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Aggregate and SCM Alkali Release

Dam Safety Technology Development Program



U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Denver, Colorado

September 2016

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Dam Safety Technology Development Program
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DSO-2016-03 (8530-2016-23)

Aggregate and SCM Alkali Release

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ACRONYMS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
ASR	Alkali silica reaction
C ₂ S	dicalcium silicate
C ₃ A	tricalcium aluminate
C ₃ S	tricalcium silicate
C ₄ AF	tetracalcium aluminoferrite
EDS	electron dispersion spectroscopy
Na ₂ O _{eq}	equivalent alkalis
RH	relative humidity
SCM	supplementary cementitious material
WDS	Wavelength-dispersive X-ray spectroscopy

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ABSTRACT

This research aims to find a better understanding of how alkalis are released from concrete aggregates and SCMs (mainly fly ash) into the concrete pore solution. This can be accomplished using existing structures information and performing alkali release testing utilizing multiple methods, in particular an electron microprobe analyzer equipped with wavelength dispersive spectroscopy. This testing can provide analytical geochemistry and quantitative microscopy to enhance understanding of how various minerals in concrete aggregates and SCMs release alkalis into concrete pore solution.

For existing Reclamation structures, records have been kept on the materials and proportions used. In this scoping study, a data search has been performed to find relevant structures and information about the initial alkalis present at the time of construction.

KEYWORDS

Alkali-silica reaction, petrography, reactive aggregate

BACKGROUND

Several Reclamation structures have exhibited damage due to ASR. Even with the use of low alkali cements with aggregates identified as deleterious, damage has been evident several years after construction. It has been shown by researchers that alkalis contained in some minerals (namely feldspar, mica, etc.) can leach out over time and contribute to the total alkalis in the pore solution. This can cause ASR to occur in structures that contained low alkali cement. This scoping study reviews Reclamation structures that have been effected by ASR. Material data such as aggregate composition and location, cement chemical composition, and mix design, have been compiled.

Literature Review

Alkali-Silica Reaction

Alkali Silica Reaction (ASR) is a deleterious chemical reaction between alkalis in cement and reactive silica in aggregates [1]. ASR has been studied extensively by Reclamation and other agencies since the 1940s.

ASR is a kinetic-type chemical reaction. In order for the reaction to initiate, a threshold level of alkalinity and moisture must be met. Activation energy is defined as the minimum energy which must be available to a chemical system with potential reactants to result in a chemical reaction. The activation energy of potential reactants (i.e. various aggregate and binder types) can therefore be used to determine whether or not a combination of materials will be reactive or not. Several researchers in the past have used the concept of activation energy to

enhance the results of ASTM C1260 by fitting the expansion with a kinematic-type model [2][3].

It is widely accepted that three criteria must be met in order for the ASR reaction to occur as shown in Figure 1 [4]. Since ASR is a kinetic type reaction, higher temperatures result in faster reaction rates. Concrete can contain reactive silica and sufficient alkalis and initiate the ASR reaction. However, sufficient moisture is essential for the swelling and expansion that causes damage. In the presence of reactive silica and alkalis, ASR gel forms around aggregate particles. When moisture is present, the gel absorbs water due to its hydrophilic nature and expands. The expansion of the gel generates a stress and causes cracking when it exceeds the tensile strength of the concrete.

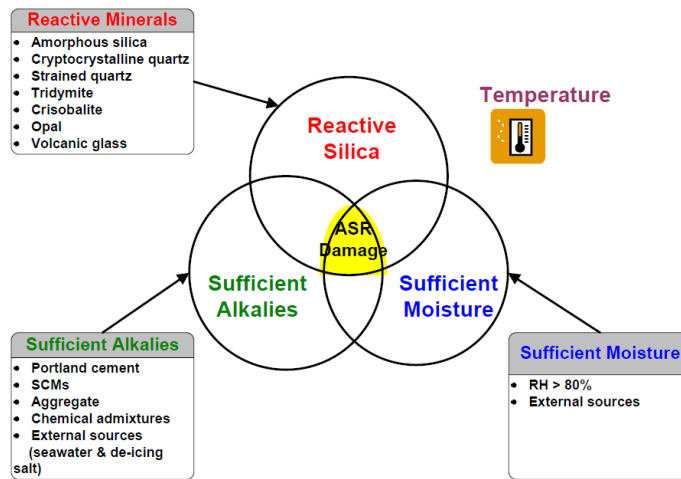


Figure 1. Criteria for ASR damage to occur. Figure from Mukhopadhyay [4].

