

ALKALI-AGGREGATE REACTION EXPERIMENTS IN ISRAEL

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ABSTRACT

Four concrete aggregate samples were tested: (1) A Mediterranean Sea quartz-sand; (2) A calcite dolomite from "Shefar-Amm", a large Israeli rock-quarry; (3) A limestone containing ~ 4% SiO₂, from a north Israeli rock quarry; (4) A complex mixture of stones, from a south Israeli river basin quarry, containing various proportions and types of amorphous SiO₂ and carbonates. Mortar or concrete specimens, containing per cubic meter 1.5 -7.5 kg Na₂O equivalent, have been prepared and tested:

The samples have been tested for AAR using five known standard methods: (I) The 24 hour chemical method; (II) The two week "NBRI" test (immersion of mortar bars in 1N NaOH solution at 80°C, with periodical length change measurements); (III) The long term (2 years) mortar bar expansion method, at 38°C in 100% relative humidity; (IV) The same as in "(III)" but on concrete prisms; (e) The same as in "(IV)" but at 22°C. A major difficulty was finding a technique to allow an equal distribution of the air humidity to cover all the sides of the specimens.

The following results have been obtained: (1,2) The quartz-sand and the calcite dolomite samples are not reactive; (3) The silica including limestone might be dangerous to use. Its expansion kinetics on concrete prisms, suggests a new case of "strong late expanding alkali-silicate/silica reaction"; (4) The mixture of silica & carbonate river stones might be dangerous to use, being suspected of a strong alkali-silica reactivity. A discussion is made on the AAR development conditions specific in Israel and on the significance of the standard AAR laboratory methods.

Keywords: Aggregate, Alkali-reaction, Carbonate, Concrete, Durability, Israel, Portland cement, Silica, Silicate, Standard requirements, Test methods.

INTRODUCTION

The Israeli standard specifications for mineral aggregates (IS-3) for Portland-cement (IS-1), the Concrete Code (IS-466) or other standards do not dwell on the AAR problems, the possibility being of deleterious alkali-reactive aggregates or do not limit a maximum amount of alkalis in the cement or in the concrete. The cement users are generally unaware of AAR and its possible effects on the durability of the concrete structures, as was the case some 10 years ago in Belgium [Van Gemerth.1989], in the United Kingdom [Hoobs.1989], in Japan [Okada.1989] and in other countries where awareness on AAR arose. The authors of the present paper contend that AAR research is important in Israel since various concrete aggregates may be suspected of different types of potential reactivity (alkali-silica, alkali-carbonate etc.). The present paper reports the results obtained after some four years of AAR research in Israel.

DESCRIPTION OF TESTED AGGREGATES

(1) A non alkali-reactive quartz-sand extracted from the Mediterranean seaside near the city of Ashdod, containing ~94% SiO₂. The sea sand is frequently used in the manufacture of concrete as a part of the fine aggregate to improve the workability of the fresh concrete made with crushed aggregate. In the manufacture of laboratory mortar bar and concrete prisms, the 0.15-0.60 mm sea sand was graded together with the 0.60-4.75 mm aggregate 2,3or4 bellow, according to ASTM C227.

(2) The Shefar-Amm aggregate is a calcitic dolomite (ASTM C294). Chemical analysis [Harel.1990] gave the following stoichiometry: 87.3% CaMg[CO₃]₂ (dolomite); 12.1% CaCO₃ (limestone); 0.30% SiO₂; 0.06% Na₂O+K₂O; 0.19% Al₂O₃+Fe₂O₃. Alkali-carbonate reaction is theoretically possible.

