

Alkali-Silica and Alkali-Carbonate Reactivity Of Some Aggregates from South Dakota, Kansas, and Missouri

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•THIS paper summarizes the two investigations concerning alkali-carbonate reactivity that have been completed at the Waterways Experiment Station. Additional investigations are in progress. These observations relate to aggregates from areas from which alkali-carbonate reaction had not been reported before this symposium. The first part describes an instance of the identification of brucite in dolomitic limestone affected by an alkali-carbonate reaction. The second part describes concrete from structures, in some of which an alkali-carbonate reaction has taken place with a limestone containing no dolomite that can be detected by X-ray diffraction. The paper raises more questions than it answers; if it stimulates additional investigation that does supply some additional answers, it will serve its purpose.

The investigations were concerned with aggregates from South Dakota, Kansas, and Missouri; the structures from which the concrete cores discussed in the second part were taken are all located in the northeastern quadrant of Kansas and the southeastern quadrant of Nebraska. For many years an increasing body of literature has stated that in part of Kansas, and in parts of other Great Plains states, there are problems relating to concrete durability that are unique. The term "sand-gravel aggregate" was coined to describe the predominant class of natural aggregates in the area. The term "cement-aggregate reaction" was coined to designate a phenomenon believed to be uniquely at work in contributing significantly to expansion and consequent damage to concrete in the area. During much of the period in which the literature on "cement-aggregate reaction" and "Kansas reactivity" was being developed, there were also developing both an improved understanding of the factors involved in the behavior of aggregates in concrete, and a conviction that physical and chemical mechanisms that control the behavior of aggregates in concrete apply generally throughout the world, whenever the participating factors and conditions come together. The ameliorative measure most widely and successfully used in combating "cement-aggregate reaction" in Kansas is the addition of some coarse aggregate to the sand-gravel aggregate concrete; this "sweetening" procedure has been believed to be most effective when the coarse aggregate added is a crushed carbonate rock.

SOUTH DAKOTA SAND

Background

In petrographic examination of sand from Watertown, South Dakota, and of mortar bars, and concrete cores containing this sand, the Corps of Engineers Missouri River Division Laboratory detected (1, 2) aggregate particles of types known to participate in alkali-silica reaction in concrete and reacted shale particles. Quick chemical tests made at MRDL on sands containing different amounts of shale particles like those that

had reacted, indicated an apparent direct relation between amount of shale and amount of dissolved silica. Length-change measurements of mortar bars to determine alkali-aggregate reactivity, made with different amounts of shale particles in the sand, showed expansion not greater than 0.025 percent at one year with as-received sand, but abundant signs of reaction. As a consequence, the MRDL raised questions about alkali-aggregate reactivity of montmorillonitic shales, and suggested that montmorillonite might be a reactive mineral.

Samples

Seven mortar bars representing portions of two sets, made with high alkali cement, that had been tested to an age of one year for length change by method CRD-C 123-57 (3); a number of shale particles separated by flotation on a liquid with a specific gravity of 2.0, from another portion of the sample of sand that was used as aggregate in the mortar bars; and about 10 pounds of the sand were obtained from the MRDL for study. The shale was the principal constituent of the sand with a bulk specific gravity below 2.0.

Tests

The tests were undertaken to identify the reactive constituent or constituents of the shale, particularly to confirm or disprove the suggestion that montmorillonitic clay was the material reacting with alkalis in the case under study. The carbonate particles in the mortar bars were investigated because reaction rims, observed as color changes, were seen in some carbonate particles or in the surrounding mortar.

Several different reacted shale particles dissected from mortar bars were pulverized, mixed with water, air-dried on glass slides, and scanned on an X-ray diffractometer, using nickel-filtered copper radiation at 30 kv and 27 ma, air-dry, and after saturation with glycerol.

A single particle and a composite of several shale particles separated from the sand by flotation were prepared for X-ray examination by the same methods. Several whole and several pulverized shale particles were placed in a solution of 0.75N potassium hydroxide (equivalent to 3 percent sodium hydroxide) for three days, and then part of the sample was washed several times and dried on a glass slide. The rest of the sample was placed in a 1.5N potassium hydroxide solution (equivalent to 6 percent sodium hydroxide) for four days, and then washed and allowed to dry on glass slides. Samples from both treatments were examined by X-ray diffraction, air-dry and after glycerol saturation.

Two carbonate particles surrounded by a thin zone of light-colored mortar on broken surfaces of one mortar bar, and one carbonate particle, with a dark rim, on a broken surface of another bar were dissected out under a stereomicroscope, and the adhering mortar removed with a dissecting needle and forceps. Each separate carbonate grain was pulverized in water, the slurry was air-dried on a glass slide, and then scanned on the X-ray diffractometer.

