

# RECLASSIFICATION OF ALKALI AGGREGATE REACTION

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## Abstract

The paper present a new classification system based on “reactivity rate” and “negative lists” of reactive constituents and aggregates designated “very fast reactive AAR”, “fast reactive ASR” and “slow reactive ASR”. The paper discusses the reaction mechanisms for alkali silica reaction (ASR) and suggests that the reaction mechanism for slow reactive aggregates are different compared to fast reactive aggregates and occur in five stages. The group “very fast reactive AAR” includes argillaceous dolomitic limestone supposed to be Alkali Carbonate Reactive (ACR) and certain very unstable siliceous constituent suggested to be Alkali Silica Reactive (ASR) and is not recommended to be used in concrete without special precautions. For the group “fast reactive ASR” and “slow reactive ASR” precautionary measures are suggested as guidance.

**Keywords:** Concrete, Alkali Aggregate Reaction, classification, reaction mechanism, precautionary measures

## 1 INTRODUCTION

Alkali Aggregate Reaction (AAR) is a complex chemical-physical reaction between constituents in the cement paste (hydroxides and alkalis) and certain alkali reactive minerals/aggregates in the concrete. The reaction may lead to volume expansion, cracking, loss of strength, and in extreme cases to the complete "destruction" of the concrete. It is important to note that AAR is a concurrent chemical reaction and physical volume expansion depending on mineral/aggregate types, aggregate sizes, and constituents in the cement paste (sodium ions, potassium ions and hydroxides), humidity, temperature and time. AAR is traditionally subdivided into 3 subgroups based on supposed different reaction mechanisms and expansion mechanisms, namely 1) Alkali Silica Reaction (ASR), 2) Alkali Silicate Reaction (ASiR) and 3) Alkali Carbonate reaction (ACR). The traditional explanation of the reaction mechanism of the two last reactions (ASiR) and (ACR) are questioned today and supposed to none exist or not to be the mechanism causing expansion of concrete.

ASR which by several publications include both “fast reactive” and “slow reactive” aggregates, is generally supposed to be caused by same chemical reaction and same expansion mechanism even the behaviour in concrete and microscopic evident/observations are different. It is obvious that a new classification system of AAR not based on the traditionally chemical reaction- and physical expansion mechanisms, which in many cases not is fully understood, is needed. Therefore the author present a new classification system of AAR generally based on reactivity rates and type of reactive minerals/aggregate rather than the traditionally reaction- and expansion mechanism. The suggested reaction types are: 1) very fast AAR, 2) fast reactive ASR and 3) slow reactive ASR. Fast reactive ASR and slow reactive ASR with some variations in the naming are well-established terms in the literature and as earlier mentioned supposed to have same reaction- and expansion mechanism which is not the case as explained in the paper.

Today “negative” list of reactive minerals/constituents or reactive rock types designated either fast reactive ASR or slow reactive ASR (or alkali carbonate reactive (ACR)) has not been published to the authors knowledge. This paper suggest classification of alkali reactive minerals/constituents and rock types to be included in the subgroup “very fast reactive”, “fast reactive” and “slow reactive” mainly based on the “negative lists” from RILEM AAR-1 (2003), Annex A.1.2 and A.1.3 [1].

For preventive and remedial measures it is important to have an updated classification system who distinguishes on how deleterious and how fast the reaction in worst cases might be and by which type of minerals and rock types in the concrete. For documented very fast reactive aggregates preventive measures are at present time unsuccessful and these types of minerals/aggregates should therefore not be used as concrete aggregate in outdoors exposed structures with humidity higher than 80 % relative humidity; except in cases long time full scale test shows the concrete is durable. Laboratory tests are not sufficient documentation and should be assessed very carefully.

## 2 HISTORY

AAR is first mentioned in the literature by Thomas Stanton in 1940 [in 2] who explained the causes of map cracking which occurred in several structures situated in California. During intensive research in the 1940s structures with AAR were discovered in several other places in the USA, and other types of alkali reactive aggregate were identified by petrographical investigations and laboratory tests.

A "black list" of alkali reactive aggregates and minerals was published by Mielenz 1947 [3]. These alkali reactive aggregates contained one or more of the following components: Opal, chalcedony, volcanic glass, devitrified glass, tridymite and possible hydromica. In the late 1950s and 1960s some reports about unidentified cement-aggregate reactions considered to be different from traditional AAR were published [4]. The structural effects of these unidentified AAR seems to be quite like traditional AAR which indicates that the mechanism of the reactions (in principle) should be the same as traditional AAR, e. g. , developing chemical alteration of aggregate particles, which leads to enlargements causing pressure and eventually structural disruption. Two different aggregate types seem to be involved in this unidentified cement- aggregate reaction, namely predominantly siliceous aggregates essentially composed by granite, quartz and feldspar - Lerch 1959 [in 4] and coarse argillaceous dolomitic limestone aggregate Swenson 1957 [5].

