INVESTIGATION OF AAR BY PHYSICO-CHEMICALS ANALYSIS IN THE CASE OF DIFFERENT CONSTRUCTIONS FROM ROMANIA

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ABSTRACT
The problem of AAR diagnosis began to be considered in the last 3-4 year by different construction's administrators from Romania, beside other possible factors of damage or destruction. The general procedures involve laboratory investigations, like psysico-mechanical, chemical and physico-chemical analysis. This paper partially describes the analytical algorithm developed for the diagnosis and investigation of ASR realized by optical microscopy, x-ray diffraction, infrared spectroscopy, scanning electron microscopy, electron microanalysis and differential thermal analysis. This analytical algorithm, completed with a special chemical sequence, was tested on real and laboratory concretes and some results are presented as two case study for ASR and ACR in Romanian constructions.
Key words:AAR diagnosis for real concretes. physico-chemical procedure. ASR and ACR case study in Romania.

INTRODUCTION
The continuing flow of conferences and papers on AAR wich demonstrates that the knowledge is still accumulating in this field of theoretical and practical research and development. The tests required for a detailed diagnosis of AAR need the expertise and the dedication of several investigations and laboratory staff, if reliable results must be obtained. The presence of AAR in concretes must be checked together with other factors as freezing and thawing, salt action, differential thermal strains, unsound aggregate, sulphate compound in soil and water, leaching, chemical attack, wear and abrasion, foundation movements, shrinkage and flexural action, rusted reinforced steel. It is very important for the laboratory staff to know and to speak the same language as the constructors, being necessary a close collaboration between engineers and laboratory staff in all stages of an ASR investigation. The general stages of AAR investigation are: site inspection and testing, sampling, laboratory investigations, assessment of site and laboratory findings, evaluation of the risk of future reaction.
When damage caused by AAR does occur, its consequences for the affected structure may appear to be serious, but, it is the general expert the deciding factor for further investigations, in situ or in laboratory. Some of the ASR macrostructural symptoms could be found at the microstructural level, or during the analytical process. Such symptoms are presented below:
1)Map cracking or pattern cracking, defined as openings on concrete surfaces in the form of a pattern of several three-armed star shapes that join up.

This can results from a decrease, increase, or both, in volume of the material near or below the surface.
2)Exudation, which means that a liquid or viscous gel-like materials can discharge through a pore, crack, or opening in the surface.
3)Efflorescence, given by salt deposits , usually white, which appear at the concrete surface, the substance having emerged in solution from within the concrete or masonry and deposited by evaporation.
4)Popout, defined as breaking away of small portions of a concrete surface due to localized internal pressure that leaves a shallow, typically conical, depression.
5)Discoloration, wich represents a change in colour from that which is normal or desired, for cement paste, reaction rims around the aggregates, filing material of the fissures and pores.

GENERAL PHYSICO-CHEMICAL LABORATORY PROCEDURE

The laboratory physico-chemical procedure developed for ASR diagnosis uses the optical microscopy, in reflexion and transmission, x-ray diffraction, infrared spectroscopy, differential thermal analysis, scanning electron microscopy and microanalysis. *Optical microscopy*, OM, the most widely used in AAR diagnosis, involves two types of examinations, in reflexion on finely ground sections, and petrografical investigations on thin sections, usually in transmission, with a quality polarizing microscope. The general flow chart for optical investigation used for ASR concrete investigation is indicated in figure 1. *X-ray diffraction, XRD*, completes the chemical and OM ASR investigation in our procedure, following a dedicated analytical flow chart which it is not related in this paper . The analysed samples are representative for the whole concrete, cement paste and aggregate, separated by crushing and sieving, or by chemical attack. It is not possible to obtain a complete separation, but this operation can reduce the influences of the matrix. There are limited data in the literature relating to ASR products, but it is possible to suppose "reaction products" as rose like crystal, "CKSH", products with structures as Okenite, CSH, Tobermorite, Gyrolite, "N"CSH-C"N"SH, $NaSi_{17}O_{13}(OH)_3.3H_2O$, $Na(K_2Na_2Ca)_{16}Si_{32}O_{80}.2H_2O$, Feldspar, Rhodesite, etc. Calcite, different alkaline carbonates, brucite and monocarboaluminate are implied as ACR reaction products. *Infrared spectroscopy*, IR, can confirm the results obtained with other analytical techniques and uses the same sample as X-ray diffraction analysis. The essential molecular IR vibrations bands are those relating to SiO_4^{2-}, SO_4^{2-}, CO_3^{2-}, OH^-, in correlation with the same reaction products indicated for the x-ray diffraction. *Scanning electron microscopy*, SEM, is an excellent tool for ASR diagnosis. The only ASR product accepted classification was made by SEM, based on the morphostructure criterion at magnifications of the order of 2000-5000. The SEM procedure was developped as algoritm for secondary and backscattered electrons with topologic, material and crystalline contrast. *Electron microanalysis* completes the general physico-chemical procedure, and in fig.2 it is presented the characteristic flow chart used for ASR diagnosis. It is very import for this analytical technique to ensure both the result representativeness and correlation with the analytical techniques.

