAX, XRD, and FT-IR are the analytical techniques used, and in this paper are indicated the chemical and possible structural composition of different AAR morphostructures. The reaction products seem to have morphostructures and chemicals compositions as in normal conditions, or real concretes, conclusions based on more than 1000 SEM-EDAX analysis. In this paper it is not discussed the influence of the high temperature cure on the cement paste.

Key words: *AAR products, chemical compositions, high temperature and alkaline solution cure, morphostructures,, SEM-EDAX, structures.*

INTRODUCTION

The temperature has an opposite and significant effect on the expansion attributed to AAR. The expansion proceeds initially faster at elevated temperatures, but this rate declines more rapidly at higher temperatures. The final values of the expansions are inversely proportional with the temperature, (Herr.1992). The first stage of ASR, respective the attack of the aggregate by the hydroxyl ions, can involve physical process too, (Poole.1992). The kinetic reaction can be influenced by the depletion of $(OH^-)/(SO_4^{2-})$ rapport in correlation with the temperature and alkalis' content, (Herr.1992). The cutoff humidity below wich ASR does not occur is proportional with the temperature, (Jones & Poole.1989). Silica gel is more viscous at high temperature, with a depletion of its migration rate in the cement paste. Between normal and high temperature cure it is possible to suppose some similitudes for reaction products, (Poole.1992, Criaud et al.1994, Andrei et al.1994, Criaud & Defausse.1995). The high temperature can produce modifications regardless of the cement hydrates and the microstructure of the tested concretes, and such effects must be considered too, when AAR reaction products are investigated.

The identification of AAR products were realized using the following criterion:

- SEM's morphostructures;
- Topologic, material and crystalline contrast, for SEM investigation;
- EDAX or electron microanalysis for chemical composition ;
- Specific colour, or refraction index, for optical microscopy;
- XRD information for related AAR products and cement hydrates ;
- Specific molecular spectra in IR for *okenite* and others cement paste hydrates.

INVESTIGATED SAMPLES

The samples were gradually selected for the analytical investigation. Cement pastes made with C2S, C3S C3A+gypsum and synthetical cements, as 1x1x4 cm prisms, were firstly analyzed. This type of samples were used to obtain and identify the influence of the high temperature cure, (5 weeks in vapour and water at 150°C), on the cement hydrates, cracking phenomena, the level of the correction for the observed expansions, the optimum sample preparation for the analytical investigations. Mortars samples of the same dimensions were investigated too. The main results presented in this paper were obtained with different 7x7x28 cm concretes made and treated as it is indicated in table 1. or in table 2 for the chemical composition of the sand and aggregate used.

Table 1. The concretes composition tested and investigated for AAR products after 5 weeks of cure at 150 °C in water and alkaline solutions.

Code	Cement	Sand	Aggr.	Na ₂ O _(equiv) [Kg.m ³]	W/C	W	S	N	K	Exp
								[Kg.m ³]	[Kg.m ³]	[%]
92/45	Airvault	Meuse	Tournaisis	3.68	0.4	y	n	2.58	38.11	0.092
92/46	"	Meuse	Tournaisis	3.68	0.4	n	y	2.58	38.11	0.223
92/53	HPR + μ silica	Meuse	Tournaisis	3.51	0.4	y	n	2.56	36.25	0.092
92/51	"	Meuse	Tournaisis	3.51	0.4	n	y	2.56	36.25	0.017
92/27	CPA	Silex	Silex	4.00	0.5	y	n	7.80	24.15	0.053
92/29	"	Silex	Silex	4.00	0.5	n	y	7.80	24.15	0.082
92/39	"	Sil.cal.	Bachant	4.00	0.5	y	n	7.86	23.59	0.075
92/41	"	Sil.cal.	Bachant	4.00	0.5	n	y	7.86	23.59	0.076

In the above table, Na₂O_(equiv) is the equivalent alkalis content of the initial mix, W/C=(water/ cement) ratio, (W) represents the cure in water, as reference, (S) indicates the cure in alkaline solution. The solutions are obtained by mixes of (NaOH=N) and (KOH=K) with water, in the indicted proportions.

Table 2. The chemical compositions of the aggregate and sand used for the concretes cured for 5 weeks at high temperature and investigated for the AAR.