From a five year study beginning in 1965 in Nova Scotia, Canada the rock types argillite, phyllite and greywacke were found to be alkali reactive and Gillott 1973 [6] hypothesises that the expansion was caused by a vermiculite like mineral in the reacted aggregates. Gillott [7, 12] suggested that the AAR should be subdivided into three main types termed: 1) alkali-silica" reaction, reactive constituent are meta stable silica as listed by Mielenz 1947 [3], 2) alkali-carbonate reaction, reactive constituents are impure dolomitic limestones and 3) alkali-silicate reaction, reactive constituents are argillite, phyllite, greywacke and possibly some granitic rocks and quartzite. The expansive constituent in phyllite and greywacke is believed to be a vermiculite like mineral.

In the seventies several international publications confirmed that more stable siliceous rocks could be alkali reactive, e.g. granite, quartzite, schist and sandstone. Lists of reported alkali reactive aggregates were published by Coull 1981 [8] and by Dolar-Mantuani 1983 [9]. The alkali reactive constituent in the "more stable" siliceous aggregates are suggested to be crypto/microcrystalline quartz, strained/granulated quartz and/or possible certain feldspar.

The Canadian Standard association, 1986 [10], renamed the alkali- silicate reaction to "Slow/Late-Expanding Alkali- Silicate/Silica Reaction (SLEASS)". The reaction is distinguished from the "classical" alkali-silica reaction by a delayed onset of expansion of concrete test prisms and the very long time span (which may be up to 20 years) before cracking becomes evident in concrete structures. Strained quartz is thought to be one reactive component in many of these alkali reactive quartz bearing rocks. In Norway a national research 1990-1993 [11] showed that all discovered alkali reactive aggregates are SLEASS type. Most of the SLEASS reactive aggregate types found in Canada have also been observed as reactive in Norway. AAR is today reported in numerous countries around the world, e.g. the USA, Australia, England, Denmark, Canada, Iceland, Germany, New Zealand, South Africa, Japan, India, Italy, Norway, France, Belgium, Sweden, India, Brazil, Argentina, Turkey, Switzerland etc. Latest "negative list" of alkali reactive constituents and rock types have been published in RILEM AAR-1 annex A1 2003[1].

## 3 SUGGESTED CLASSIFICATION

### 3.1 General

AAR is suggested to be divided into the following subgroups which are explained in the following and in table 1, 2 and 3 as: Subgroup 1: very fast reactive AAR, Subgroup 2: fast reactive ASR and Subgroup 3: slow reactive ASR

Subgroup 1 “very fast reactive AAR” include the formerly alkali carbonate reaction (ACR) and some very unstable silica constituents. Because of the uncertainty and ongoing discussion whether ACR is alkali silica reaction or caused by dedolomitization and/or expansion by clay minerals the designation AAR should be used until the reaction mechanisms are clarified and accepted. The damaging effect in concrete occurs very fast from days (laboratory) to less than one year depending on the environmental exposures. Subgroup 2 and subgroup 3 “fast reactive ASR” and “slow reactive ASR” are by most publications supposed caused by the same reaction and expansion mechanism but as suggested in the paper the expansion mechanism in slow reactive aggregates is different from fast reactive aggregates as well as the behaviour in concretes and use of efficient preventive measures. Fast reactive ASR shows damaging effect generally within few years but for slow reactive ASR it sometimes takes 10 years or more before sign of AAR can be observed in the concrete.

It has to be mentioned that climatic conditions differ significantly between countries as well as the micro climates around the structures and therefore differences on reaction rates and reaction pattern should be expected. Classification of aggregates and naming can be different too, due to different geological traditions. Internationally one should therefore expect “differences” in the behaviour of the reaction, differences in the rate of the reaction and type of reactive aggregates with same name. Even differences are expected to occur internationally the characteristic of the reaction and type of minerals/rock type between the reaction types is more or less similar.

### **3.2 Very fast reactive AAR**

Deleterious damage occurs from few days (in laboratory) to less than one year in structures. The reaction mechanism are alkali carbonate reaction (some researcher believe this is alkali silica reaction) and alkali silica reaction. Reactive minerals/constituents are fine dolomite crystals?, expansive clay minerals?, disseminated sub microscopic opal/quartz/chalcedony, certain siliceous volcanic glass (hydrated or devitrified), certain artificial glass and possibly in rare cases cristobalite and tridymite. Reactive rock types are certain argillaceous dolomitic limestone (ACR), certain rhyolites with volcanic siliceous glass, artificial alkali-silica rich glass and undispersed silica dust, see table 1. Undispersed silica particles have reacted deleterious in laboratory test cubes stored in water at 20 °C with crack widths up to 3 mm after 7 days, Jensen 1989 [28]

### **3.3 Fast reactive ASR**

Deleterious damage in structures occurs mostly within 10 years. The chemical reaction mechanism is alkali silica reaction and expansion by water uptake of swelling gel. Reactive minerals/constituents are opal, opaline silica, chalcedony, chalcedonic silica, certain volcanic and artificial glass and cryptocrystalline quartz. Reactive rock types are siliceous limestone, metamarl, opaline sandstone, rhyolite, andesite, basalt with glass or opal, porous flint, certain chert and flint or any rock containing sufficient content of the reactive minerals, see table 1.

