ALKALI-SILICA REACTION PRODUCTS FROM SEVERAL CONCRETES:

OPTICAL, CHEMICAL, AND X-RAY DIFFRACTION DATA

by

Alan D. Buck* and Katharine Mather**

Abstract

Alkali-silica reaction products from six different concretes were
examined by X-ray diffraction and light microscope, and four of the gels
were chemically analyzed. Most of the reaction products were crystalline
in considerable part and were composed of one or more of four phases.
Two of the phases were tentatively identified as variants on CSH(I) and
CSH(II).

Introduction

Bryant Mather (1), McConnell, Mielenz, et al (2), (3), and Krogh (4)
provided optical or chemical data or both on alkali-silica reaction
products. Poole (5) reported electron-probe spot-microanalyses within
rims developed on the Beltane opal in specimens containing high-alkali
cement, stored at 40°C over water for periods up to 28 days. He found
that in a specimen examined after 28 days at 40°C, containing cement with
6% NaCl added at the time of manufacture, there was 45.77% CaO in the
reaction-rim material close to the cement interface. In the specimen
examined after 7 days at 40°C containing cement with 2% NaCl added during
manufacture there was 54.06% of CaO in the reaction-rim material close to
the interface. In both specimens calcium had moved through the reaction
rim into the opal. These electron-probe microanalyses clearly show the
mobility of calcium into the alkali-silica reaction product.

We have collected X-ray diffraction and light microscope data and
made chemical analyses of reaction products from six different concretes
affected by alkali-silica reaction. We have only four chemical analyses

* Chief, Petrography and X-Ray Branch, Engineering Sciences Division,
  Concrete Laboratory, U. S. Army Engineer Waterways Experiment Station,
  Vicksburg, Miss. 39180, USA.
** Chief, Engineering Sciences Division, Concrete Laboratory, U. S.
  Army Engineer Waterways Experiment Station, Vicksburg, Miss. 39180,
  USA.

of the reaction products from these six concretes but we believe that the chemical analyses are reliable because every sample was hand-picked by a geologist or a chemist who knew how to recognize alkali-reaction product and understood that it was better to have a small pure sample than a larger contaminated one.

Age of Specimens

Five of the concretes came from structures ranging in age from 24 to 40 years when the samples were taken. The sixth sample was from a concrete beam prepared in the Concrete Laboratory and stored in seawater near St. Augustine, Florida, for about 2 years. A sample of reaction product from this concrete was examined when the beam was about 3 years old. A fresh reaction product sample, obtained from the beam after an additional 20 years of storage in laboratory air, was examined by X-ray diffraction.

Reactive Aggregates

The aggregates believed to be reactive in these concretes included three distinct groups. They were: opal; mixtures of quartzite and quartz with or without chert; and granite gneiss.

X-Ray Diffraction Data

Table 1 shows the X-ray diffraction data for eight samples from the six concretes. There are eight samples because three recognizably different types of gel from the Charleston dry dock (6) concrete were examined separately. X-ray diffraction spacings believed to be due to impurities such as quartz or forms of calcium carbonate are shown in Table 1 with the spacings underlined. The data suggest several dangers and possibilities:

    a. We can only comment where we have optical information as well as X-ray diffraction information or several X-ray diffraction patterns on how many phases may be present in the samples, leaving out obvious impurities and characteristic secondary reaction products such as calcite, vaterite, and aragonite. We suspect that most of the "gel" reaction products are mixtures of amorphous alkali-silica gel and slowly crystallizing calcium-silicate hydrates that may contain some alkali.

74

with opal as the reactive constituent (7) was amorphous to X-rays. The gel was still amorphous although some calcite, vaterite, and aragonite had formed when a new specimen was examined by X-ray diffraction after 20 more years of storage in laboratory air.

       c. The crystalline materials in the other reaction product samples may consist of three phases. One has long spacings at 0.132 and 0.122 nm. A second has a long spacing at 0.113 to 0.115 nm. The third and most abundant type has a 0.105- to 0.108-nm spacing. All three phases appear in the samples from the Charleston dry dock.

       d. An 0.85- to 0.88-nm spacing occurs in five of the seven partly crystalline samples. It is associated with the 0.113- to 0.115-nm peak in two of these cases and with the 0.105- to 0.108-nm peak in two others. This association may mean that the 0.105- to 0.108-nm and the 0.113- to 0.115-nm peaks represent one phase with a variable long spacing and an 0.8^+-nm spacing. Absence of a longer spacing with the 0.86-nm peak in one case may indicate a situation like that in CSH(I) where the long spacing does not always appear. The 0.85- to 0.88-nm peak may arise from an altogether different phase. This second possibility is considered probable.