Aggr.	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	MgO	TiO ₂	SO ₃	LOI
Meuse	52.85	3.52	0.40	0.42	0.00	0.10	0.42	0.02	0.00	42.00
Sil.cal.	14.74	69.11	1.58	0.57	0.17	0.19	0.13	0.04	0.13	12.44
Silex	0.22	97.43	0.35	0.42	0.04	0.17	0.00	0.04	0.07	1.63
Tournaisis	45.29	11.89	1.59	0.58	0.03	0.52	1.28	0.08	0.00	37.42
Bachant	39.74	0.67	0.11	0.13	0.04	0.02	13.60	0.00	0.08	45.98

The drying of the sample was realized for 24-48 hours in low vacuum, with lithium chloride solution for 15% RH at the normal temperature. For backscattered SEM, EDAX and optical microscopy, the samples were immersed in epoxy resin and finely grounded to 0.65 microns. Specially microprelevations were picked up under stereo microscope from the interesting areas, for X-ray diffraction and FT-IR analysis. Very thin 10x10 cm slices were investigated by optical microscopy and backsattered SEM + EDAX too.

MORPHOSTRUCTURES

The morphostructural identification of AAR reaction products was realized by SEM with secondary, (SE), and backscattered electrons, (BSE), on fractured or simply cut surfaces. The criterion necessary for this identification are topologic, (SE, BSE), material, (BSE, ES-with negative voltage for the detector), and crystalline contrast, (SE with low voltage tension on the detector).

In the reactive aggregates, AAR products seem to be as amorphous or polymorphous gel, with granular, blades and botroydals deposits and/or crystallisations. The blades are rhombic and present a good crystallisation, with the tendency of grouping, by superposing, of such blades, 2 or 3. Sometimes, the grouping blades seem to transform in rhombohedral form, approximately crystallized.

At the *cement paste-reactive aggregate interfaces*, AAR products are as compact amorphous and polymorphous gel, figures 1 and 2. Between these gels and the cement paste appear the cracking phenomena, more frequently in the case of carbonatic aggregate.

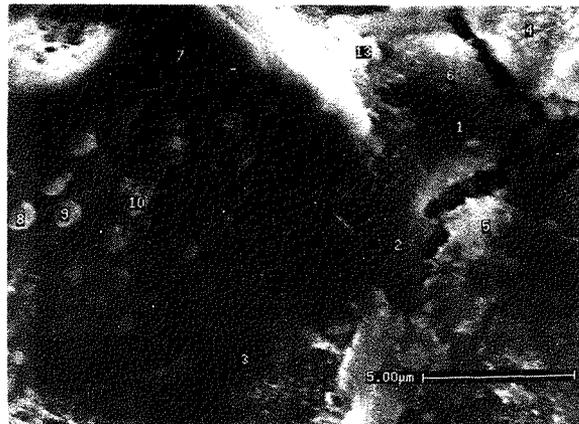
Figure 1. ASR product as stratification of polymorphous silica gel, with fissures coming from the silex aggregate to the cement paste. The molar S/C rapport of the point (1) obtained by EDAX, is 1.8, and point (2), the fibber on the gel, contains high percentage of S.

(5 weeks at 150 °C in alkaline solution).



Figure 2. Reactive carbonate aggregate grain, (7), with botroydals reactions products, (8), (9), (10), on the corroded surface. The phenomena of cracking appear between the compact and amorphous AAR gel, (1), (2), (3), (6), and the hardened cement paste, (4), (5).

(5 weeks at 150 °C in alkaline solution)



In the *free space of the cement paste*, there were found crystallized AAR products, as blades, botroyidals, fibbers, rods, lamella, more frequently in the case of Silex aggregate. The occurrence of silica gel is low, more probably near reactive aggregate. The blades are rhombohedral, and are associating, 2 or 3, and can form morphostructures as rods, figure 3. The botroyidal structure, with spherical aspect, seems to be in intimate mixture with the fibbers, figure 4.

Figure 3. SEM image for ASR crystallized products in the free spaces of the hardened cement paste, as blades like crystals associated with rods like crystals, for the concrete made with aggregate silex and cured for 5 weeks at 150 °C in alkaline solution. The blades seem to associate, 2 or 3, and can transform to rhombohedral crystallized structures.