### **3.4 Slow reactive ASR**

Deleterious damage in structures occurs after more than 10 years. The chemical reaction mechanism is alkali silica reaction and expansion mechanism from crystallisation pressure caused by cryptocrystalline reaction products inn reacted aggregate and less by water uptake of swelling gel. Reactive minerals/constituents are cryptocrystalline and microcrystalline quartz, highly strained quartz with sub grain development and re-crystallized quartz. Reactive rock types are sandstone, siltstone, clay stone, phyllite, argillite, quartzite, mylonite, cataclasite, metarhyolite, certain greywacke, certain hornfels, certain granite and

gneiss or any rock containing sufficient content of the reactive minerals, see table 1. Many of the reactive rock types were formerly included in the subgroup “alkali silicate reaction” (ASiR) but this term is not recommended to be used because the reaction mechanism suggested by Gillott 1975 [7, 12] not has been confirmed by later research. The reactive rock types are the same as SLEASS type suggested by Canadian researcher.

#### **4 CHARACTERISTIC OF REACTIONS**

The behaviour in concrete and microscopic observations differs often significantly between the reaction types as described in table 2 and the following.

##### **4.1 Very fast reactive AAR**

For very fast reactive siliceous constituents and rock types the behaviour and microscopic observations are similar to fast reactive ASR except the rate of reaction and used of preventive measures which in most cases not is efficient. Siliceous very fast reactive minerals/aggregates are described further under fast reactive ASR. The behaviour in concrete and reaction signs caused by argillaceous dolomite limestone (ACR) differ significantly from other alkali reactive aggregates and is described in the following. It has to be mentioned that ACR worldwide is rather rare and often only some few beds in same quarries are ACR reactive. Reactive argillaceous dolomite limestone contains often (but not always) disseminated fine dolomite rhombs and sometimes clastic quartz and feldspar particles. In concrete the reaction is caused by coarse particles and pessimum relation is not observed. Concrete expansion test show rapid expansion curves. In microscope peripheral inner calcite rims and outer calcite rim in the contact zone to the cement paste sometimes occur. Generally reaction products are difficult to observe in thin section but can sometimes be observed (e. g. gel in cracks) by large magnifications. Internal cracking and cracks running out in cement paste are easily observed in UV-light (fluorescence impregnated thin section) and confirm the reaction. SEM/EDX analyses are recommended for ACR.

##### **4.2 Fast reactive ASR**

Fast reactive ASR is common worldwide and the behaviour, signs of reaction and the reaction mechanism are well described in published literature. However, as mentioned a clear distinction between fast reactive ASR and slow reactive ASR and mineral-rock types has not been given in the literature to the author’s knowledge. Fast reactive ASR is generally caused by reaction in fine particles in the sand fraction and less common in coarser particles (porous chert). Pessimism relation caused by varying content of reactive constituents and particle sizes has been documented and included in some national recommendations. Characteristic for fast reactive ASR (and very fast reactive AAR) is rapid expansion in most expansion tests. However, some accelerated test [25] does not recommend testing of porous chert because expansion not occur even the aggregate is reactive. By microscopy amorphous gel (sometimes recrystallized) often are abundant in cracks in aggregates and cement paste and air voids. Sometimes a “portland free” zone occurs around reacted aggregates and gel filled cracks due to reaction with siliceous gel and calcium hydroxide (portlandite) in the cement paste. Internal cracking and cracks running out in cement paste is easily observed in UV-light (fluorescence impregnated thin section) and confirm deleterious reaction. Dissolution of constituents internal in reacted aggregates is observed in late stages of the reaction.

##### **4.3 Slow reactive ASR**

Slow reactive ASR is today probably more common and extent world wide than fast reactive ASR. In literature slow reactive ASR and fast reactive ASR are believed to be same reaction even several important differences occur in behaviour and microscopic analyses. In concrete the reaction is caused by coarse particles

(> 1 mm) [11] and pessimum relation is not observed, same as for ACR. Delayed expansion compared to fast reactive aggregates occurs in expansion test but over longer time expansion can be higher than fast reactive aggregates (same in structures). In microscope cryptocrystalline reaction products can be observed in aggregates and in the centre of “larger” air voids. Amorphous gel is seldom observed in reacted aggregates and occurs here in cracks in the contact zone to the cement pasta. In reacted slow reactive aggregates often one main crack occurs in the particle. Amorphous (sometimes recrystallized) gel occurs in cracks in cement paste and air voids. In larger air voids filled with cryptocrystalline reaction products amorphous gel is observed peripheral in contact to the cement paste. In many slow reactive aggregate a dense outer rim in the reacted aggregates can be observed in reflected light on polished slaps and UV-light in fluorescence impregnated thin section. Internal cracking and cracks running out in cement paste is easily observed in UV-light (fluorescence impregnated thin section) and confirm deleterious reaction. Dissolution of constituents internal in reacted aggregates is observed in late stages of the reaction.