Many aggregates, both coarse and fine, contain silica or silicate material. Not all forms of silica within the aggregate will result in ASR. In general, metastable silica and alumina-silicate glasses are known to be highly reactive with alkalis in concrete. This includes opal, chalcedony, tridymite, crisobalite, some disordered forms of quartz, and acid volcanic quartz. Forms of reactive silica in aggregates are summarized in Table 3. The form of silica is not the only factor that controls aggregate reactivity. The amount and nature of distribution (homogeneous or inhomogeneous) of reactive constituents can determine whether or not ASR will form. Additionally, the aggregate porosity will influence the ingress of OH^- , Na^+ , and K^+ ions into the aggregate [5]. Higher porosity or pore connectivity increases rate of ASR.

Table 1. Forms of reactive silica in aggregates susceptible to ASR (Mindess et al. [1])

Reactive Component	Physical Form	Rock Type	Occurrence
Opal	Amorphous	Opaline limestone (e.g. Spratt limestone), chert, shale, flint	Common as minor constituent in sedimentary rocks
Silicate Glass		Volcanic glasses (rhyolite, andesite, dacite) and tuffs; synthetic glasses	Regions of volcanic origin; river gravels originating in volcanic areas; container glass
Chalcedony	Microcrystalline Quartz	Silicious limestones and sandstones, cherts, and flints	Widespread
Cristobalite (Tridymite)	Crystalline but metastable	Opaline rocks, fired ceramics	Uncommon
Strained Quartz	Disordered due to strain effects	Metaquartzite, sands, gravel, sandstones, many metamorphic rocks (e.g. granite gneiss and schists)	Common

Sufficient moisture must be present to initiate expansion of the alkali-silica gel. The gel is hygroscopic, meaning it attracts and holds water molecules from the surrounding environment. Under 80% RH, there will be minor expansion, but above 80%, expansion increases exponentially [6]. Even if concrete appears dry, the interior can maintain high RH above 80%.

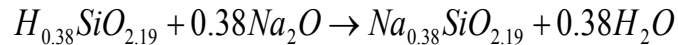
The third factor required for ASR to cause damage is alkalis. Concrete pore solution contains hydroxyl (OH^-) and alkali ions (i.e. Na^+ and K^+). The alkalis come primarily from the cement as alkali sulfates which are immediately released into the pore solution when water is introduced. Supplementary cementitious materials (SCMs), certain aggregates, chemical admixtures, seawater, and deicing chemicals can also contribute additional alkalis. Many researchers have reported a threshold concentration of hydroxyl ions in the pore solution in the range of 0.2M to 0.3M (pH=13.3 to 13.5). A reactive aggregate has low potential to react if the alkali level in the concrete is below the threshold level. Generally, a cement having an alkali equivalent (Na_2O_e) of less than 0.6% is considered “low alkali” cement.

If all three reactants are present in the concrete (reactive silica, water, and alkalis), the reaction will initiate. In general, there are four steps in the chemical reaction:

1. Neutralization of surface silanols of the reactive silica by the alkali base
2. Breaking up of siloxane bonds (Q4) by hydroxyl ions to form Q3 tetrahedrons
 - a. OH^- reacts with Si-O-Si bonds to form silanol bonds

3. Dissolution of silica due to continued hydroxyl ions attack on the Q3 tetrahedron to form silica ions and small polymers
4. “Gelation” of expansive ASR silica gels from the silica saturated pore solution

The entire chemical reaction was summarized by Glasser [7] as:



The ASR product itself is not deleterious, the issues arise when it absorbs water and swells, causing cracking.