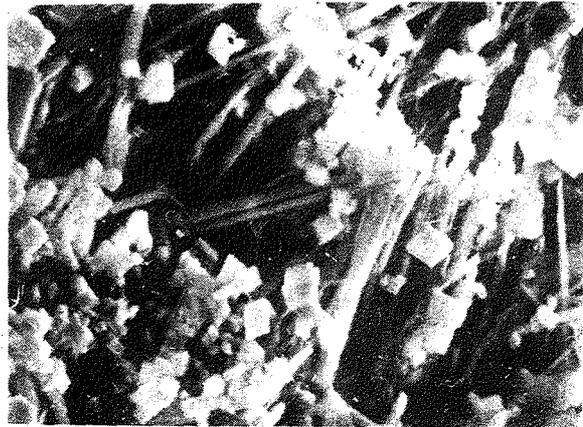
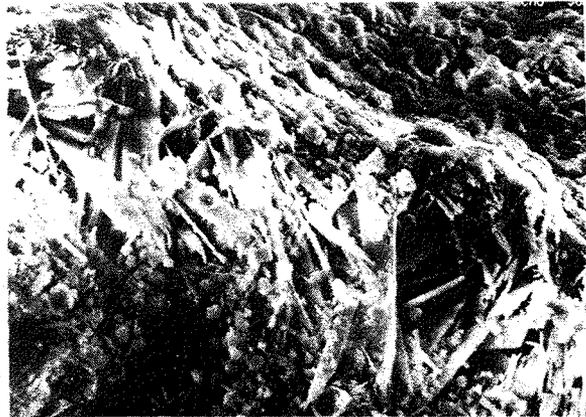


Figure 4. SEM image for ASR products like "botroyidals", associated with fibbers, or very long lamella, in the free spaces of the hardened cement paste of a concrete made with aggregate silex, treated for 5 weeks at 150 °C in alkaline solution.



The term "fibber" can indicate very thin section of the lamella disposed in the plane of the section explored by the electronic beam. The lamella form in pores and fissures, with triangular aspect, more or less elongated. In figure 5 it is presented this ASR crystallized morphostructure, placed between one pore and the reactive grain silex aggregate.

Figure 5. ASR products crystallized as lamella in the hardened cement paste of a concrete made with silex aggregate, and cured for 5 weeks at 150 °C in alkaline solution. The reaction products from this image are developed between the reactive siliceous aggregate and one pore, from the pore to aggregate.



CHEMICAL COMPOSITION OF AAR PRODUCTS

The chemical composition of the reaction products was analysed by EDAX. The table 3 indicates the synthesis of the results grouped for the siliceous aggregates, and table 4 presents a similarly syntheses, but in the case of the carbonates aggregate.

Table 3. Synthesis for the chemical ASR products identified in the concretes made with silex aggregate and cured for 5 weeks at 150°C in water and alkaline solution.

Localisation	SiO ₂	CaO	Na ₂ O	K ₂ O	Al ₂ O ₃	Morphostructure
Aggregate	84-99,99	0-18	0-0.5	0-0.6	-	Amorphous gel
idem	80-95	4.5-18	0-0.8	0-0.8	-	Blades on gel
idem	64-95	3-35	-	0-2.5	-	Botroyidals on gel
Reaction rim	51-60	34-44	-	2-3.5	-	polymorphous gel
Cement paste	59-60	31-36	-	4.7-6.1	-	Blades ass.with fibbers
idem	59-60	30-35.6	-	5.6	6.2	Botroyidals ass.with rods
idem	49-53	43-48	-	1.2-1.5	-	Fibrous
idem	58	34.6	-	1.6	5.8	Lamella
idem	61	35.5	-	3.5	-	Long lamella
idem	63.3	30.2	-	2.2	-	Lamella ass.with rods

The chemical compositions of the reactions products are ordered and grouped in the limits of the experimental errors. The correction method of the EDAX concentrations was "PAP" with background corrections for oxygen. The concentrations are selected by combining the topologic, morphostructural and material contrast and different statistics criterion applied to the molar rapports of Si, Al, Na, K, to calcium.

Table 4. Synthesis of the chemical composition for AAR products identified in the concretes made with carbonatic aggregate, after the cure for 5 weeks in water and alkaline solution at 150 °C.

Localisation	SiO ₂	CaO	Na ₂ O (MgO)	K ₂ O (SO ₃)	Al ₂ O ₃ (Fe ₂ O ₃)	Morpho- structure
Aggregate	18.5-47.2	26.7-52.7	-	0-0.2	0-1.1	Gel, neostructures
idem	1.5-8	89.6-95	0-1.1	0-0.3	0.3-1.5	Idem
idem	46.5-86.4	1.9-23.9	1.1-3.0 (2.2-8.9)	0.8-19.4 (1.9-4.2)	2.2-16.7 (0.7-7.6)	amorphous gel
Reaction rim	18-47.3	26.7-52.7	-	0.1-0.2	0.3-7.1	amorphous gel
idem	37.3-85.1	7.7-59.3	0-2.4 (0.2-4.1)	0.3-10 (0-0.9)	1.1-22.4 (0-2.0)	idem
Cement paste	52-56	30-40	0.9-5.3 (0-4.2)	3.2-7.4 (0.5-1.3)	1.8-4.0 (-)	amorphous gel
idem	56-60	29-35	1-2.4 (0-2.5)	4.3-6 (0.5-1.3)	1.7-2.2 (-)	Fibrous
idem	30-42	19.4-28.1	0-9.4 (2.9-18.2)	0.3-1.3 (31.2- 40.2)	10-24.5 (-)	Rods