## 5 REACTION AND EXPANSION MECHANISMS

Reaction mechanisms are shortly described for Alkali Carbonate Reaction and Alkali Silica Reaction in the following. For slow reactive aggregates which have different behaviour and signs of reactions compared to traditionally ASR a sequential development of slow reactive reaction is suggested by Jensen 1993 [11].

### 5.1 Very fast AAR - Alkali Carbonate reaction

The traditional explanation of the reaction mechanism of ACR are questioned today and supposed not to existing or not to be the mechanism causing expansion of concrete. Today 3 different reaction mechanisms are suggested in the literature.

- 1 Dedolomitization and swelling of clay minerals by Gillott 1964 [12]
- 2 Expansion caused by dedolomitization by Tang & Deng [13], Tong [14], Lopez-Buendia 2008 [15]
- 3 Alkali Silica Reaction by Katayama [16]

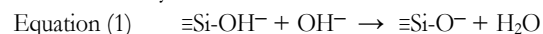
The controversy of alkali carbonate reaction and a state of art on the reaction mechanism is given by Jensen [17, 18] and not discussed further in the paper.

For very fast ASR caused by unstable siliceous constituents - aggregates the chemical reaction and expansion mechanism is supposed to be the same as for fast reactive ASR, but more deleterious, which is described in the following.

### 5.2 Fast reactive ASR - Alkali Silica Reaction

#### *Chemical reaction*

Alkali Silica Reaction was first described by Powers & Steinour 1955 [19a, b] and confirmed by later research. According to Dent Glasser & Kataoka 1981 [20a,b] the reaction can be described in two stages: First a straight acid-base reaction where the hydroxide from the solution reacts with the acidic silanol groups and second “neutralization” by alkali ions. The charge on the terminal oxygen atoms produced in this way is balanced by the alkali ions that simultaneously diffuse into the structure:



If the alkali hydroxide concentration is high enough a further reaction takes place, given enough time:



This reaction not only removes and neutralizes the surface hydrogen ions, but also severs the siloxane bridges that hold the whole mass together and increases its capacity to absorb alkali ions and water. The reaction depends on the concentration and Ph of the solution produced. In the limits, the “mass” disintegrates completely. For poorly crystallized hydrous silica (as opal) which is particularly vulnerable penetration of alkalies and hydroxide into the interior- of the reactive particle is rather fast. In well crystallized or other forms of silica (quartz) the attack of alkalis and hydroxide is

rather slow and mainly takes place at the surface of the particle.

#### *Expansive mechanism*

Powers & Steinour 1955 [19a, b] described the reaction to be determined by reactive silica, calcium hydroxide and alkali in the concrete. The initial attack of alkalis and calcium hydroxides on reactive silica builds up a zone of non-expansive lime-alkali-silica complex around the reactive particle. During further attack on the reactive silica particle, lime and/or alkali diffuse through the non-expansive layer to react with silica. If the ratio of lime to alkali outside the layer is sufficient high, lime is delivered to the reaction site fast enough, and a non-swelling lime-alkali-silica complex (in chemical equilibrium) is produced. On the other hand, if the ratio of lime to alkali is not sufficient high outside the layer a swelling alkali-silica complex which is not in equilibrium with lime is produced. "Expansion is produced when the alkali-silica complex imbibes water. The initial, most damaging expansion probably occurs while the reaction product is still solid, though expansion may occur after the product becomes plastic or fluid, if initially formed cracks have no outlets. The force is that of swelling pressure or osmotic pressure the two being fundamentally alike".

### **5.3 Slow reactive ASR**

#### *Chemical reaction*

The chemical reaction is supposed to be the same as given by Dent Glasser & Kataoka 1981 [20a, b] namely first an acid-base reaction and second neutralization by alkali ions. In well crystallized quartz which is the dominating alkali reactive mineral in slow reactive aggregates the attack of hydroxide ions and alkali ions is rather slow and takes place at the surface of the particle explaining why the reaction takes long time to be deleterious.

#### *Expansive mechanism*

The long time span before reaction can be observed in concrete as well as the observation of dense rims and cryptocrystalline reaction products in reacted aggregates suggest the reaction is different from fast reactive ASR. Typically reaction signs in slow reactive aggregates obtained by petrographical observations (from polished concrete, thin section incl. fluorescence technique and by SEM/EDX) can be summarized in several reaction stages Jensen 1993 [11]:

Stage 1) Initial stage. No sign of reaction is visible.