About 50 carbonate rock grains were selected from sand retained on the No. 8 sieve in the sand sample, one-half by appearance and one-half by testing with dilute hydrochloric acid, as resembling the types which had developed reaction rims in the mortar bars. Portions of broken particles from each group were pulverized in water to produce composite slurries which were dried on glass slides, and X-ray patterns made of them. Saturated surface-dry weight and volume of the particles in each group were determined, and the specific gravity was calculated. Each group was then stored in 0.75N sodium hydroxide solution for almost 11 months. The particles were then washed, and the volume redetermined. Each group was examined with a stereomicroscope, pulverized in water to make a composite, dried on glass slides, and examined by X-ray diffraction. Twenty to thirty additional carbonate particles from the sand retained on No. 8 sieve were selected after examination with a stereomicroscope. They were divided into four groups; each group was pulverized and examined by X-ray diffraction as tightly packed powders.

TABLE 1
COMPOSITION OF SHALE PARTICLES DETERMINED
BY X-RAY DIFFRACTION

Shale Particles	Relative Amounts of Constituents in Samples				
	Low Cristobalite- Tridymite	Quartz	Montmo- rillonite	Illite	Feldspar
Unreacted (portion of separated fraction added to mortar bars)	Major	Major	Major	Minor	Very minor
Reacted (found in mortar bars)	Not found	Major	Major	Major	Minor
Reacted experimentally (3 days in KOH solution) ¹	Minor	Major	Major	Major	Minor
Reacted experimentally (4 additional days in KOH solution) ²	Not found	Major	Major	Major	Minor

¹Part of same sample as that in line 1, after 3 days in KOH equivalent to 3% NaOH.

²Second part of same sample, after 4 more days in KOH equivalent to 6% NaOH.

Results

Alkali-Silica Reaction.—The gray and brown shale particles were tabular with rounded corners and edges. Broken surfaces of unreacted shale particles appeared to be ordinary shale and looked unlike broken surfaces of the reacted shale in the mortar bars. The reacted particles were easy to distinguish in the mortar bars because they exhibited thin, hard peripheral shells with radial cracks, and soft, moist centers shrunk away from the shells, and gel-filled voids were common at or near the surfaces of the shale particles. The composition of the unreacted shale and the reacted particles in the mortar bars differed (Table 1). The unreacted particles contained a large amount of opal of the type described from Kansas by Swineford and Franks (4) as low cristobalite-tridymite (SiO_2) with a large amount of quartz (SiO_2) and minor montmorillonitic clay, clay-mica (illite), and feldspar. There was no evidence of low cristobalite-tridymite opal in the reacted particles. Any form or combination of cristobalite or tridymite is readily soluble in alkaline solutions and capable of producing alkali-silica reaction in concrete.

The (001) basal spacing of the montmorillonite in the reacted particles, air-dry and glycerol-saturated, measured about 12A and 14A, respectively, while the basal spacings of the montmorillonite in the unreacted particles measured about 15A and 18A, air-dry and glycerol-saturated, respectively.

X-ray examinations of unreacted shale after two intervals of storage in potassium hydroxide solution showed progressive decrease and eventual disappearance of the low cristobalite-tridymite peaks and a change in the (001) basal spacing of the air-dry and glycerol-saturated montmorillonitic clay from about 15A and 18A, to about 12A and 14A, which are the values found in potassium-bearing montmorillonitic clay (5). The changes indicated that all of the low cristobalite-tridymite dissolved, and that the potassium ions of the solution replaced the exchangeable cations naturally present in the clay.

The experimental results explained the differences between reacted and unreacted shale particles, and also the shale-mortar reaction in the mortar bars. The low cristobalite-tridymite opal, not the montmorillonite, was the apparent source of the reactive silica in the alkali-silica reaction. If the montmorillonitic clay in the shale had contained exchangeable sodium or potassium, and the cement had been low in alkali, cation exchange between shale and paste might have displaced the alkalies in the clay by calcium, releasing alkali ions. However, the cation exchange that actually occurred removed alkalies from availability to participate in alkali-silica reaction.