(3) A limestone aggregate sample containing ~4% SiO₂ that turned out to be particularly interesting for alkali reactivity research. This sample, supplied from a quarry situated in the north of Israel, was known to be a "pure limestone" and was considered to be a comparative blank (non alkali-reactive) sample. *The chemical analysis corroborates the assumption of non-reactivity:* The sample is not suspected of alkali-silica reactivity since it contains less than 5% insoluble residue in HCl [Fournier & Berube.1993] and is not susceptible to alkali-carbonate reactivity according to a new CSA test, consisting of plotting on a graph, the CaO/MgO ratio as function of the Al₂O₃ content: for a CaO/MgO ratio ≥ 24 and for a content of ≤ 0.37% Al₂O₃ the sample is placed on the non ACR zone of the graph (CSA A23.2-26A-94) The limestone sample was studied by several AAR methods which led to inconclusive results. *The non-reactivity assumption was finally refuted* when our investigations comprised simultaneously: (a) high alkali content concrete specimens, stored in 38°C wet air; (b) measurements at late ages (11 months and more); (c) testing by the AS/SR version of the concrete prism expansion method. *For the above conditions, concrete containing this aggregate, does show a strong late-expanding alkali-silicate/silica reaction.*

Note: The former edition of the CAN/CSA-A.23.1-M90&CAN/CSA-A.23.2-M90 including the AAR regulations (as A23.1-90-Appendix B or A23.2-14A) were replaced in June 1994 when our concrete specimens were 18 month old. The AS/SR designation no longer exists in the new edition.

(4) Aggregates from a South Israeli (Negev) river basin quarry, representing a *complex mixture of stones* containing various proportions and types of amorphous SiO₂ and carbonates (amorphous silica minerals colored from bright brown to white, hard limestone - bright colored, hard dolomite - brown colored) or *fragments of the above described stones* (silica stone with chalk and limestone inclusions, chalk and limestone with or without silica inclusions, and calcitic dolomite). A visual examination of the laboratory sample, shows that a third of the coarse aggregates (grain size 14-19 mm) granules are silica minerals or carbonates including silica minerals. The sample is strongly suspected to be potentially alkali reactive, especially for ASR.

EXPERIMENTAL PROCEDURES

The 24 hour ASTM C289 chemical test with an altered graph (Fig.1)The test consisting of the immersion of graded aggregate sample in 1N NaOH solution for 24 hours at 80°C, is followed by chemical analysis of the filtered solution for dissolved silica (Sc) and for reduction of alkalinity (Rc). The results are plotted on a graph

showing four regions of aggregates: (A) "innocuous"; (B) "generally non-reactive", but in this field the interference of carbonates in the reaction between SiO_2 and NaOH leading to inconclusive results requiring long term mortar bar or concrete prism expansion methods; (C) "highly reactive, potentially deleterious", but if the pessimus (worst) percentage of reactive silica is exceeded, the mortar bars might display non significant expansions; (D) "deleterious reactive". The original ASTM C-289 graph comprises only three regions, the (A+B) region being considered innocuous. The ASTM chemical test was excluded from the last CAN/CSA. We think that it should be considered as a more suitable alternative method for future AAR test of siliceous limestone aggregates. The alternative method consists of performing the ASTM procedure on the insoluble residue obtained by dissolution of the carbonates in concentrated hydrochloric acid [Dron.1992, Berube & Fournier.1993]. In order to find the worst proportion of reactive particles the chemical method has been altered in the French standard NF-P18-589.