Stage 2) Development of a peripheral thin rim in reacted aggregate. This rim will be more distinct in later stages of the reaction. The peripheral contact zone between aggregate/cement paste is attacked by aggressive solutions derived from the cement paste. The access of the aggressive solution into the aggregate occurs via the interfaces between mineral crystals/grains located in the contact zone to the cement paste. Due to dissolution of silica and possibly also precipitation of reaction products (in situ) interfacial cracks (and matrix) near the contact zone are tightened or "glued" together and becomes denser. The dense outer rim in reacted aggregate could be considered to act like a semi permeable membrane to the movement of alkali ions, hydroxyl ions and possibly to calcium ions, too, - as suggested by Hansen 1944 [in 19a, b] and Jones 1989 [21].

Stage 3) Development of inter granular cracks in reacted aggregates with and without visible (in thin section) reaction products. Aggressive solutions penetrate further inward via interfacial cracks/matrix and react with the mineral crystals/grains and development of precursor gel which by time recrystallized to cryptocrystalline reaction products. The reaction widens up interfacial cracks between mineral crystals/grains and a premature "main" crack will in most cases be developed (as well as minor cracks) [11]. The main crack will in most cases be oriented parallel to the preferred orientation/lamination of the rock. In homogeneous and granular rocks main crack will be more erratically orientated but will often be developed along and under the dense peripheral outer rim. In later stages cracks will expand in width and length and prolong to the outer edge of the aggregate.

Stage 4) The pressure from precursor gel and recrystallized precursor gel in aggregate exerts the tensile strength of the cement paste and cracks runs out in the cement paste. Precursor gel and/or cryptocrystalline reaction products with origin inside the aggregate "flows" via the main cracks (and other cracks in later stages) into the cement paste and react with aggressive solutions derived in the cement paste. The chemical environment in the cement paste is different from the one in the aggregate and prevents crystallization of the precursor gel. Alternatively cryptocrystalline reaction products transform into amorphous gel when it comes in contact to the cement paste. A significant borderline can often be observed in thin section where cryptocrystalline reaction products occur inside the aggregate and amorphous gel in the contact zone to the cement

paste and in the cement paste. Cryptocrystalline reaction products in "larger" air voids are suggested to be precursor gel who has flowed into these air voids without contact to the cement paste. Therefore these air voids must be adjoining reacted aggregates. Observations in thin sections of larger air voids filled with cryptocrystalline reaction products often show thin amorphous gel linings in the contact zone to the cement paste. Such amorphous gel lining is probably caused by reaction between precursor gel and the cement paste. SEM/EDX investigations also confirm that reaction products from aggregates and "larger" air voids (curettage) more or less are morphologically and chemically similar.

Stage 5) Further volume expansion of the aggregate will enlarge crack(s) and more reaction products is able to flow into the cement paste. In more advanced stages of AAR cracks which are more or less filled with gel, connect other reacted aggregates, with consequence of more severe expansion of the concrete. Due to increased gel production and hereby dissolution of silica minerals, loss of materials in the aggregate, will be visible as enlarged crack(s) and empty spaces.

It has been observed in sawn faces from laboratory concrete prism samples that "precursor" gel exuded from reacted coarse mylonite and metarhyolite aggregates (without contact to the cement paste). By time the gel hardened and cryptocrystalline reaction products developed. SEM/EDX analyses showed that morphologically and chemically the reaction products were similar to the reaction product observed in reacted aggregates from field concrete, but generally contain less calcium [11]. These observations shows that precursors gel first develop internal in the aggregates and by time recrystallized to cryptocrystalline reaction products. It is likely that crystallization pressure from crystallization of precursor gel and cryptocrystalline reaction products is higher than the pressure from precursor gel itself. In later stages of the reaction swelling of amorphous gel in the cement paste will contribute to the expansion of the concrete.

## 6 PRECAUTIONARY MEASURES

Precautionary measures to reduce the risk of AAR are given in many national recommendations and by RILEM Committee TC 219-ACS "RILEM Recommended Specification: AAR-7.1 (Alkali Silica Reaction) [22] and AAR-7-2 (Alkali Carbonate Reaction) [23]. For ACR the key issue is to combating the reaction by identify potentially susceptible carbonate aggregate by a specific techniques given in RILEM-0 Annex A [24] (petrographic analyses and expansion tests according to the accelerated mortar bar test RILEM AAR-2 [25 and RILEM AAR-5 [26]. It is specified that "the primary strategy, given the present level of knowledge and understanding is focussed on identifying and avoiding the use of such aggregates. However, experiences suggest that some dolomitic carbonate aggregates may be usable in concrete in which the cement contains high replacement levels of blastfurnace slag". For Alkali Silica Reaction RILEM AAR-7.1 gives recommendations for aggregate reactivity as "low", "medium" and "high" without specifying which type of mineral/constituents and rock types are included in the groups. The group "low aggregate reactivity" corresponds to the aggregates identified as non-reactive according to RILEM AAR-0. For aggregates containing substantial proportion of opal are likely to be more reactive than "high reactivity aggregates" and should not be used in concrete or should be proven by performance tests etc. Such aggregates fall outside the recommendations.