  The identification of the crystalline materials in the partly crystalline gel from the several concretes is uncertain. A thorough effort to identify the spacings in the diffraction charts of the gel from the New Savannah Bluff Lock and Dam concrete (9) with reactive granite gneiss coarse aggregate led to the possibility that the 0.105- to 0.108-nm material might be jennite (9) or a CSH(II) (14), and the 0.85- to 0.88-nm material tricalcium-silicate hydrate (9). No alkali silicate hydrates fitted. Tricalcium-silicate hydrate has been prepared by autoclaving at 200°C and is not known to have been reported from normal ambient temperature material. However time may proxy for temperature in some reactions, and it may be easier for a calcium-silicate hydrate to crystallize within an amorphous flexible alkali-silica gel than in a cement paste. Table 1 does show in almost all the samples the three familiar spacings at 0.307, 0.282, 0.182-nm, that appear in well hydrated cement paste. However in these patterns there are many other lines, usually representing substances less crystalline than quartz (the universal contaminant) but as well crystallized as most of the constituents of anhydrous portland cement.

These diffraction patterns show a gel-like hump, suggesting that the important part of the compositions including Na_2O, K_2O, part of the SiO_2, and part of the water remain as gels or the equivalent to hydrated glasses.

If Table 1 contains items that seem recognizable to people who see it, we would very much appreciate some discussion from any of them.

Light Microscopy and Chemical Analyses

The light microscope and chemical results in Tables 2 and 3 complete the information that we have on the reaction products in these six concretes affected by alkali-silica reaction. We always look for gel in concrete suspected of alkali-silica reaction since if gel is present it is unequivocal evidence that the reaction took place, and therefore have considerable familiarity with appearance of gel in immersion mounts in plane light, and with crossed polarizers, and have determined a number of indices of refraction of gel. We are also very familiar with gel viewed using the stereomicroscope. We also usually analyze the reaction products to assure that they contain considerable SiO_2 and some alkali. No determination of alkalies was made on the samples from Oliver Lock probably because we did not yet have a flame photometer.

Conclusions

Our tentative conclusions are as shown below. It appears that alkali-silica reaction product in its early stages contains very little calcium, a high concentration of silica, and more total alkali than calcium (Table 3, Beam 1850). Calcium moves into the product from the large supply available in the cement paste and calcium hydroxide, but moves at varying rates over unknown distances. Examination of concrete thin sections, comparing sections of normal concrete and that affected by alkali-silica reaction, shows that crystalline $Ca(OH)_2$ is depleted in parts of the mortar where reaction has proceeded.

Ultimately, at ages in field structures at least as low as 24 years (Table 1, Charleston Naval Dry Dock No. 2) complex products develop. They include products giving X-ray diffraction spacings that suggest that part at least of the products is related to CSH(I) (13) and possibly to CSH(II)

76

(14). CSH(I) and CSH(II) both have variable long spacings. It may be a
consequence of the composition of these complex, probably mixed, products
that they differ from sample to sample in their crystalline parts but
share a family resemblance. This similarity which exists regardless of
the type of reactive aggregate, with the possible exception of opal,
suggests that the same mechanism is involved in five of the cases discussed
here. This in turn suggests that division of silica bearing aggregates
into those that participate in the alkali-silica reaction and those that
participate in an alkali-silicate reaction may be a misleading practice.

Acknowledgment

References

(1) Mather, Bryant, Cracking of Concrete in the Tuscaloosa Lock, Highway
Research Board Proc Thirty-First Annual Meeting, 1952, pp 218-233.