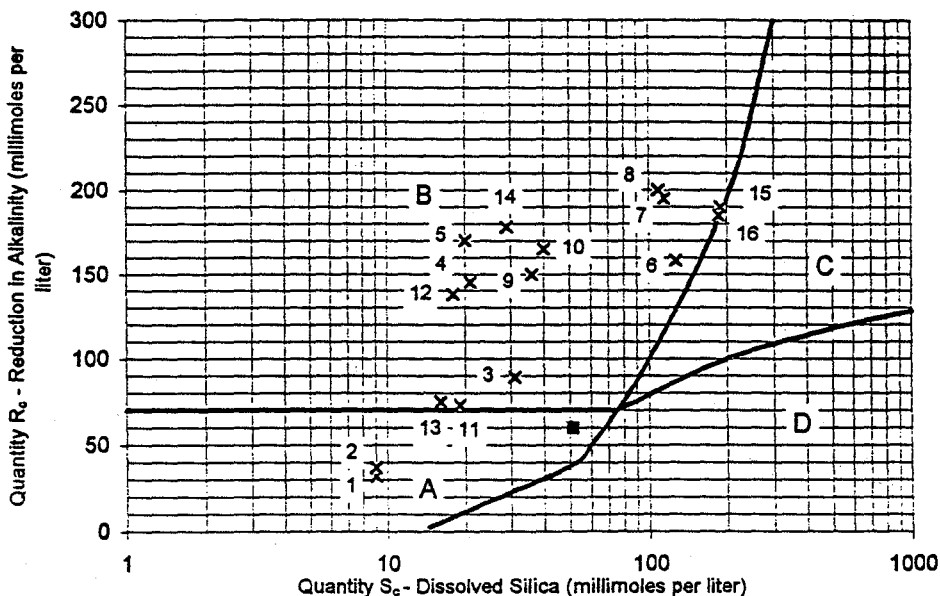


Fig.1 Evaluation of the AAR results by the 24 hour chemical method ASTM C289 with an altered graph. S_c is plotted on a logarithmic scale [Bredsdorf et al 1960, Romanian Standard STAS 5440]:
x1...x5 - Limestone aggregate samples, **x6...x16** - Aggregates from a river basin quarry
x6...x8 - 20% silica stones + 40% carbonates + 20% sea sand, **x9 & x10** - 6% silica stones + 54% carbonates + 20% sea sand, **x11 & x12** - 60% carbonates + 40% sea sand, **x13 & x14** - 100% carbonates, **x15 & x16** - 100% silica stones ■ - Sea sand sample from Ashdod

(II) The 2 week NBRI mortar bar test (ASTM C1260 or CSA A23.2-25A). Mortar bars, 25 by 25 by 285-mm ASTM C227, are maintained at 80°C , one day in water up to the zero reading and afterward in 1N NaOH solution. Fournier & Berube (1993) and CAN/CSA A23.1-94. Appendix B suggested the following mortar bar expansion limits

in 14 days: $<0.10\%$ for innocuous aggregates and $\geq 0.15\%$ for deleterious aggregates. Shayan et al (1988) suggested that: (i) mortar bar expansion of 0.10% in 10 days and 0.10% in 22 days to be taken as indicating reactive aggregate of short induction period and long induction period, respectively; (i,i) for some slowly reacting carbonate rocks a concrete prism test is more suitable than mortar bars for assessing alkali reactivity.

(III) The long term mortar bar test. (ASTM C227 and CAN/CSA A23.1-90. Appendix B). The reactivity limits are 0.05% at 3 months or 0.1% at 6 months or more, for mortar bars with high alkali content (1.25% Na_2O equivalent relative to the cement weight or $7.5 \text{ kg Na}_2\text{O}$ equivalent per 1m^3 of mortar) maintained at 38°C , in wet air According to [Hooton & Rogers.1989] the absorbent material used in the ASTM containers might cause diminished expansions due to the alkali-leaching of the mortar bars. The test is not included in the 1994 edition of CSA Standard. For our future work we consider an alternative method which would replace the mortar bars 25 by 25 by 285 mm with mortar prisms 40 by 40 by 160 mm according to the European RILEM experience [Grattan-Bellew.1989] and to the Japanese standard JIS A 5308..

(IV) The long term concrete prism expansion methods. Two versions (ACR and AS/SR) of the former CSA A23.2-14A, and the French Standard NF P18-857 were applied. Each former version of the CSA was intended to test concrete aggregate suspected to suffer from alkali carbonate reaction (ACR) or Alkali Silicate/Silica Reaction (AS/SR). The main difference between the two former versions is the storage temperature of the specimens in moist air, being 23°C for ACR and 38°C for AS/SR. The former CSA was replaced in June 1994 with the new CSA A23.2-14A-M94. The main modifications are: (i) the cement content increased from 310 to 420 kg/m^3 and an alkali content of 1.25% Na_2O equivalent (eq.) by mass of cement, resulting in an increase of the alkali content in concrete from 3.90 to $5.25 \text{ kg Na}_2\text{O eq./m}^3$; (i,i) a 38°C storage temperature in moist air is required for all the specimens, independent of the AAR type. The French standard looks like the new CSA, with a cement content of 410 kg/m^3 , corresponding to $5.13 \text{ kg Na}_2\text{O eq./m}^3$ of concrete.