The concentrations for ASR products of the concretes made with aggregate siliceous, are presented as individual points in the diagram (%K₂O)/(%CaO) versus (%SiO₂)/(%CaO) in figure 6. Figure 7 indicates the repartition of the EDAX concentrations for ASR products identified in the concretes made with reactive carbonate aggregate as (%K₂O+%Na₂O)/(%CaO) versus (%SiO₂)/(%CaO).

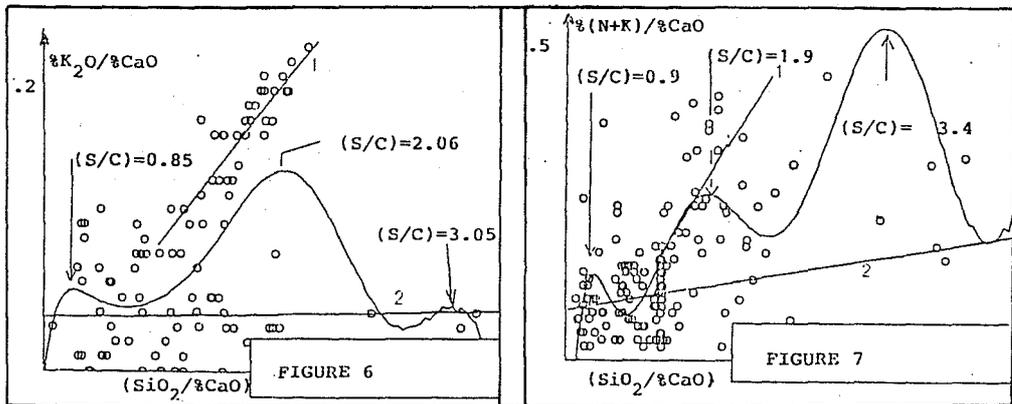
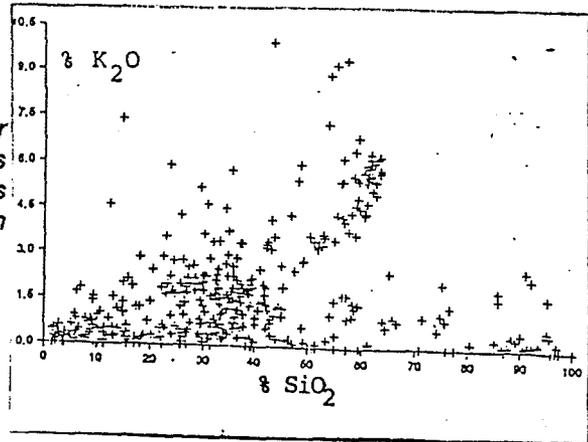


Figure 6. Repartition %K₂O/%CaO versus %SiO₂/%CaO for EDAX analysis of ASR products from concretes with siliceous aggregate cured 5 weeks at 150 °C in alk.sol. **Figure 7. Repartition %(K₂O+Na₂O)/%CaO versus %SiO₂/%CaO for EDAX analysis of ASR products identified in concretes with reactive carbonate aggregate cured 5 weeks at 150 °C in alkaline solution.**

(Line (1) approximates ASR crystallized products, line (2) is obtained by eliminating the points making line (1), and the curve with 3 maxima is the order 9 interpolation of the all points. The slashes indicate the maximum probability positions of the alkalis content and the corresponding %SiO₂/%CaO rapport).

The content of K₂O seems to be correlated with SiO₂, as it is presented in figure 8 that cumulates more than 1000 EDAX analysis realized for the concretes from the first table, investigated for ASR reaction products and cement hydrates at the end of the high temperature cure at 150°C.

Figure 8. %K₂O versus %SiO₂ for ASR and cement hydrates products identified the concretes cured for 5 weeks at 150 °C in alkaline solution.