(2) McConnell, D.; Mielenz, R. C.; Holland, W. Y.; and Greene, K. T.;
Cement Aggregate Reaction in Concrete, Proc. Am. Conc. Inst. vol 44,
Journal ACI vol 19 No. 2, pp 93-128.

(3) McConnell, D.; Mielenz, R. C.; Holland, W. Y.; and Greene, K. T.;
Petrology of Concrete Affected by Cement-Aggregate Reaction, The
Geological Society of America, Engineering Geology (Berkey) Volume,
Nov. 1950, pp 225-250.

(4) Krogh, Hanne, Examination of synthetic alkali-silica gels, pp 131-163,
Symposium on Alkali-Aggregate Reaction: Preventive Measures,
Reykjavik, August 1975, The Building Research Institute, Keldnaholt/
Reykjavik, Iceland.

(5) Poole, A. B.; Electron Probe Microanalyses of reaction zones at
cement/opal interfaces, The Effect of Alkalies on the Properties of
Concrete, Proceedings of a Symposium Held in London, Sept. 1976.

(6) Buck, Alan D.; and Mather, Katharine; Concrete Cores from Dry Dock
No. 2, Charleston Naval Shipyard, S. C., Miscellaneous Paper C-69-6,
U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.
39180, USA.

(7) Buck, A. D., Seawater Exposure Tests, Alkali-Aggregate Reactivity;
draft report, U. S. Army Engineer Waterways Experiment Station,
Concrete Laboratory, June 1958.

(8) Buck, Alan D., Tests of Concrete Core, Fort Meade, Md., 21 January
1977; letter report to U. S. Army Engineer District, Baltimore, Md.

(9) Buck, A. D., Tests of Cores from New Savannah Bluff Lock and Dam,
18 October 1977; letter report to U. S. Army Engineer District,
Savannah, Ga.

(10) Mather, K. and B., Disintegration of Concrete from Tuscaloosa Lock
and Dam, U. S. Army Engineer Waterways Experiment Station, 25 August
1949.

(11) McDonald, J. E.; Campbell, Roy L.; An Investigation of Concrete
     Condition, William Bacon Oliver Lock and Spillway, Miscellaneous
     Paper C-77-5, June 1977, U. S. Army Engineer Waterways Experiment
     Station, Vicksburg, Miss. 39180.
(12) Buck, Alan D.; and Mather, Katharine; Examination of Fontana Dam
     Concrete Cores, 3 May 1974; letter report to Tennessee Valley
     Authority.
(13) Taylor, H. F. W., The Calcium Silicate Hydrates, Proc. International
     Symposium on the Chemistry of Cement, Tokyo, 1968, The Cement
     Association of Japan, Dec. 31, 1969, vol II, pp 1-26.
(14) Gard, J. A.; and Taylor, H. F. W.; Calcium Silicate Hydrate (II)
     (C-S-H(II)), Cement and Concrete Research, vol 6, pp 667-678, 1976.

79

Table 1

X-Ray Diffraction Data on Alkali-Silica Reaction Products from Six Concretes*

Fort Meade 45 Years I** — d	I	New Savannah Bluff L and D 40 Years II** † — d	I	Oliver Lock 38 Years III† — d	I	Fontana Dam 33 Years IV** † — d	I	Charleston Naval Dry Dock No. 2 — From 1/4-in. Void 24 Years V** † — d	I	Tan, Layered, Translucent Gel VI — d	I	Composite for Chemical Analysis VII** † — d	I	Beam No. 1850 3 and 23 Years VIII** † — d	I
												1.318	vw		
												1.217	w		
							1.132	vw	1.147	w			1.150	vw		
		1.077	w					1.064	vw	1.077	w	1.072	vw		
0.858	s	0.850	vs	0.884	w	0.861	w	0.858	w			0.858	vw		
												0.696	vw		
0.665	w	0.661	w	0.660	vw	0.660	w	0.660	w			0.664	w		
										0.646	vw	0.646	w		
				0.564	vw										
0.503	w	0.498	vw	0.501	vw	0.498	vw	0.499	w			0.501	vw		
						0.472	vw								
		0.424	s					0.425	vw			0.426	w	Amorphous; crest of halo at	
														0.390	s
						0.386	vw							0.386	w
												0.379	vw		
		0.366	w					0.368	vw						
				0.359	w	0.357	w	0.359	w			0.358	w	0.359	w
0.356	s	0.356	m					0.354	w			0.351	w		
		0.339	w												
0.335	s	0.333	vs			0.335	vw	0.335	w			0.334	s	0.341	w
		0.328	m			0.329	vw							0.334	
0.324	w							0.324	vw					0.330	w
		0.318	w							0.318	vw	0.318	vw		
0.311	w					0.314	vw	0.312	vw						
		0.306	m	0.307	m	0.305	m			0.306	w				
		0.303	s	0.303	m			0.303	vw	0.301	w	0.304	w	0.305	m