Alkali Release from Aggregates or SCMs

Typically, limits are set on the amount of alkalis present in the cement in order to mitigate ASR. Generally, a cement having an alkali equivalent (Na_2O_e) of less than 0.6% is considered “low alkali” cement. However, some structures using a low alkali cement have still exhibited ASR damage [8]. It is possible for aggregates or supplementary cementitious materials (SCMs) to contribute alkalis to the pore solution. With the addition of alkalis, the threshold of 0.2M to 0.3M can be met, even when using a low alkali cement [9].

Several alkali-bearing materials can potentially contribute alkalis to the pore solution of concrete. Feldspar is the most common and has been widely studied. Others include impure limestone aggregate, mica, nepheline, and zeolites [10]. Constantiner and Diamond directly measured the concentration of alkalis in pore solutions from mortars with and without alkali-bearing feldspar [9]. The rate of alkali release from the aggregates was constant for the four months of the test. The study concluded that feldspars do release alkalis into the pore solution of concrete and that they can participate in ASR if reactive aggregates are present. Grattan-Bellew investigated the release of alkalis from limestone aggregate [11]. The limestone contained a high amount of alkalis, $0.85 Na_2O_{eq}$.

SCMs, particularly fly ash, also contain alkalis that can be released into the pore solution and participate in ASR. The alkali content of fly ash can be specified in three ways: 1) available alkalis, 2) water soluble alkalis or 3) total alkalis [12], [13]. The effect of alkalis from fly ash into the pore solution has been studied by Diamond et al. in the 1980s [14], [15]. From his studies, it was concluded that Na_2O and K_2O could be released and thus augment the alkali hydroxide content of the pore solution. It was noted that the sodium from the high-calcium ashes (Class C) contributed to the alkali hydroxide concentration more so than the potassium from the low-calcium ash (Class F).

Analysis Methods for Evaluating Existing Structures

Analysis of existing cores from structures affected by ASR is of interested for researchers investigating the alkali release phenomenon. The concentration of

alkalis throughout the paste can be measured to enhance understanding of how various minerals in concrete aggregates and SCMs release alkalis into concrete pore solution.

Electron Probe Microscopy

Electron probe microscopy, also referred to as electron microprobe analysis, is a technique used to establish the composition of small areas on specimens. A beam of accelerated electrons is focused on the surface of a specimen using a series of electromagnetic lenses, and these energetic electrons produce characteristic X-rays within a small volume (typically 1 to 9 cubic microns) of the specimen. The characteristic X-rays are detected at particular wavelengths, and their intensities are measured to determine concentrations. All elements (except H, He, and Li) can be detected because each element has a specific set of X-rays that it emits [16].

Wavelength Dispersive Spectroscopy

Wavelength-dispersive X-ray spectroscopy (WDXRF or WDS) is a method used to count the number of X-rays of a specific wavelength diffracted by a crystal. The wavelength of the impinging X-ray and the crystal's lattice spacings are related by Bragg's law and produce constructive interference if they fit the criteria of Bragg's law. Unlike the related technique of energy-dispersive X-ray spectroscopy (EDS), WDS reads or counts only the X-rays of a single wavelength at a time, not producing a broad spectrum of wavelengths or energies simultaneously [17]. WDS is up to 100 times more sensitive than an electron dispersion spectroscopy (EDS) system for trace element detection.

Reclamation Dams Exhibiting ASR

At least 23 Reclamation Dams have exhibited ASR damage. In many early cases, the cement had a high alkali content which in conjunction with reactive aggregate and moisture, led to ASR damage. Cement composition analysis in the 1930s did not typically include alkali content and the cements used in construction did not have a specified upper limit on alkali content.