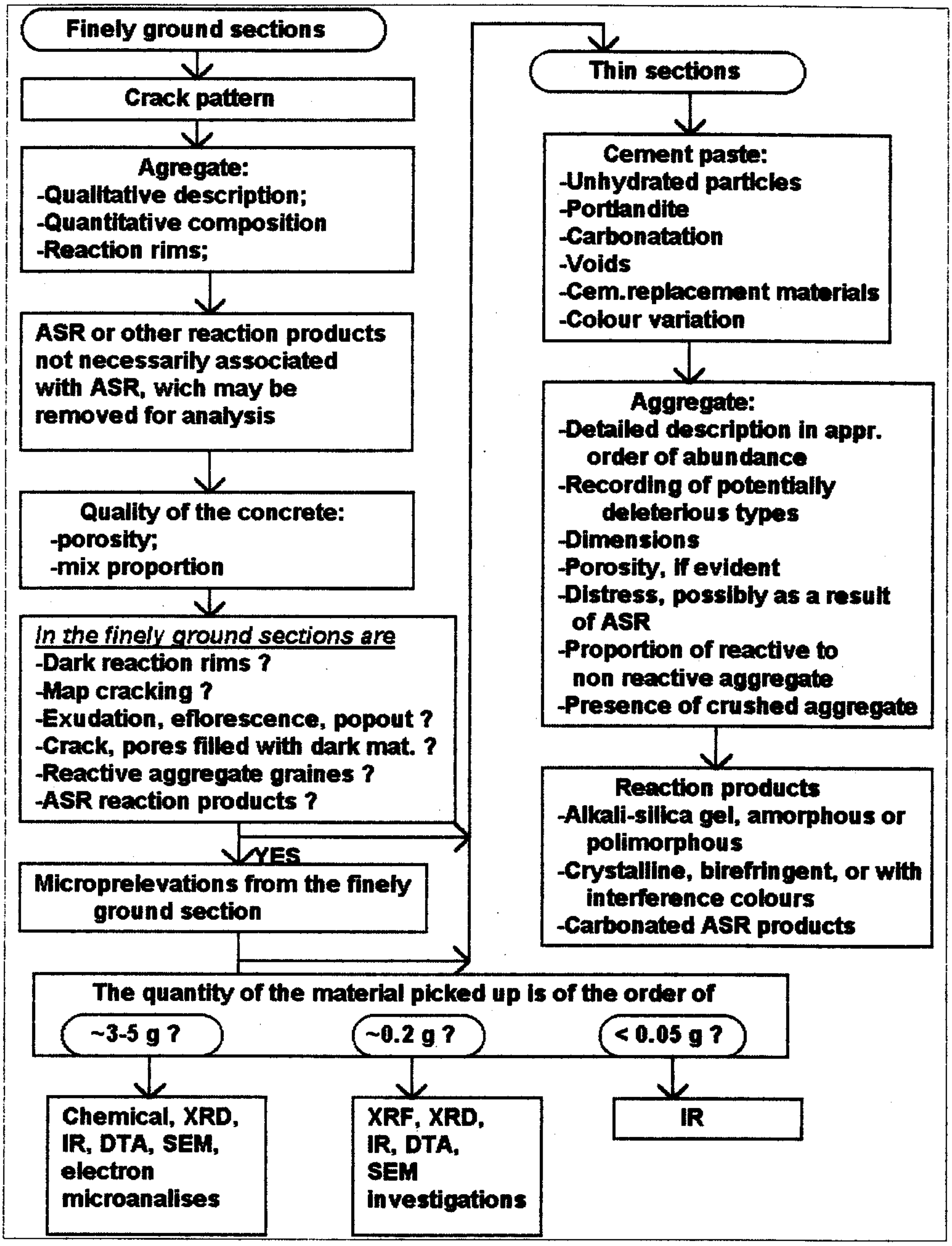

Figure 1. Flow chart for the concrete diagnosis and/or investigation of ASR by optical microscopy and connections with other analysis.