TABLE 2

COMPOSITION OF CARBONATE PARTICLES IN SANDS FROM VICINITY OF WATERTOWN, SOUTH DAKOTA, AS DETERMINED BY X-RAY ANALYSIS

Samples	Relative Amounts of Constituents in Particles				
	Dolomite	Calcite	Brucite	Quartz	Feldspar
Particles with reaction rims in mortar bars:					
Piece A	Major	Major (dol.)	Minor	—	—
Piece B	Major	Minor	Very minor	Trace	—
Piece C	Major	Minor	Very minor	—	—
Particles in sand:					
Natural state ¹	Major	Major to none	—	Trace	Trace
After 11 months in 3% NaOH solution ²	Major	Minor	Minor (cal.)	Trace	Trace

¹ Results are an average of six patterns; two represent samples before immersion in sodium hydroxide and four are general samples selected to show composition.

² Results are for group selected by appearance and by acid testing.

TABLE 3

PHYSICAL DATA¹ FOR CARBONATE ROCK PARTICLES FROM WATERTOWN, SOUTH DAKOTA, SAND USED IN MORTAR BARS

Dolomite or Dolomitic Limestone Particles Retained on No. 8 Sieve	Natural State			After 11 Months in 3% NaOH Solution	
	Weight (g)	Specific Gravity ²	Volume (ml)	Volume (ml)	Volume Increase (%)
22 particles selected by appearance	1.54	2.80	0.55	0.60	9.1
26 particles selected by acid testing	2.06	2.94 ³	0.70	0.75	7.1

¹ Measured while particles were saturated surface-dry.

² Specific gravity of pure dolomite is 2.85 ± 0.01 ; that of pure calcite is 2.71.

³ Probably acid testing developed small pits on surfaces of particles and surface water was not completely removed from these pits when an effort was made to bring the particles to saturated surface-dry condition. Therefore this value, calculated from measured weight and volume determined by displacement ($2.06/0.70 = 2.94$), is higher than it should be.

Alkali-Carbonate Reaction.—Some of the white chalky carbonate particles on broken surfaces of the mortar bars had dark rims or were bordered by a thin band of light-colored mortar. X-ray examination of three of the particles (Table 2) revealed that each was composed of dolomite, calcite, and brucite ($\text{Mg}(\text{OH})_2$) in that order of abundance. The amount of brucite was small, but it was definitely present. Because brucite is an improbable constituent of a dolomitic limestone, this composition indicated that some of the dolomite had altered to brucite in the mortar bars; this is the dedolomitization reaction previously reported in concrete (6, 7). The composition of similar carbonate particles in their natural state was determined to see if such particles would produce brucite in an alkaline solution, and to see if the reaction would produce in sand-sized grains expansions detectable by a simple physical test. Carbonate rock particles from the sizes coarser than the No. 8 sieve in the sample from the source of the sand used in the mortar bars were selected to resemble those with reaction rims in the mor-

tar bars (Table 3). Most of the particles had spots of the manganese oxides ("wad") scattered over their surfaces, and some were stained with iron oxides. The particles in the group selected by appearance and in the group selected by acid testing were divided into three lithologic varieties based on grain size, wad coatings, and iron-oxide coatings. The varieties were not successfully distinguished after storage in sodium hydroxide solution for 11 months because of bleaching and chemical changes. For this reason, all of the particles in each group were pulverized into a composite sample after measurement of volume and before X-ray examination. The particles as received varied in composition from dolomite to dolomitic limestone with traces of quartz and feldspar (Table 2). There was no detectable brucite. X-ray examination of the samples after storage for 11 months in 0.75N sodium hydroxide solution showed that some of the dolomite had been altered to calcite and brucite; much less new brucite was apparent than new calcite. (The apparent difference in quantity may result from the low linear absorption coefficient for copper radiation of magnesium hydroxide as compared with calcium carbonate.) Measurements of the particles before and after the 11 months storage in alkaline solution showed a detectable increase in volume.

Conclusions

Alkali-Aggregate Reaction.—The shale particles had participated in alkali-silica reaction, and X-ray diffraction examination of reacted shale particles from the mortar bars and of shale particles from the sand not used in mortar bars showed differences. The unreacted particles contained a large amount of low cristobalite-tridymite opal (4) which was missing in the reacted particles. Any kind of opal can participate in alkali-silica reaction in concrete. Both unreacted and reacted shale contained some montmorillonitic clay, but the clays in the two conditions differed in basal spacing. The reason for this difference was shown to be cation exchange in which divalent cations in the clay (probably Ca and Mg) were replaced by potassium ions from the cement. Thus, the source of reactive silica in the shale particles was apparently low cristobalite-tridymite opal and there was no evidence that montmorillonitic clay participated in alkali-silica reaction in portland cement concrete.