ACR expansions are considered deleterious: depending on the micro-climate to which the structure is to be exposed, if the length change exceeds 0.010% after 3 months or $0.025\text{-}0.040\%$ after 12 months (former CSA); independent of the micro-climate, if the length change exceeds 0.015% after 3 months or 0.025% after 6 months or 0.030% after 12 months (ASTM C1105). *AS/SR expansions were considered deleterious by the former Canadian standard,* depending on the micro-climate to which the structure is to be exposed, if the length change exceeds $0.040\text{-}0.075\%$ after 12 months. *The new Canadian Standard considers that expansions are deleterious,* independent of the AAR type, if the length change exceeds 0.040% after 12 months, noting that "in critical structures such as those used for nuclear containment or large dams, a lower expansion limit may be required" (CAN/CSA A23.1-94. Appendix B). *The French test conditions* [NF-P18-589] are more strict than the Canadian. To the best of our knowledge there are no French standard limits for critical AAR expansions, a 0.040% limit at 8 months seems to be accepted by scientists to indicate reactivity but it is still being discussed [Corneille & Bollotte.1994]. However it seems that the interpretation of the French test results is covered by the Canadian standard limits.

In the future *significant AAR compositions for mortar bars and concrete prisms methods* are to be prepared taking into account the experimentally found worst pessimum") content of the reactive particles (NF-P18-589 and Corneille & Bollotte.1994)

AAR STUDIES ON MEDITERRANEAN SEA QUARTZ- SAND

The samples of Mediterranean Sea quartz-sand are placed in region A, "innocuous aggregates" of the ASR reactivity graph (Fig. 1)

AAR STUDIES ON SHEFAR-AMM CALCITIC DOLOMITE

All the four AAR test methods gave results that did not indicate alkali reactivity for the investigated concrete aggregate sample.

AAR STUDIES ON SILICEOUS LIMESTONE AGGREGATE

The methods I, II and III gave inconclusive results or gave results that did not indicate alkali-reactivity for this aggregate. Only the fourth method (IV) showed under certain conditions deleterious alkali- aggregate reactivity.

(I) The 24 hours chemical test ASTM C289 On the graph (Fig.1) five tested samples are placed as follows: two samples in region A, three others on the doubtful region B, due probably to the presence of carbonates interfering with the reaction between NaOH and the dissolved silica. In order to clarify if the tested aggregate is reactive, long term tests (III) or (IV) are required by ASTM C33.

(II) The 2 week NBRI mortar bar test After 14 days of storage at 80°C in 1N NaOH solution, an average expansion of 0.08% was recorded showing no alkali reactivity for the tested concrete aggregate.

(III) The long term mortar bar test ASTM C227 Even for mortars with high alkali content, obtained by adding NaOH in the mixing water, the length changes were small (up to 0.013 % in 2 years), less than the reactivity limits

(IV) The long term concrete prism expansion methods

Concrete mixtures, experimental variants and results. These studies comprise four concrete mixtures and six experimental variants (Table 1). Each experimental variant was labeled with the name of the concrete mixture (M1, M2, M3 or M4) and the temperature (in °C) of the wet air environment in which the specimens were stored. Storage temperatures were 22°C or 38°C. The experimental variant M4/38 is in accordance with the requirements of the new Canadian and French specifications