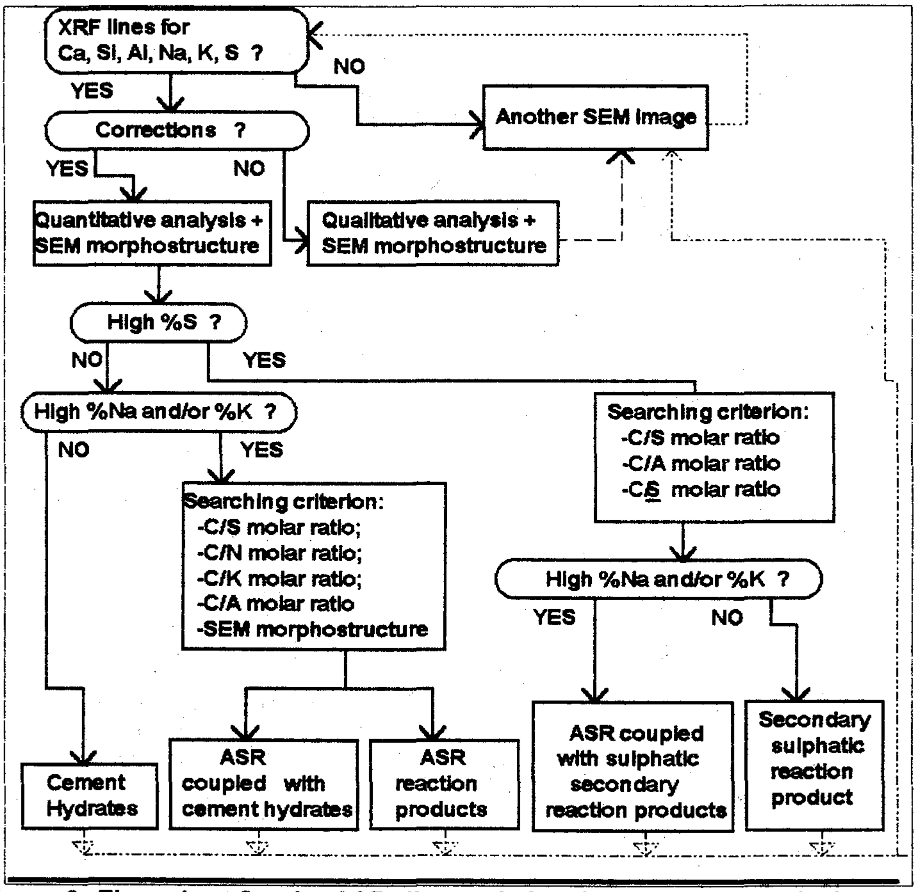

Figure 2. Flow chart for the ASR diagnosis by electron microanalysis

CASE STUDY FOR ASR-CHANNEL LINING VINATORI

In the region of Bicaz there are in service many dams and several channels. The main administrator observed very serious deteriorations of the channel lining at Pîngăraţi. There are map cracking, movements and concrete disintegration. Cores were extracted from the variable level of the water, below and above, both from affected and reference area too. The sample arrived in laboratory with very limited information, only codes and indications about the environmental humidity. The customer's assumption was that "ASR damaged the concrete structure". The physico-chemical procedure, completed with chemical analysis, were applied for every core. The equivalent alkalis content for concretes was between 1.19% and 1.56%, coming specially from the aggregate. The mineralogical composition of the investigated concrete was: (40-45)% Quartz, (12-20)% Calcite, (10-15)% Feldspar, (10-15)% Illite-micas, ~5% Clorite, ~2% Gypsum, and amorphous compounds, of the order of 10-15%.

The main component of the aggregate is siliceous, containing quartz as discrete grains, quartzite micro and crypto-crystalline, gneiss, schist, flint as chalcedonic silica. Reaction rims are frequently associated with $Ca(OH)_2$, cement hydrates, granular carbonate and cracks, approximately coloured as ferric oxides' impregnations. Acicular reaction products were identified near reactive aggregate grains. The hardened cement paste is completely hydrated, with carbonated areas, and low distribution of the fissures. The fissure pattern observed by OM seems to be generated by freezing and thawning, leaching, ASR and secondary sulfatic reactions, these being the damaging factors. SEM and electron microanalysis indicated ASR reaction product like amorphous and polymorphous silica gel, crystallized products like rods, lamella, in associations with CSH I, II and sulphate compound, fig.3. ASR reaction products are frequently carbonated, specially at the cement paste level. Silica gel and sulphate crystallized reaction products are very unstable in the SEM being altered by the electronic beam. The chemical composition for ASR reaction products, observed at SEM with morphostructure as compact like gel, it was obtained by the electron microanalysis, with the following compositional ranges as bellow :