Carbonate Rock Reaction.—Rims consisting of dark borders in the carbonate rock or of thin bands of light-colored mortar surrounding the carbonate rock were observed around carbonate particles on broken surfaces of the mortar bars. The carbonate rocks contained dolomite, calcite, and a small amount of brucite ($\text{Mg}(\text{OH})_2$). X-ray analysis of selected carbonate particles from the sand used in making the mortar bars showed them to be dolomite or dolomitic limestone with small amounts of quartz and feldspar; no brucite was found. The volume, weight, and specific gravity of some of the carbonate particles from the sand were determined; two groups of these particles were then placed in 3 percent sodium hydroxide solution for 11 months, and their volume and mineralogical composition were again determined. The volume of the groups had increased from 7.1 to 9.1 percent; some of the dolomite had been converted to calcite and brucite by dedolomitization. The absence of brucite in carbonate particles in their natural state, its presence in particles with reaction rims in mortar bars, and the presence of brucite plus the volume change of the carbonate particles after storage in sodium hydroxide solution for 11 months all indicate that some dedolomitization (6, 7) had occurred in the mortar bars, and that the reaction rims, in this case, were observable evidence of this reaction. This is believed to be the first time that carbonate rock reaction has been reported in Corps of Engineers specimens, and the first instance in which brucite has been directly identified among the products of alkali-carbonate reaction in concrete or mortar.

AGGREGATES FROM KANSAS AND MISSOURI

Background

In 1960, representatives of the Waterways Experiment Station and of other agencies concerned with research on the behavior of aggregates in concrete held discussions on the investigational attack required to elucidate the mechanisms involved in "cement-aggregate reaction" as manifested by "sand-gravel aggregates," typically in Kansas.

At about this same time representatives of the Kansas City District and the Missouri River Division (MRD) Offices of the Corps of Engineers were making aggregate investigations for Milford Dam, proposed for construction on the Republican River near Milford, Kansas. As has been the case in all serious considerations of aggregate suitability and of anticipated concrete performance in Kansas in the last several decades, it was difficult to establish a rational basis for selecting aggregates that might be used with confidence that the concrete structures in which they were employed would provide the desired service. These difficulties arise primarily from a lack of knowledge of the factors that contribute to poor performance of concrete in the area, because no fundamental investigational work has been done on the problem.

During the aggregate investigation for Milford Dam, representatives of the District and the MRD made several trips to examine structures, on one of which they were joined by a representative of the Office, Chief of Engineers, and by one of the authors of this paper.

The aggregate investigation for Milford Dam has already shown that the Towanda limestone, quarried near the Milford Dam site, was physically superior to most coarse aggregate from sources economically available. The principal question remaining was whether it would be advisable to list the sands produced from the Republican River and the section of the Kansas River just east of the confluence of the Republican River and the Smoky Hill River among the approved sources of fine aggregate. The answer was not readily apparent, because these sands make up the bulk of the product known as sand-gravel aggregate, and because aggregates from the particular reaches of the Republican River under consideration include some of those which have been associated with "cement-aggregate reaction."

The examinations of structures and the aggregate tests that had been made did not provide conclusive answers, and thus the WES representative suggested that four cores be taken, three from structures examined during the inspection trip and one additional core from a 10- to 15-yr-old concrete structure containing sand from the Republican River or the Kansas River at Junction City, and limestone coarse aggregate. Examination of these cores was expected to provide additional evidence helpful in reaching a decision on whether or not to include Republican River sand, and Kansas River sand from the region just downstream of the confluence of the Republican and Smoky Hill Rivers, among the approved sources of fine aggregate.

Samples

Eight 6-in.-diameter diamond-drilled concrete cores from structures in Kansas and Nebraska were received late in 1961 or early in 1962. All contained crushed limestone coarse and sand-gravel or natural fine aggregate. Information on the structures and materials is given in Table 4.

Tests

Each core was examined when received to determine its general condition, whether old cracks were present, whether any chemical reactions after drilling were indicated by deposits on the drilled surface, and whether there was any evidence of freezing and thawing, sulfate attack, alkali-silica reaction or any other reaction between aggregate and cement paste. After the preliminary examination, each core was placed in a separate container and covered with water to let the dry concrete regain moisture and to determine whether soaking at room temperature would produce any signs of reaction not present in the concrete as received. After one or more days of soaking, each core was re-examined to find whether any changes had taken place, and one or more surfaces were sawed and examined for evidences of alkali-silica reaction that had taken place before drilling. After this examination the sawed surfaces were scrubbed with acetone to remove cutting oil, and the pieces of the core were soaked and re-examined after one to three days to determine whether any sign of the progress of alkali-silica reaction was developing.