(Continued)

Table 1 (Continued)

		New Savannah							Charleston Naval Dry Dock No. 2						
Fort Meade 45 Years		Bluff L and D 40 Years		Oliver Lock 38 Years		Fontana Dam 33 Years		From 1/4-in. Void 24 Years		Tan, Layered, Translucent Gel		Composite for Chemical Analysis		Beam No. 1850 3 and 23 Years	
I**		II** †		III†		IV** †		V** †		VI		VII** †		VIII** †	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
0.299	m	0.298	w					0.298	w			0.300	w		
		0.293	m									0.293	m		
0.291	s	0.290	m			0.290	vw	0.290	m			0.289	m		
0.284	w	0.282	w	0.283	vw			0.283	w			0.282	w		
0.276	vw			0.279	vw					0.278	vw				
						0.274	vw							0.274	w
		0.272	m									0.271	w	0.271	w
		0.270	w												
0.263	w							0.261	vw			0.261	vw		
0.255	w											0.253	vw		
		0.248	vw			0.250	w							0.250	w
Pattern		0.245	w			0.241	vw	0.245	vw			0.245	w	0.238	vw
not run												0.232	vw		
to higher		0.228	m			0.229	w	0.227	vw			0.228	vw		
angles		0.223	w			0.223	vw					0.223	w		
						0.221	vw	0.221	vw						
		0.215	vw	0.214	w							0.213	vw		
		0.212	s					0.212	vw						
		0.209	vw			0.210	w	0.209	vw						
		0.206	m			0.206	w	0.205	vw			0.206	vw	0.207	vw
												0.200	vw		
		0.197	m	0.198	vw	0.198	w					0.198	vw	0.198	w
		0.191	vw			0.192	m	0.192	vw						
		0.188	w			0.188	w	0.188	vw			0.187	vw	0.188	w
		0.183	w	0.184	w	0.184	w			0.183	vw	0.183	vw		
		0.182	s			0.182	w	0.182	w			0.182	w	0.182	w
				0.181	w			0.181	w						

(Continued)

Table 1 (Concluded)

	Fort Meade 45 Years I**		New Savannah Bluff L and D 40 Years II** †		Oliver Lock 38 Years III†		Fontana Dam 33 Years IV** †		Charleston Naval Dry Dock No. 2 — From 1/4-in. Void 24 Years V** †		Tan, Layered, Translucent Gel VI		Composite for Chemical Analysis VII** †		Beam No. 1850 3 and 23 Years VIII** †	
	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
							0.178	m								
			0.175	m					0.175	w					0.175	w
			0.174	w									0.174	w		
			0.167	w	0.167	vw										
					0.164	vw	0.163	w								
							0.160	w								
							0.159	vw								
							0.157	vw								
							0.156	vw								
			0.154	s	0.154	vw	0.154	vw					0.154	vw		
Aggregate:	Quartzite, quartz; quartz sand		Granite gneiss, natural sand		Quartzite, sandstone, quartz, chert		Metamorphic subgraywacke and phyllite coarse and fine		Quartzite, quartz, and quartz sand						5% opal-bonded quartzite, chert gravel, quartz sand	
Alkali:	Not known		Not known		Not known		0.75% max				Not known				1.0%	

* Spacings are given in nanometres. Nanometres times 10^{-1} = Angstroms.
** Sample contained quartz.
† Sample contained calcium carbonate as calcite, vaterite, or aragonite. Lines of the compounds mentioned in these notes are underlined. Only the sample in column VIII contains aragonite in recognizable amounts. It was stored for two years in warm seawater. The quartz, calcite, vaterite, and aragonite spacings are underlined. Spacings at left and estimated intensities on right within each column. Intensities: vs = very strong; s = strong; m = moderate; w = weak; vw = very weak.