STRUCTURAL INFORMATIONS FOR AAR PRODUCTS

The structural informations are obtained mainly by x-ray diffraction. The samples were picked up from a flat 7x7 cm² section, around of the all aggregates, from reaction rims, and the neighbored cement paste. The siliceous aggregate presented two colours for his reaction rims described below:

- Rose colour, with crystallized products as calcite, tobermorite 11 A, C₂SH, and tuscanite, $K(Ca,Na)_6(Si,Al)_{10}O_{22}(SO_4,CO_3,OH)_2.H_2O$;

- Brown colour, with crystallized products as calcite, tobermorite 11 A, Calcium Hydrogen Silicate Hydroxide Hydrate, $Ca_9(Si_6O_{18}H_2)(OH)_8.2H_2O$.

Minerals like albite, microcline, quartz, calcite, dolomite are coming from the aggregate. The cement hydrates are characteristic for the temperature and pressure conditions of the cure, as C₂SH, Tobermorite, Okenite, Gyrolite, Hillerbrandite, Scawtite, C₃AH₆, Mg(OH)₂, Ca(OH)₂ are rare. In completion of XRD investigations, we realized very complex statistical calculus, by selecting different ranges of (%SiO₂)/(%CaO), Andrei et al.1994.

CONCLUSIONS

Informations about the experimental conditions and the results of the expansion of accelerated tests are presented by Criaud & Defausse.1995. Regardless of the reaction products obtained at 150°C, it seems that they have similarly textures as amorphous and polymorphous gel, individual or associated blades, botryoidals, fibrous, rods, lamella, like as for normal or real conditions. The ASR products have a broad range for the chemical compositions.

The structures of AAR products can be supposed by combining x-ray diffraction, FT-IR and SEM-EDAX investigations. The physico-chemical processes are very complex during the high temperature and alkaline cure, the alkaline solution being depleted in Na and K, which precipitate in concrete.

For the crystallized ASR products, represented by the points grouped along the lines (1) from the figures 6 and 7, it is possible to have the following statistically correlations:

-From $CS_{1.1}K_{0.04}H_x$ to $CS_{2.05}K_{0.13}H_x$, line (1) $[(\%K_2O)/(\%CaO)] = -0.1 + 0.145x [(\%SiO_2)/(\%CaO)]$, for the siliceous aggregate ;

-From $CS_{1.1}(N+K)_{0.05}H_x$ to $CS_{2.05}(K+N)_{0.15}H_x$, line (1) $(\%K_2O + \%Na_2O) = -0.05 + 0.148 [(\%SiO_2)/(\%CaO)]$, for the reactive carbonate aggregate ;

-Three maxima of the alkali's content for $(\%SiO_2)/(\%CaO)$ ratio at (0.85-0.9), (1.9-2.0), and (3.05 - 3.4), for all ASR products identified in our study.

Most of the crystallized ASR products had the molar ratio $SiO_2/CaO = 1.8$.

Reaction products with very high content of Al, S, Si and Ca and in association with ASR gel, there were found with a maximum probability for $(SiO_2/CaO)_{molar\ ratio} = 1.8$. Between the cement hydrates and AAR products can exist different interactions, and it is very difficult to identify without special precautions. The use of complementary analytical techniques and statistical computations it will be very helpful for this field of research.

REFERENCES

Andrei, V., 1992, "Study of the concrete microstructure after the cure at 150°C, Vol.1-5, Stage Rep. CNRS-BRITEST Convention, Techodes sa.

Andrei V., 1994, AAR Monography, Rep.CEPROCIM SA, C180-MTC.

Andrei V, Criaud, A., Colombet, P., 1994, "Secondary Reactions Associated with AAR at 150 °C Investigated by SEM-EDAX", Presented at the 4th NCB Int.Seminar on Cement and Building Materials, New Delhi, India.

Criaud, A., Defuasse, C., Andrei, V., 1994, "An Accelerated Method for the Evaluation of ASR Risk of Actual Concrete Compositions", Presented at the 3rd CANMET/ACI Conf.on Durability of Concrete, Nice, France.

Criaud, A., Defuasse, C., 1995, *Materials and Structures*, 28, 32-42.

Herr, R., Wieker, W., 1992, "The Hydroxide-Sulphate Ion Equilibrium in Cement Paste Pore Solutions and Its Significance to the Theory of AAR in Concrete" Procc.9th Int.Conf.on AAR in Concrete, London, England, 440.

Jones, T.N., Poole A.B., 1989, Procc.8th Int.Conf.on AAR, Kyoto, Japan, Ref.5 from Poole, 1992.

Poole, A.B., 1992, "ASR Mechanisms of Gel Formation and Expansion" Procc.9th.Int.Conf.on AAR in Concrete, London, England, 782.