Where cores KC-1, -4, and -5 were examined, rims of different color from the rest of the piece could be seen just inside the boundaries of many of the pieces of car-

TABLE 4
AGE, LOCATION OF STRUCTURE, COMPOSITION OF CORES, AND MEAN
ANNUAL RAINFALL FOR COUNTY OF LOCATION

Speci- men	Date Placed; Age (yr)	Structure and Location	Horiz. or Vert. Core	Aggregate and Source		Mean Annual Rainfall (in.)
				Coarse	Fine	
KC-8	1918 43	World War I sewage plant, now swimming pool, Camp Funsten, Ft. Riley, Kan.	V	1-in. maximum limestone	Republican or Kansas River near Junction City, Kan.(?)	31.8
KC-1	1924 37	Abandoned high- way pavement, Scandia, Kan.	V	2½-in. maximum crusher-run limestone; National Stone quarry, Louisville, Nebraska(?) ¹	Republican River, Clay Center, Kan.(?)	25.9
KC-9	1927 34	Right abutment of highway bridge, Clark's Creek, Geary County, Kan.	H	2½-in. maximum crusher-run limestone, Cottonwood formation(?)	Republican River, Clay Center, Kan.(?)	31.8
KC-7	1945 16	Swimming pool, officers' club Ft. Riley, Kan.	H	1-in. maximum crushed lime- stone	Republican River, More Sand Co., Junction City, Kan.	31.8
KC-6	1947 14	West wall of garage, Harlan County Dam, Neb.	H	1-in. maximum crushed lime- stone, Loring quarries, Bonner Springs, Kan.	Republican River, More Sand Co., Junction City, Kan.	20.9
KC-4 KC-5	1949 12	Building, Harlan County Dam, Neb.	H	1-in. maximum crushed lime- stone, Pixley Mine, Independ- ence, Mo.	Kansas River, Turner, Kan.	20.9
KC-11	1955 6	North wall, compressor room, boiler plant, hospital, Ft. Riley, Kan.	H	1-in. maximum crushed lime- stone, Towanda formation, Milford, Kan.	Republican River, More Sand Co., Junction City, Kan.	31.8

¹ It has also been suggested that the aggregate came from the old Kerford quarry.

bonate coarse aggregate. In KC-1 there were also partial rims, or projecting lobes, in the paste next to parts of the edges of some of the carbonate coarse aggregate. These rims suggested that the reactions between carbonate coarse aggregates and alkalis in portland cement might have taken place in these concretes. These reactions include dedolomitization, described by Hadley (6), and the rim formation discussed in several publications by John Lemish and various coworkers (8-13). Therefore, parts of the rims in the aggregate particles, the centers of rimmed particles, and parts of the cement paste immediately bordering rimmed carbonate rocks were dissected out and examined by X-ray diffraction to see whether the reported compositions and reaction products of dedolomitization were present. Slices of each core containing carbonate aggregate were etched with hydrochloric acid by the procedure described by Lemish et al. (9) or in 10 percent acetic acid solution. A sample of limestone from the source of the coarse aggregate used in cores KC-4 and -5 was examined by stereomicroscope and by X-ray diffraction to see whether it was similar to the stone in those cores. Cracks, the kind of aggregate with which they were associated, carbonate coarse aggregate with and without rims, and chert or cherty limestone were counted on sawed slices of several cores.

Pieces of each variety of carbonate rock in the cores were selected after the outer surfaces, sawed slices, and etched slices of the cores had been examined. The color of each variety was named by comparison with the Rock-Color Chart (14). The rock was broken out of the concrete and freed of mortar, ground, and examined by X-ray diffraction. The crushed coarse aggregate in cores KC-7, -8, and -9 contained chert or cherty limestone that had developed rims and, in some cases, internal cracks. The reacted chert was sampled and examined by X-ray diffraction, and in immersion liquids to determine whether any chalcedonic silica, with indices of refraction below the lower index of quartz, was present.

A sample of mortar was taken from each core, away from coarse aggregate, examined under the stereomicroscope to be sure that no coarse aggregate was included, and was then crushed and sieved over the No. 100 sieve. This procedure concentrates fine aggregate in the fraction retained on the sieve and cement paste in the fraction passing the sieve. Each fraction was ground to pass the No. 325 sieve, packed in a sample holder so as to minimize preferred orientation, and examined by X-ray diffraction.

Thin section blanks, chosen from interesting areas of each core, were impregnated under vacuum with an epoxy resin formulation, mounted with epoxy resin, and prepared for microscopical examination. Thin sections prepared several years ago from cores from the McPherson test road (15), which contained Republican River sand-gravel from Wakefield, Kansas, with each of two cements with and without the addition of 30 percent crushed Moline limestone, were re-examined for comparison.