In cases where potentially deleterious aggregates were used, dams were recorded to have used a low-alkali cement, but the records of the cement composition could not be located. Unfortunately, many mix designs were determined using laboratory standard cement and not necessarily the same cement used in the field. Of the 23, 6 dams have information on the original materials used, including alkali content of the cement and are summarized in the following sections.

Bartlett

Bartlett Dam is located on the Verde River northeast of Phoenix, AZ. A thorough aggregate and concrete mix design program was completed in 1937 before construction [18]. Mix designs were based on two sources of coarse aggregate and two sources of fine aggregate. In one source of coarse aggregate there were

trace amounts of feldspar, and one of the sands was composed primarily of feldspar, as well as small amounts of mica.

The cement used for laboratory testing was classified as “MC” which is a blend of modified cements as used at Grand Coulee. During this time, a “modified cement” was similar to a Type II cement. The chemical analysis did not include total alkalis.

In 1942, observation of “cement-aggregate reaction” in a portion of the walkway across the dam was noted [19]. According to the memo, modified cement was used in the lower elevations of buttresses 9 and 10 and the low heat cement was used elsewhere. The construction took place at the same time as Parker Dam and the four low-heat cements used were furnished by the same mills. Chemical composition is summarized in Table 2.

Table 2. Chemical composition of low-heat cements used in Bartlett and Parker Dams

Chemical Analysis	PV	PC	PM	PR
	Victorville	Colton	Monolith	Riverside
SiO ₂	26.60	22.71	22.72	22.11
Al ₂ O ₃	3.14	5.17	5.71	5.27
Fe ₂ O ₃	1.53	5.07	5.74	5.45
CaO	63.71	59.89	59.84	58.97
MgO	2.12	3.06	1.16	4.27
SO ₃	1.76	2.04	2.07	1.68
Ignition Loss	1.12	1.43	1.68	1.55
Insoluble Residue	0.12	0.06	0.13	0.08
Na ₂ O	0.13	0.69	0.81	0.82
K ₂ O	0.42	0.56	0.61	0.31
Na ₂ O _{eq} ¹	0.41	1.06	1.21	1.02
Compound Composition	PV	PC	PM	PR
C ₃ S	28.9	23.6	17.9	23.6
C ₂ S	54.5	47.1	51.6	45.6
C ₄ AF	4.6	15.4	17.4	16.6
C ₃ A	5.7	5.1	5.4	4.7

$$^1 \text{Na}_2\text{O}_{\text{eq}} (\%) = \text{Na}_2\text{O} (\%) + 0.658 \times \text{K}_2\text{O} (\%)$$

According to a 1990 coring report, there was little evidence of ASR occurring, but the gel became evident when the cores were moistened. It was concluded that there was potential for ASR due to the high alkalinity of the cements used and the potentially deleterious aggregates, however, there was insufficient moisture present to allow for the gel to expand and cause damage [20].

El Vado

The aggregate from El Vado Dam was provided by L.G. Everist Company from the Rio Brazos plant [21]. The gravel is mostly quartz pebbles, quartose sandstone, schistose quarts, granite-quartz diorite, schist, gneiss, amphibolites,

miscellaneous metamorphic rocks, acidic, intermediate glassy and silicified volcanic with minor amounts of chert and miscellaneous silicified rocks. Alkali-reactive materials comprised about 18% of the gravel. The sand was composed of the same rock types found in the gravel with the addition of feldspar grains, and minor amounts of opal, palagonite, zeolite, and miscellaneous detrital materials. About 16% of the same is alkali-reactive. The aggregate was considered suitable for concrete provided a low-alkali cement is used.

A Type II, low-alkali cement from the Ideal Cement Company in Tijeras, New Mexico. No record of chemical composition was located.

In 2009, cores were taken from the spillway structure floor and wing wall structure. Overall, the concrete was determined to be petrographically sound. However, there was evidence of minor deterioration due to ASR on various reactive particles.