In this paper precautionary measures for cement alkali content and cement replacement by low lime fly ash and ground granulated blastfurnace slag have been enclosed in table 3 including recommendations from RILEM AAR-7.1 and 7.2. It specifies that these recommendations only should be uses as guidance because several uncertainties occur as mentioned in the paper. In table 3 the group "fast reactive ASR" conform to "high aggregate reactivity" and "slow reactive ASR" to "medium aggregate reactivity" by RILEM AAR-7.1. However because it is not specified which type of reactive constituents and rock type the RILEM groups contains the recommendations should be taken with care as mentioned.

In table 3 the cements equivalent  $\text{Na}_2\text{O}$  is given too. For fast reactive ASR the maximum equivalent  $\text{Na}_2\text{O}$  is suggested to be 0.6 % corresponding to the limit and term "low alkali cement" used many places. According to Rilem AAR-7.1 low alkali cement can generally be applied but for some aggregate types in some regions ASR damages has been reported in concrete specimens made with low alkali cements. For slow reactive ASR the equivalent  $\text{Na}_2\text{O}$  is suggested to be 0.8 % in table 3. This limit is base on long term experience in Denmark where the max. equivalent  $\text{Na}_2\text{O}$  seldom is higher than 0.8 with some few cases on

max. 0.9 %. In Denmark natural aggregate deposits contain various amounts of several types of Norwegian slow reactive rock types which have been transported from Norway to Denmark by glaciers during the Wiesel ice age (ended about 12000 years ago) and intermixed with other local aggregates e.g. flints. During decades numerous petrographic examinations in thin sections of Danish concretes containing slow reactive Norwegian aggregates ASR has never been reported caused by Norwegian slow reactive aggregates. In Denmark fast reactive porous flint from local sources is the main alkali reactive concrete aggregates which have reacted in many concrete structures. It is surprising that recommendations by RILEM and other places not have requirement to the alkali content in cements, but requirements to total amount of alkalis in concretes calculated as kg eq.  $\text{Na}_2\text{O}/\text{m}^3$  concrete. This because alkali silica reaction is a plain acid-base reaction terminated by alkali ions and that the solubility of silica increase exponential towards higher pH values. The concentration of hydroxide ions (pH value), increases significantly with a very good correlation to increased alkali content in cements, as shown by Diamond 1989 [27]. Calculations according to Diamond of the pH value in pore solution from Norwegian high alkali cement with 1.2 weight % eq.  $\text{Na}_2\text{O}$  gives a pH value on 13.92 which is very high and can explain why so many slow late reactive aggregates have reacted in Norway and not in Denmark where the pH value is lower.

## 7 CONCLUDING REMARKS

The paper suggests a new classification system based on “reactivity rates” and type of constituents/aggregates rather than reaction mechanism as former classifications. It is the aims that the new classification system including “negative lists” of reactive constituents and aggregate types and suggested precautionary measures can be used as a technical and practical “tool” for assessing constituents and aggregates for use in durable concrete. Limit values of reactive constituents and aggregates should be based on national experiences and recommendations.

## 8 REFERENCES

- [1] RILEM Recommended Test Method AAR-1 (2003): “Detection of potential alkali-reactivity of aggregates-Petrographic method”, Materials and Structures, vol. 36, Aug.-Sept. 2003, pp 480-460
- [2] Nerenst, P., 1957: “Generell on Alkali Reaction in Concrete”. Committee on Alkali Reactions in Concrete, The Danish National Institute of Building Research and The Academy of Technical Science. Progress Report Serial A No. 1, Denmark (in Danish)
- [3] Mielenz et al. ,1947: "Cement-Aggregate Reaction in Concrete", Journal of the American Concrete Institute, Detroit, Vol. 19 No. 2, pp 93-129
- [4] Bredsdorff,P., et al. ,1963: " Chemical Reactions in Concrete Involving Aggregate" , Special issue 128, Chemistry of Cement, Proceedings of the Fourth International Symposium, Washington, USA, pp. 749-806
- [5] Swenson, E.G. (1957): “A reactive aggregates undetected by ASTM test”, ASTM Bulletin, American Society for testing and Materials, No 226, 1957, pp48-51
- [6] Gillott, J.K. et al. ,1973: "Alkali-aggregate reaction in Nova Scotia IV. Character of the reaction", Cement and Concrete Research, vol. 3, pp 521-535, Pergamon Press, Ltd, USA
- [7] Gillott, J. E., 1975: "Practical Implications of The mechanisms of Alkali- Aggregate Reactions". Proceeding 3th International Conference on Alkali- Aggregate Reaction, Preventive Measures, Reykjavik, August 1975
- [8] Coull , W. A., 1981: "Characteristics and Service Record of Commonly used South African Aggregates". Proceeding 5th Int. Conf. on alkali-aggregate reaction in concrete, Cape Town - South Africa pp 17. S252/37
- [9] Dolar-Mantuani, L.,1983: " Handbook of concrete aggregates-A petrographic and technological evaluation", pp 345, Noyes Publication, USA
- [10] The Canadian Standard association, 1986. Supplement No. 2-1986 to CSA Standards CAN3-A23.1-M77 and CAN3-A23.2 - 77, appendix B
- [11] Jensen V. (1993): “Alkali Aggregate reaction in Southern Norway” Doctor Technicae Thesis, p 262, Norwegian Institute of Technology, University of Norway
- [12] Gillott J. E. (1964): “Mechanism and Kinetic of Expansion in the Alkali-Carbonate Rock reaction” Canadian Journal of Earth Science. Volume 1, 1964, pp 121-145
- [13] Tang Mingshu & Deng Min (2008). Progress on the Studies of Alkali-Carbonate Reaction” Proc. 12<sup>th</sup> Int. Conf. AAR, pp 51-59, Beijing, China
- [14] Tong L. (1994): “Alkali-Carbonate Rock Reaction” Doctor Thesis, Nanjing Institute of Chemical Technology, p 219, Nanjing China
- [15] Lopez-Buendia A.M. et al (2008): “Influence of Dolomite Stability on Alkali-Carbonate Reaction” Proc. 13<sup>th</sup> Int. Conf. AAR, Trondheim, Norway