Because the cores were conspicuously dry when received, although they had presumably been drilled with water and some had reached the laboratory within a few days after drilling, it appeared desirable to determine whether the concretes were potentially capable of expansion if they were exposed to water or high humidity. Two prisms approximately 4 in. by $1\frac{1}{2}$ in. by $1\frac{1}{2}$ in. were cut from each core, except KC-7 and KC-9, and a ball bearing cemented to the center of each end face of each prism with an epoxy resin to provide a reference point. After the resin had hardened at room temperature for several days, one prism from each core was stored over distilled water in an individual polyethylene container, and the other prism was stored in another individual polyethylene container and covered with distilled water to a depth of $1\frac{1}{2}$ in. The containers had tight-fitting lids, and a piece of heavy polyethylene large enough to overlap each side of the container at the top was laid over the opening before the lid was pressed down. The humidity in the container reached a level high enough for moisture to condense on the underside of the polyethylene sheet if an inch of water were placed in the bottom of the container.

Each prism was equilibrated for 72 hr at room temperature, and its reference length then measured with a micrometer graduated to 0.0001 in. The prisms stored above water were measured at 28-day intervals, at room temperatures ranging from 23.0 to 27.1 C. The other prisms were subjected to a cycle like that of ASTM Designation:

TABLE 5
CONSTITUENTS OF THE MORTAR FRACTION IDENTIFIED BY X-RAY DIFFRACTION

Constituent	Cores															
	Finer than No. 100 Sieve								Coarser than No. 100 Sieve							
	KC-1	KC-4	KC-5	KC-6	KC-7	KC-8 ¹	KC-9	KC-11	KC-1	KC-4 ²	KC-5 ²	KC-6 ³	KC-7 ⁴	KC-8 ⁵	KC-9	KC-11
Sulfoaluminate																
32H ₂ O	3	—	tr	tr	—	—	tr	tr	tr	tr	tr	tr	—	—	tr	tr
11H ₂ O	—	—	—	—	—	—	tr?	—	—	—	—	tr	—	—	—	—
C ₄ AH _x	—	—	—	—	?	—	—	—	—	—	—	—	tr	—	—	—
Monocarboaluminate	tr	3	3-	3	3+	3+	3+	3-	—	tr	tr	tr	tr	tr+	3	—
Hydrogarnet	tr	tr	tr	tr	—	tr	tr	?	tr	—	—	—	—	tr	—	—
Ca(OH) ₂	3	3	2	3	2	3	2	2	3	3-	3-	3-	3	3	3-	tr
Calcium silicate hydrate	Present in all samples; most lines overlapped by others								pr	pr-	pr	pr	pr	pr	pr	pr
Residual unhydrated cement	Traces probably present in all samples								tr	tr-	tr	tr	tr	?	?	pr
Quartz	Most prominent constituent of all samples; probably less abundant than the sum of the feldspars if the whole mortar is considered								1	1	1	1	1	1	1	1
Feldspar	More potassium than plagioclase feldspar, except in KC-5, and -6								1-	3	1	2	2	2+	2	2
Calcite	1	1	3	2	1	1	3	1	3	3	3	3	3	2	3	3

¹Extra line at 10.1 Å.

²Extra line at 9.2 Å.

³Extra line at 10.2 Å.

⁴Extra line at 10.4 Å.

⁵The metastable calcium aluminate, 2CaO·Al₂O₃·8H₂O, is also present, and minor mica.

Note: 1 = major; 2 = moderate; 3 = minor; tr = trace; pr = present; ? probably present. KC-2, -3, -10 sand-gravel concretes; others contain carbonate coarse aggregates. The calcite in the sand-gravel concretes represents both occasional calcareous grains in fine aggregate and secondary calcite.

TABLE 6
LENGTH CHANGE OF SAWED CONCRETE PRISMS STORED IN SEALED CONTAINERS OVER WATER

Specimen	Reference Length After 4 Days in Water (in.)	Length Change (%)													
		32 Days	60 Days	88 Days	116 Days	144 Days	172 ¹ Days	200 Days	228 Days	256 Days	284 Days	312 Days	340 Days	368 Days	
KC-1	4.4585	+0.034	+0.054	+0.074	+0.074	+0.074	+0.070	+0.065	+0.061	+0.061	+0.053	+0.051	+0.049	+0.063	
KC-4	4.5615	+0.022	+0.044	+0.063	+0.059	+0.061	+0.057	+0.059	+0.055	+0.061	+0.053	+0.050	+0.053	+0.066	
KC-5	4.7485	+0.038	+0.057	+0.067	+0.067	+0.063	+0.072	+0.074	+0.069	+0.074	+0.074	+0.078	+0.082	+0.099	
KC-6	4.5085	+0.029	+0.051	+0.058	+0.062	+0.060	+0.060	+0.058	+0.055	+0.064	+0.055	+0.055	+0.058	+0.067	
KC-8	4.4977	+0.022	+0.044	+0.071	+0.064	+0.064	+0.056	+0.062	Not read	+0.064	+0.078	+0.100	+0.098	+0.076	
KC-11	4.4698	+0.022	+0.060	+0.092	+0.081	+0.078	+0.056	+0.065	Not read	+0.065	+0.072	+0.087	+0.098	+0.081	

¹Water in all containers changed after 172 days.