Hoover

Hoover Dam was built between 1933 and 1935. The massive scale of the project required extensive research on the materials used for the project. The aggregate used in Hoover Dam was from the Arizona pit and the composition is summarized in Table 3. The chemical composition of the aggregate was also investigated (Table 4). As a whole, there were trace amounts of alkalis. The basalt, granite and quartzite contained 8.12%, 4.8%, and 0.95% alkalis, respectively. Those three rocks comprised 68.7% of the coarse aggregate.

Table 3. Petrographic analysis of aggregate from the Arizona Deposit for use in concrete at Hoover Dam

Rock or Mineral	Percent by Weight	
	Gravel	Sand
Limestone	31.3	13.1
Granite ¹	35.7	-
Basalt	19.4	-
Quartzite	13.6	-
Chalcedony	-	10.6
Quartzite	-	67.8
Feldspar	-	8.5

¹ Includes granite, gneiss, soda granite porphyry, granite pegmatite, granite gneiss, and granite gneiss porphyry.

Table 4. Chemical analysis of rock types from Arizona aggregate for use in concrete at Hoover Dam

Component	Percentage			
	Basalt	Granite	Quartzite	Conglomerate
Loss on Ignition	2.04	0.43	0.98	0.25
Moisture	0.61	0.4	0.45	0.19
CO ₂	1.43	0.03	0.53	0.06
SiO ₂	50.02	72.74	94.5	98.81
Al ₂ O ₃	18.85	6.88	1.22	0.4
Fe ₂ O ₃	9.62	9.24	1.36	0.32
CaO	8.98	0.57	0.36	0.19
MgO	2.4	5.95	0.65	0.53
MnO	0.075	0.0027	0.0026	trace
Na ₂ O and K ₂ O	8.12	4.8	0.92	trace

Several low-heat cements were evaluated for use in Hoover Dam. The chemical composition of one such cement is in Table 5. Unfortunately, alkalis were not measured in any analysis of cements used in Hoover.

Table 5. Chemical composition of low-heat cement used in Hoover Dam

Chemical Analysis	Percent (%)
SiO ₂	23.09
Al ₂ O ₃	4.64
Fe ₂ O ₃	1.95
CaO	65.54
MgO	1.60
SO ₃	1.38
Ignition Loss	1.38
Compound Composition	Percent (%)
C ₃ S	52.9
C ₂ S	26.3
C ₄ AF	5.9
C ₃ A	9.0

Palisades

Palisades Dam is located on the Snake River about seven miles upstream from Irwin, Idaho. The aggregate investigations took place in 1946. There were four sources of sand and two sources of gravel. The aggregate from two pit areas were identified as being suitable for concrete “provided...low-alkali cement is specified” [22]. The gravel contained primarily limestones, sandstones, and quartzites with small quantities of siliceous limestones, dacites, and chalcedony which are known to be deleterious with a sufficient concentration of alkalis. The sand contained predominantly sandstones, limestones and quartzites. The fines

were primarily quartz and feldspars. Highly-reactive chalcedony, rhyolites, tuffs and opals comprised 10-15% of the sand.

The cement used was from the Idaho Portland Cement Company in Inkom, Idaho. The cement was a Type I, low-alkali cement with properties seen in Table 6. From Table 6, the calculated equivalent alkalis ($\text{Na}_2\text{O}_{\text{eq}}$) is 0.49%. This value is under the threshold to initiate the alkali-silica reaction. Fly Ash was used in some mixtures. It was from the Combustion By-Products Company from Fisk Station, Chicago, Illinois. No chemical data was provided.

Table 6. Chemical composition of Type I, low-alkali cement used in Palisades Dam

Chemical Analysis	Percent (%)
SiO ₂	22.67
Al ₂ O ₃	5.06
Fe ₂ O ₃	1.80
CaO	65.34
MgO	1.55
SO ₃	1.57
Ignition Loss	0.95
Insoluble Residue	0.25
Na ₂ O	0.10
K ₂ O	0.59
Compound Composition	Percent (%)
C ₃ S	52.6
C ₂ S	25.4
C ₄ AF	5.5
C ₃ A	10.4

In 2009, cores were taken from the weir wall and spillway chute wall and examined by the Materials Engineering and Research Laboratory [23]. Concrete from the weir wall showed deterioration from freezing and thawing and ASR. Concrete from the chute wall did not show any deterioration from ASR, although there were some potentially deleterious particles of chert and volcanic glass.