(48-92)%SiO_2 (5-42)%CaO (3-22)%Al_2O_3 (0-1)%K_2O (0-5)%Na_2O

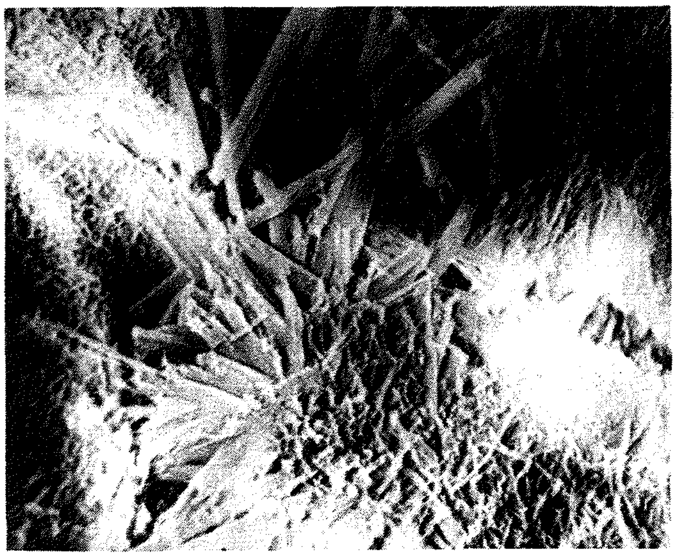

Figure 3. SEM image for the cement paste morphostructure damaged by ASR products associated with secondary sulphate reaction products.

The final conclusion of the laboratory repport was that ASR and secondary sulphate reaction are implied in the concrete deterioration, but the assement of the contractor was that the ASR contribution, as damaging factor, is of the order of 20-25%.

CASE STUDY FOR ACR - ADDUCTION CHANNELS FROM DRAGAN-REMETI

The Dragan-lad hydrotechnical construction, located in the region of Transilvania, is in service from 1980. The initial concrete mix was made with a special cement for dams, coarse dolomite aggregate, 3-40 mm, and river sand mixed with very fine dolomite powder obtained during the rock grinding. The ACR reactivity of the aggregate was tested by STAS 5440/70, (ASTM C227 mortar test). The external concrete damage symptoms are as massive and contiunous calcite efflorescence, "popouts" with irregular depths and forms, cracking and cement paste loosing.

The actual concrete investigations were conducted in close cooperation between contractor and Ceprocim laboratory. For the final results assembling and conclusions the Polytechnic University of Bucharest it was implied. The laboratory investigations, (chemical, XRD, IR, DTA and optical microscopy were done on cores, (transversal and longitudinal cut sections) and crushed samples from damaged areas. Eight different cores, with the chemical and mineralogical compositions indicated in tables 2 and 3, were used for this paper.

TABLE 2. *Concrete mean chemical analysis*

Compound	1	2	3	4	5	6	7	8
SiO_2	22.70	24.70	33.77	29.21	26.73	21.51	31.56	20.05
CaO	24.53	24.04	22.08	22.89	22.03	24.70	21.58	25.23
Al_2O_3	3.33	2.44	4.09	2.95	2.84	2.81	4.94	3.18
Fe_2O_3	1.20	1.41	1.00	1.61	1.62	1.40	1.78	1.79
MgO	13.00	13.03	9.09	11.73	13.35	13.96	9.33	13.69
SO_3	0.89	0.67	0.59	0.65	0.47	0.51	0.41	0.71
Na_2O	0.44	0.58	0.66	0.59	0.53	0.42	0.58	0.67
K_2O	0.44	0.53	0.69	0.63	0.56	0.42	0.59	0.59
TiO_2	0.59	0.58	0.55	0.59	0.52	0.62	0.58	0.60
Ins.	14.95	27.99	36.31	32.60	29.22	23.63	36.18	24.43
LOI 580 °C	5.96	7.48	5.32	5.73	5.69	6.52	6.55	5.71
LOI 1050 °C	33.20	31.96	26.80	29.10	31.03	34.05	28.48	33.75

TABLE 3. *Concrete mean mineralogical composition.*

Compound	1	2	3	4	5	6	7	8
Dolomite	50	45	45	45	45	45	40	50-55
Calcite	5	5	5	5	5	5	<5	5-7
Quartz	20	15-20	20-25	20	20-25	15-20	25-30	15
Feldspar	5	5	5	<5	5-10	5	5	5
Illite	5	5	5-10	5	-	-	5	5
$Ca(OH)_2$	<5	1-2	<5	2-5	1-2	1-2	2-3	2-3
$Mg(OH)_2$	-	x	?	?	x	?	?	?