- [16] Katayama T. (2010): "The so-called alkali-carbonate reaction (ACR). Its mineralogical and geochemical details, with special reference to ASR", Cement and Concrete Research, Volume 40, Issue 4, April 2010, Pages 643-675. Special Issue: ICAAR 13, Trondheim, Norway, June 16-20, 2008
- [17] Jensen V. (2009): "Alkali Carbonate Reaction (ACR) and RILEM AAR-0 annex A: Assessment of potentially reactivity of carbonate rocks", 12<sup>th</sup> Euroseminar on Microscopy Applied to Building Materials, 15.-19. September 2009, Dortmund, Germany
- [18] Jensen V 2012: "The controversy of alkali carbonate reaction: state of art on the reaction mechanism", Proc. 14<sup>th</sup> Int. Conf. AAR, Texas, USA
- [19a] Powers, T. C. & Steinour, H. H., 1955: "An Interpretation of Some Published Researches on the Alkali-Aggregate Reacton. Part 2. A Hypothesis Concerning Safe and Unsafe Reactions with Reactive Silica in Concrete". Journal of The American Concrete Institute V 26 No 8, Title No 51-40, USA
- [19b] Powers, T. C. & Steinour, H. H., 1955: "An Interpretation of Some Published Researches on the Alkali-Aggregate Reaction. Part 1. The Chemical Reactions and Mechanism of Expansion". Journal of The American Concrete Institute V. 26, No 6, Title No 51-26, USA
- [20a] Dent Glasser, L. S. D. & Kataoka, N., 1981: "The Chemistry of "Alkali-Aggregate Reactions". Proceeding 5th Int. Conf. on alkali-aggregate reaction in concrete, Cape Town- South Africa, S252/23
- [20b] Dent Glasser, L. S. D., Kataoka, N., 1981: "The Chemistry of "Alkali-Aggregate" reaction", Cement and Concrete Research, Vol 11 pp 1-9, USA
- [21] Jones, T. N., 1989: "Mechanism of Reactions Involving British Chert and Flint Aggregates" . Proceeding 8th International Conference on Alkali-Aggregate Reaction, July 17-20, Japan, pp 135-140
- [22] RILEM Recommended Specification: AAR-7.1. International Specification to Minimise Damage from Alkali-Reactions in Concrete. Part 1 Alkali-Silica Reaction. RILEM/TC-ACS/11/09
- [23] RILEM Recommended Specification: AAR-7.2. International Specification to Minimise Damage from Alkali-Reactions in Concrete. Part 2 Alkali-Carbonate Reaction. RILEM/TC-ACS/11/17
- [24] RILEM Recommended Test method AAR-0: Outline Guide to be used of RILEM Methods in Assessment of Alkali-Reactivity Potential of Aggregates" RILEM/TC-ACS/11/24
- [25] RILEM Recommended Test Method AAR-2 (2000): "Detection of Potential Alkali-Reactivity of Aggregates: A - The Ultra-accelerated Mortar-bar Test" Materials & Structures, Vol. 33, No 229, 2000, 283-289 (revised edition of AAR-2, including AAR-2.1 & AAR-2.2, in preparation)
- [26] RILEM Recommended Test Method AAR-5 (2005): "Rapid Preliminary Screening Test for Carbonate Aggregates". Materials & Structures, Vol. 38, No 282, 2005, 787-792
- [27] Diamond, S., 1989: "ASR Another Look at Mechanisms". Proceedings 8th International Conference on Alkali-Aggregate Reaction, July 17-20, Japan, pp 83-94
- [28] Jensen V. 1989, Confidential and unpublished results