Table 2

Light Microscope Data on Alkali-Silica

Reaction Products from Six Concretes*

Source of Gel	Description of Gel
Fort Meade (8)	Clear to brownish in plane light. With crossed polarizers, crystalline material black, gray, and white in a texture like finely granular chert. Amorphous material also present. $n < 1.520$
New Savannah Bluff Lock and Dam (9)	Apparently crystalline with crossed polarizers, texture like finely granular chert. $n = 1.460 - 1.500$
Oliver Lock (10)(11)	White to translucent bluish, laminated, often with shrinkage cracks, brittle where dry. Also in pockets and lining cracks, clear to translucent, rubbery to brittle; usually the outer shell of the lining if two varieties are present in one void. By microscope, there were three varieties: with crossed polarizers one anisotropic, with aggregate polarization, low birefringence, and wavy extinction with a misshapen black cross as in strained glass; the second with crossed polarizers had a very fine-grained pepper and salt appearance resembling chert or fine grained calcium hydroxide; the third variety was clear, isotropic, with fewer inclusions than the other types. Ranges of indices of refraction: pepper and salt type $n = 1.478$ to $n = 1.511$; in the type with aggregate polarization $n = 1.480$ to $n = 1.502$; isotropic gel formed after the cores were drilled $n = 1.465$ to $n = 1.487$. The 1976 samples were similar.
Fontana Dam (12)	Semicrystalline; first order gray birefringence in crossed polarized light. $n < 1.480$
	Salt and pepper type in crossed polarized light. $1.482 > n < 1.502$
	Alternating growth layers of clear and of tan translucent gel; some of the clear material is amorphous. $1.480 > n < 1.520$

(Continued)

Table 2 (Concluded)

Source of Gel	Description of Gel
Charleston Dry Dock (6)	
Gel from 1/4-in. void	Transparent in plane light, crystalline salt and pepper texture with crossed polarizers. n about 1.494
Tan layered gel	Layered structure with fibers normal to layers; fibers appear to be uniaxial +; 1.510 < n < 1.544
Composite	Amorphous and crystalline material in clear and brownish fragments.
Beam 1850 (7)	Amorphous with 1.460 < n < 1.500

* See Table 1 for type of aggregate.

Table 3

Chemical Analyses of Alkali-Silica Reaction Products from Four Concretes

Constituents, Percent by Weight	Oliver Lock Sample 1*	Sample 2**	Fontana Dam 33 Years	Charleston Dry Dock 24 Years	Beam 1850 3 Years
SiO_2	49.82	61.73	50.70	66.00	85.91
Al_2O_3	1.15	2.17	not determined	1.88†	not determined
Fe_2O_3	0.81	0.47	not determined	not determined	not determined
CaO	21.11	12.28	4.76	11.54	1.25
SO_3	0.16	0.00	not determined	not determined	not determined
Cl^-	not determined	not determined	not determined	0.39	not determined
Na_2O	not determined	not determined	6.75	1.30	2.41
K_2O	not determined	not determined	6.68	19.00	0.60
Insoluble residue	5.58	8.1	not determined	not determined	not determined
Moisture loss at 105°C	34.6	9.81	not determined	not determined	5.22
Moisture loss at 200°C	--	--	not determined	not determined	3.09
Moisture loss at 450°C	--	--	not determined	17.23	
Ignition loss	--	14.84	24.80 at 550°C	not determined	

* Scraped from the wall of the 36-in. core hole 16-19 June 1948.
** Collected from pockets in cores from holes 20-1 and 60-1 after cores dried in laboratory air.
  Analyses made in 1948 and 1949.
† Assumed to be Al_2O_3 but contained at least some iron. Structure was 10 to 11 years old.