According to the specifications of the ACR version of the former Canadian standard, the small length changes recorded for specimens M4/20, prove that the tested aggregate is not alkali carbonate reactive, resulting logically from the chemical analysis according to the new CSA requirements(CSA A23.2-26A-94). Fig. 2 shows the length changes vs. time up to 2 years for the six experimental variants. The length changes for each specimen of the experimental variants M1/22, M1/38, M2/38, M3/22 and M4/22 are small, sometimes within the error of measurement, and they are placed on the hatched surface. Trying to distinguish, at different ages, the non-reactive, the marginally or the very reactive aggregates, the expansion kinetics of each of the three specimens of the experimental variant M4/38 is compared with Canadian characteristic AAR expansion curves comprised in the former CSA. This comparison shows that the tested aggregate generates a strong late-expanding alkali-silicate/silica reaction. It is also obvious that in comparison with the Canadian limits the beginning of the expansions appears much later and in a sudden manner at ~11 month, with subsequent expansions developing abruptly to very high values.

Table 1 Concrete mixtures and experimental variants for AAR testing

Name of the concrete mixture	M1	M2	M3	M4
Water-cement ratio (w/c)	0.63	0.62	0.54	0.52
Portland Cement content in concrete (kg/m ³)	310	310	410	410
Additional alkalis through the mixing water	No	Yes	No	Yes
Alkali content (as Na ₂ O equivalent) provided from the cement and from the mixing water				
-Relative to the cement weight (%)	0.47	1.25	0.47	1.25
-Relative to the concrete (kg/m ³)	1.46	3.90	1.93	5.13
Slump of the fresh concrete (mm)	0	0	~80	~80
Density (kg/m ³)	2360	2350	2350	2370
Compressive strength (MPa):				
-7 days	31	21	38	23
-28 days	42	34	55	34
-180 days			66	59
Average expansion at 2 years (%):				
-Storage in 100% humid air at 22±2°C	-0.005	-	-0.008	0.002
-Storage in 100% humid air at 38°C	0.007	0.011	-	0.188
Negative (-) values represent shrinkage changes				

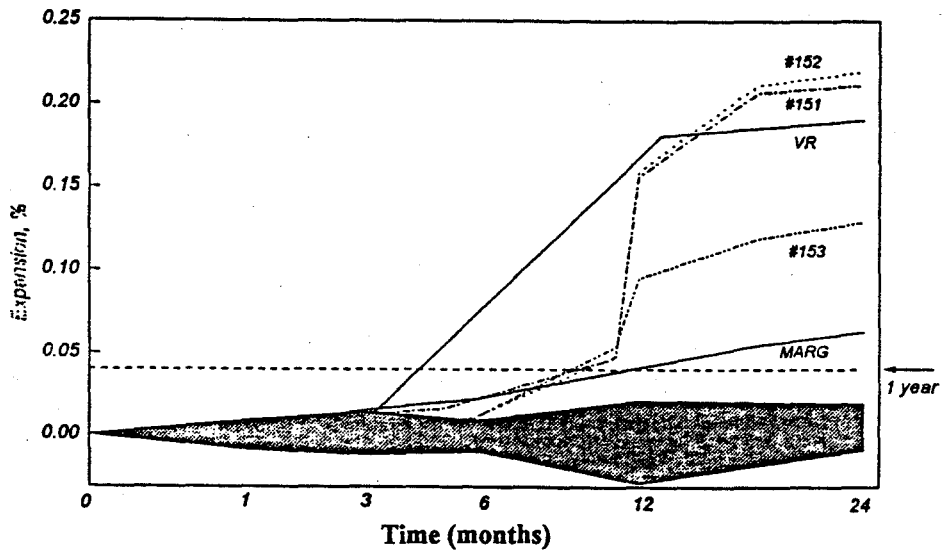


Fig 2 Expansion kinetics for the experimental variants studied, compared with the Canadian "characteristic expansion curves for concrete prisms made with the greywacke-slow/late-expanding alkali-silicate/silica reactive aggregates" (time is plotted on a square cubic root, the graph is adopted from page 100 of the former CSA A23.1-90): MARG - Expansion behaviour of marginal reactive AS/SR aggregate; VR - Expansion behaviour of very reactive AS/SR aggregate #151, #152, #153 Expansion kinetics for each of the three M4/38 specimens; The hatched surface - Expansion kinetics for M1/22, M1/38, M2/38, M3/22 and M4/22).