Note: Air temperature in storage room ranged from 26.7 to 23°C; temperatures of water equilibrated with the room ranged from 26.4 to 22.1°C.

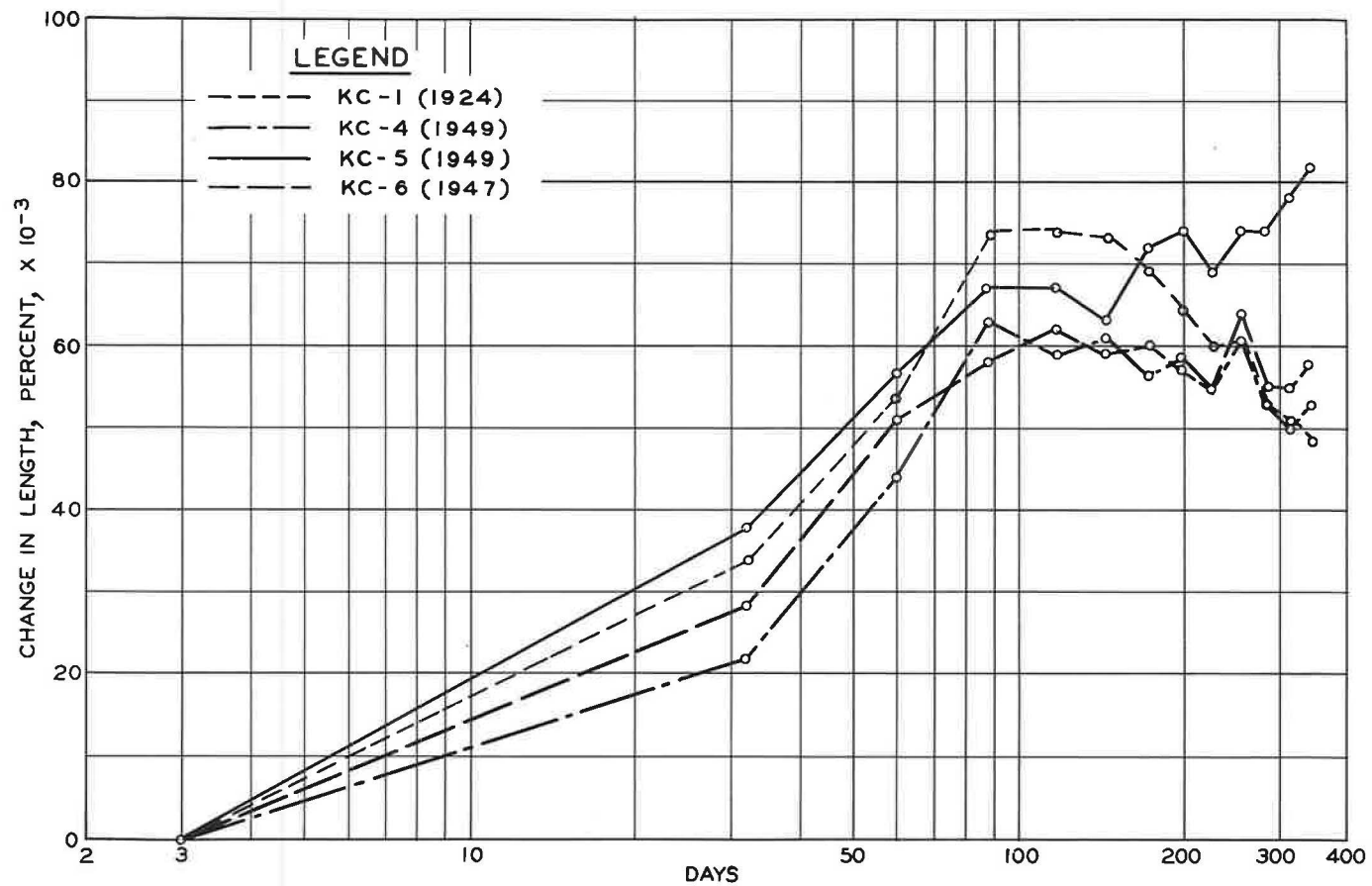


Figure 1. Expansion, during storage over water at 25 ± 2 C, of sawed concrete prisms from a pavement at Scandia (KC-1) and from office building and garage at Harlan County Dam.