Parker

Parker Dam is located on the Colorado River straddling the state border of California and Arizona. It was completed in 1938 and extensive cracking was noted two years after in 1940. The gravel was primarily granite with less than 15% basalt. There was approximately 7% feldspar in the gravel. The sand consisted primarily of quartz with approximately 22% feldspar. The full petrographic composition is summarized in Table 7.

Table 7. Petrographic analysis of aggregates from Bill Williams Deposit for use in concrete at Parker Dam

Name of rock or mineral	Percent by Volume	
	Gravel	Sand
Andesite	2.2	3.2
Andesite (amy.)	0.2	-
Andesite (porp.)	1.8	-
Andesite tuff	0.2	-
Aplite	1.4	-
Basalt	14.9	2.9
Basalt (vesi.)	3.4	-
Chert	2	-
Chlorite	-	3.2
Diorite	4.2	1.8
Feldspar	7.4	22.3
Felsite	2.4	3.4
Granite	20.9	-
Granite (rot.)	0.2	-
Granite gneiss	17.3	-
Hornblende	-	3.5
Limestone	1	-
Magnetite	-	0.7
Mica	-	0.5
Pegmatite	3.6	-
Quartz	3.2	53.9
Quartzite	5.4	-
Rhyolite	2.4	2.2
Rhyolite tuff	1.2	-
Sandstone	2.2	2.3
Schist	2.2	0.2

Four low-heat cements were used in the construction of Parker Dam as summarized in Table 2. According to construction reports, the brand PM was used entirely in the last stages of the work [24]. This includes the superstructure part of the dam, specifically all of the concrete above the elevation of the spillway crest and all of buttresses 11, 12, and 13 of the trash rack structure. The lower portions of buttresses 1 through 10 used a “modified type of cement” and the upper portions contained a mixture of the four low-heat cements. The rest of the dam bellow the spillway crest was built with the four brands, used indiscriminately. All brands except PV had high alkali contents.

The cores revealed expansive sodium silicate gel around the aggregate which confirmed the presence of ASR.

Seminole

Seminole Dam is located on the North Platte River in Carbon County, Wyoming. The dam was built from 1936 to 1938. Cores drilled in 1951 were sent to the Reclamation laboratories in Denver for a petrographic investigation. Three small areas of silica gel were discovered on the core surface after being stored in the fog room. It was uncertain if the gel was present in the core before being exposed to moisture. The gel was formed on an opal particles. From aggregate testing, neither sand nor gravel was considered deleteriously reactive with high alkali cement. The cement used during construction contained 0.81% K_2O and 0.32% Na_2O [25]. Seminole is currently severely affected by ASR. Although ASR products were discovered in the 1950's, the presence of gel and resulting deterioration was accelerated in the 1980's.

CONCLUSIONS

- It is possible for alkalis to leach out from aggregates over time. Feldspar, volcanic glasses, mica, nepheline, and zeolites are known to release alkalis into the pore solution.
- Some Reclamation dams could have experienced the alkali release phenomena. For example, El Vado and Palisades used low-alkali cement but showed minor deterioration from ASR several years later. These dams may be of interest for analysis using electron probe microscopy or wavelength dispersion microscopy.
- Some supplementary cementitious materials are used to mitigate ASR, particularly fly ash. Studies have shown that some alkalis can be released into the pore solution over time and participate in ASR. The additional alkalis from fly ash typically less than those from the aforementioned alkali-bearing aggregates.
- Bartlett, Parker, and Seminole dams suffered from ASR damage due to the use of reactive aggregates and cement with a high alkali content. The presence of ASR products is not surprising.

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