AAR STUDIES ON A SOUTH ISRAELI (NEGEV) RIVER BASIN QUARRY

(I) **The 24 hours chemical test ASTM C289.** Eleven mixtures were tested: The results are plotted on the Sc/Rc graph (samples 6 to 16, Fig. 1). All the 11 samples are placed in zones B and C, with a recommendation to study that reactivity by accelerated and long term expansion methods.

(II) **The 2 week NBRI mortar bar test.** An average thermal expansion of 0.066% was recorded for mortar bars after 24 hours of storage at 80°C in water. From the "zero measurement", the average expansions recorded for the bars stored at 80°C in 1N NaOH solution were: 0.078% after 7 days; 0.112% after 10 days; 0.120% after 11 days; 0.143% after 14 days. The expansion values after 14 days exceeds 0.150% for three of the eight bars studied at the same time. The expansions are at the limit of the deleterious values according to CAN/CSA A 23.1-94 and according to the limits suggested by Shayan et al (1988).

(III,IV) **Long term expansion methods.**

Mortar bar test ASTM C227 For mortars with high alkali content, obtained by adding NaOH to the mixing water (up to 1.25% relative to the cement mass), the recorded average expansions were : 0.029% after 6 month, 0.038% after 12 month, 0.035% after 24 month. The recorded expansions are under the limits of 0.1% at 6 month..

Concrete prism expansion methods Expansions measurements were performed on prisms prepared with 410 kg. cement per cubic meter of concrete. The alkali content was increased up to a Na₂O equivalent of 1.25% relative to the cement mass by the addition of NaOH to the mixing water. For storage in a humid air at 22°C the length changes are small, within the error of measurement. For the concrete prisms stored in humid air at 38°C, the following average expansions were recorded: 0.025% after 6 months, followed by a stabilized expansion of 0.034-0.042% up to 30 month. According to CAN/CSA, the expansions are at the limit of deleterious expansion. *The very heterogeneous composition of the quarry* does not allow us to reach definite conclusions regarding the reactivity of all the aggregates in the quarry.

DISCUSSION

One can summarize the first AAR results obtained on Israeli aggregates as follows:

- (1) Four aggregates were tested, two of them might be dangerous to use: a limestone including ~4% silica and a mixture of silica & carbonate river stones. Consequently, it is highly recommended to continue and to develop the AAR studies in Israel.
- (2) The long term expansion kinetics of concrete prisms with the limestone aggregate suggests a new case of "strong late expanding alkali-silicate/silica reaction". This behaviour was not foreseeable by accelerated test methods and becomes obvious after some 11 months of measurements. Based on a detailed AAR study of Quebec rock-quarries, Fournier & Berube (1993) concluded that carbonate aggregates containing less than 5% insoluble residue or involving expansions less than 0.1% after 14 days in the NBRI method are innocuous. However, our limestone concrete aggregate sample which passed both requirements is a deleterious aggregate. Unfortunately, the field of validity of each accelerated test method depends on the chemical, physical and geological peculiarities of the tested aggregate.
- (3) The mixture of silica & carbonate river stones might be dangerous to use, being suspected of a strong alkali-silica reactivity.

For future AAR research based on the results shown here we would propose the following: (i) improvements to the NBRI mortar bar expansion method [Shayan et al.1988] and the use of autoclave methods [Fournier & Berube(1993) and the French standard NF P18-590]are to be taken in account to predict the AAR behaviour of slowly reacting aggregates; (i,i) alternative methods to the 24 hours ASTM chemical method,described in the "EXPERIMENTAL PROCEDURE", are to be taken in account for the AAR test the reactivity of the carbonate aggregates.

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