The actual concrete mix compositions was obtained using special corrections for chemical, XRD and IR analysis for the mean concrete sample, solubilizated fraction, insoluble and hardened cement paste, (for MgO from dolomite, CaO from dolomite and calcite too, for Al_2O_3, SiO_2, Na_2O and K_2O from soluble illite).

It was possible to approximate the actual mix proportions, table 4, and the actual chemical compositions for the hardened cement paste, table 5.
The coarse aggregate contains 90-95% dolomite, with 3% insoluble, (as 80-85% quartz and 15-20% feldspar), and it has a granular texture. The dolomite grains bigger than 16 mm are frequently fissured with a propagation in the cement paste. The fissuration seems to be in more extent for concrete coming in contact with the water. The reaction zone between dolomite and the hardened cement paste is as "positive" type and the dark colour can be associated with very fine reactive siliceous grains. The dolomite grains have a gradient colour from inside to the reaction zone in correlation with presence of the granular calcite. The calcite is identified among the coarse grains fissures. The cracks' aspects, without filling materials, at the level of the cement paste or near the aggregate, can indicate a leaching phenomenon.

TABLE 4. *Calculated concrete mix compositions.*

Compound	1	2	3	4	5	6	7	8
Total aggr.	85%	80%	90%	80%	85%	75%	85%	85%
Carbonate	63%	63%	56%	63%	59%	67%	53%	71%
Sand	31%	37%	44%	37%	41%	33%	47%	29%
S/C	0.43	0.59	0.79	0.59	0.69	0.49	0.89	0.41
"C"/Aggr.	0.15	0.20	0.10	0.20	0.25	0.25	0.15	0.15

(Total aggr.=The aggregate percentage in concrete; Carbonate, Sand= Aggregate component's percentage normalized for %Total aggr.; S/C= Sand/Carbonate percentage ratio , "C"/Aggr.="Hardened cement paste" / Total aggregate percentage ratio.)

The sand/carbonate ratio may indicate an increasing of the siliceous component, from the initial ratio of 0.33, caused by the calcite exudation on the concrete's surface as allkali-carbonate reaction product produced obtained during the dedolomitization reaction. The brucite content is at the limits of XRD and IR analytical techniques. The MgO content for the hardened cement paste seems to be bigger than the initial limits imposed for the used cement.

TABLE 5. *Chemical compositions calculated for the hardened cement pastes.*

Compound	1	2	3	4	5	6	7	8
SiO_2	18.04	16.12	18.59	18.79	18.24	14.45	16.36	18.54
CaO	55.62	59.18	57.36	57.71	55.23	53.08	66.68	48.64
Al_2O_3	6.67	7.12	9.02	6.79	7.71	5.00	5.27	9.61
Fe_2O_3	3.14	3.00	3.74	5.14	3.64	3.15	3.10	5.83
MgO	9.54	9.53	6.13	7.14	12.61	19.93	5.43	8.16
SO_3	5.82	3.76	3.62	4.36	2.74	3.15	2.17	6.89
Na_2O	0.72	0.65	0.68	0.71	0.72	0.68	0.49	1.07
K_2O	0.59	0.71	0.74	0.79	0.78	0.55	0.38	0.97
Na_2O_{eq}	1.10	1.11	1.15	1.22	1.23	1.04	0.74	1.69

The fine aggregate, < 3mm, contains quartzite, illite, feldspar, and there were identified tipical aspect for ASR, specialy for quartzite.

The study of the old repports, (10-15 years ago), indicated that the problem of AAR was either unknown and/or neglected. Based on the actual state in the AAR field, it is possible to afirm that the ACR and ASR deterioration began after two years of service. The contractor assessed laboratory findings with other physico and mechanical tests and concluded that reparations are needed, being also proposed the closing of the exploiting carrier for future hydrotechnical constructions in the region of Dragan-lad.

CONCLUSIONS

The ASR diagnosis involves the use of a complex and elaborated analytical step-by-step procedure. For that it was created a specially physico-chemical algorithm wich involve Optical Microscopy, Chemical X-ray Fluorescence Analysis combined with wet techniques, X-ray Diffraction, Infrared Spectroscopy, Differential Thermal Analysis, Scanning Electron Microscopy with secondary and backscattered electrons and electron microanalysis. It is not possible to indicate a versatile technique, and that is why we tried all possible information and analytical criterion, including site observations and testing, a close cooperation with the constructor, a transfer of actual level of the knowledges of ASR. There are signs that some of Romanian constructions may prescrit ASR and ACR damages, but it is not only the laboratory who decides the final diagnostic. The procedure was tested for dams, roads, industrial constructions and monuments.

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