## 9 TABLES

TABLE 1: Reactive minerals and rock types, <i>list from RILEM AAR-1 2003, ANNEX A.1.2 and A.1.3 [1]</i>		
Reaction type	Reactive minerals	Reactive rock types
Very fast reactive AAR	<i>fine dolomite crystals?, expansive clay minerals?, disseminated sub microscopic opal/quartz/chalcedony, certain siliceous volcanic glass (hydrated or devitrified), certain artificial glass and possibly in rare cases also cristobalite and tridymite.</i>	certain argillaceous dolomitic limestone (ACR), certain rhyolite, tuff and siliceous volcanic rock with volcanic siliceous glass, artificial alkali-silica rich glass and <i>undispersed silica dust</i>
Fast reactive ASR	opal, opaline silica, chalcedony, chalcedonic silica, certain volcanic and artificial glass and cryptocrystalline quartz. Possible alkali contribution from feldspar	siliceous limestone, <i>metamarl</i> , opaline sandstone, rhyolite, andesite, basalt with glass or opal, <i>porous flint</i> , certain chert and flint or any rock containing sufficient content of the reactive minerals.
Slow reactive ASR	cryptocrystalline and microcrystalline quartz, highly strained quartz with sub grain development and re-crystallized quartz. Possible alkali contribution from feldspar.	sandstone, siltstone, clay stone, phyllite, argillite, quartzite, mylonite, cataclasite, metarhyolite, certain greywacke, certain hornfels, certain granite and gneiss or any rock containing sufficient content of the reactive minerals.
<i>Cursive not included in RILEM AAR-1, ANNEX A.1.2 and A.1.3 [1]</i>		
Note 1: Alkali Carbonate Reaction might be alkali silica reaction which exclude dolomite crystals and expansive clays		
Note 2: Many of the slow reactive rock types were formerly included "Alkali Silicate Reaction" (ASiR) and SLEASS		

Reaction type	Behaviour in concrete	Microscopic characteristic
Very fast reactive AAR	<u>Alkali carbonate reaction (ACR):</u> Reaction caused by coarse particles. Pessimism relation not observed. Rapid expansion in concrete expansion tests.  <u>Silicious constituents:</u> same as fast reactive ASR, see next	<u>Alkali carbonate reaction (ACR):</u> Fine dolomite rhombs. Peripheral calcite rim and outer calcite rim in contact zone to cement paste. Reaction products difficult to observe in thin section (but sometimes possible). Internal cracking and cracks running out in cement paste. SEM/EDX analyses recommended <u>Silicious constituents:</u> see fast reactive ASR
Fast reactive ASR	Reaction caused mostly by fine particles and less coarse particles? Pessimism relation caused by varying content of reactive constituents and particle size. Rapid expansion in expansion tests.	Amorphous (sometimes recrystallized) gel in aggregate and cement paste. "Portland free" zone around reacted aggregates and gel filled cracks. Internal cracking and cracks running out in cement paste. Dissolution of constituents internal in reacted aggregates.
Slow reactive ASR	Reaction caused by coarse particles (> 1 mm). Pessimism relation not observed. Delayed expansion in expansion tests.	Cryptocrystalline reaction products in aggregates. Amorphous (sometimes recrystallized) gel in cement paste and contact zone. Dense peripheral rim in reacted aggregates. Internal cracking and cracks running out in cement paste. Dissolution of constituents in reacted aggregates. Main crack in aggregate.

Reaction type	eq. Na <sub>2</sub> O	kg eq. Na <sub>2</sub> O/m <sup>3</sup> concrete	Low lime fly ash, blast furnace slag
Very fast reactive AAR	<i>No limits can be recommended</i>	<i>No limits can be recommended</i>	<i>No precautionary measures are known For some argillaceous dolomitic limestone high replacement of blastfurnace slag</i>
Fast reactive ASR	Max 0,6 %	<i>Min. 2.5 – 3.0</i>	<i>Min. 40 % fly ash replacement Min. 50 % blastfurnace slag replacement</i>
Slow reactive ASR	Max 0,8 %	<i>Min. 3.0 – 3.5</i>	<i>Min. 25 % fly ash replacement Min. 40 % blastfurnace slag replacement Min. 8 % silica fume replacement Min. 15 % metakaolin replacement</i>
<i>Low reactivity (correspond to non-reactive in RILEM AAR-O)</i>	No requirement	<i>None required</i>	<i>Any fly ash replacement Any fly slag replacement</i>

Limits from RILEM AAR-7.1(cursive) [22]. Fast reactive ASR values from "high reactivity aggregates" and slow reactive ASR values from "medium reactivity aggregates". RILEM AAR-7.1 specifies not which types of aggregate are highly reactive or medium reactive so the values shall be used with care.