TABLE 7
LENGTH CHANGE OF SAWED CONCRETE PRISMS SUBJECTED TO A CONROW CYCLE

Specimen	Reference Length After 4 Days in Water (in.)	Length Change (%) After		Length Change (%) After Designated Time ¹ in Water at Room Temperature													
		Stored in Water		Stored in Air		1 Day		7 Days		28 Days		56 Days		84 Days		112 Days	
		29 Days at Room Temp.		7 Days at 55 C		7 Days		7 Days		Days		Days		Days		Days	
KC-1	4.4170	+0.020	+0.057	-0.041	-0.025	0	+0.032	+0.032	+0.032	+0.038	+0.059	+0.041	+0.038	+0.027	+0.032	+0.029	+0.034
KC-4	4.5725	+0.028	+0.136 ^a	-0.015	-0.004	+0.024	+0.085	+0.112	+0.048	+0.050	+0.057	+0.061	+0.076 ^b	+0.061	+0.051	+0.061	+0.079
KC-5	4.7290	+0.027	+0.027	-0.057	-0.025	-0.006	+0.038	+0.051	+0.044	+0.051	+0.053	+0.046	+0.049	+0.051	+0.046	+0.051	+0.061
KC-6	4.5485	+0.040	+0.057	-0.033	-0.004	-0.005	-0.042	+0.055	+0.053	+0.059	+0.059	+0.053	+0.051	+0.057	+0.059	+0.057	+0.015 ^d
KC-8 ^e	4.5303	+0.033	+0.108	-0.035	-0.004	+0.042	+0.132	+0.132	+0.132	+0.146	+0.148	+0.161	+0.159	+0.159	+0.166	+0.172	+0.168
KC-11 ^f	4.4753	+0.036	+0.159	-0.009	+0.036	+0.087	+0.217	+0.230	+0.230	+0.237	+0.239	+0.239	+0.239	+0.241	+0.244	+0.241	+0.241

¹First day in water at room temperature is 54th day since start of test; water in all containers changed after 112 days.

^aBall bearing fell out, was replaced; later readings may not be significant.

^bHigh reading was checked several times. Reason for high reading unknown.

^cRust deposit on ball bearing, was scratched off, left pit in bearing; reading is not valid.

^dTests of these prisms started at later date than first six.

Note: Air temperature in the storage room ranged from 26.2 to 22.9 C; temperatures of water equilibrated with the room ranged from 26.4 to 22.4 C.

C 342-61T (Potential Volume Change of Cement-Aggregate Combinations, the Conrow Test) (16, 17), except that the temperature range of the room in which the containers were stored was greater than that permitted in the test procedure.

Results

Table 5 contains the results of X-ray examinations of the cement paste concentrates. Table 6 and Figures 1 and 2 show the length-changes of concrete prisms exposed at high humidity, and Table 7 and Figures 3, 4 and 5 show the length changes of prisms exposed to a Conrow cycle. All of the descriptions of carbonate coarse aggregates from the cores are grouped in Table 8.

KC-1.—The sample was an unreinforced vertical core 8³/₈ in. long from an abandoned highway pavement at Scandia, Kan., placed about 1924. The coarse aggregate was very pale orange to dark yellowish-brown, somewhat shaly limestone (Table 8), apparently crusher-run stone ranging from 2¹/₂-in. maximum size to passing the No. 4 sieve. The high proportion of sand retained on the No. 50 and No. 100 sieve suggested that the fine aggregate had been used in the grading in which it had been obtained. The source of the cement is not known. The paste was grayish in most of the concrete; the mortar was well consolidated with a few irregular voids up to ³/₈ in. in maximum dimension. A few small pockets of white opaque gel were found, and two fresh gel spots developed on the surface of one piece of the core after several days of soaking. The finished surface was weathered, and worn so that the sand grains stood in relief above the paste. The core showed a few short cracks, believed to be old because the paste bordering them differed in color from the rest. A deposit that was relatively resistant to hydrochloric acid formed an irregular layer just below the pavement surfaces.

Carbonate coarse aggregate and associated reactions.—Some of the pieces of coarse aggregate had darker shells at the outer border next to the mortar. When pieces of the concrete were broken, the darker shells stuck to the mortar and the paler centers fell out. Some dark-shelled pieces of coarse aggregate were bordered by brownish lobes or tongues of mortar,

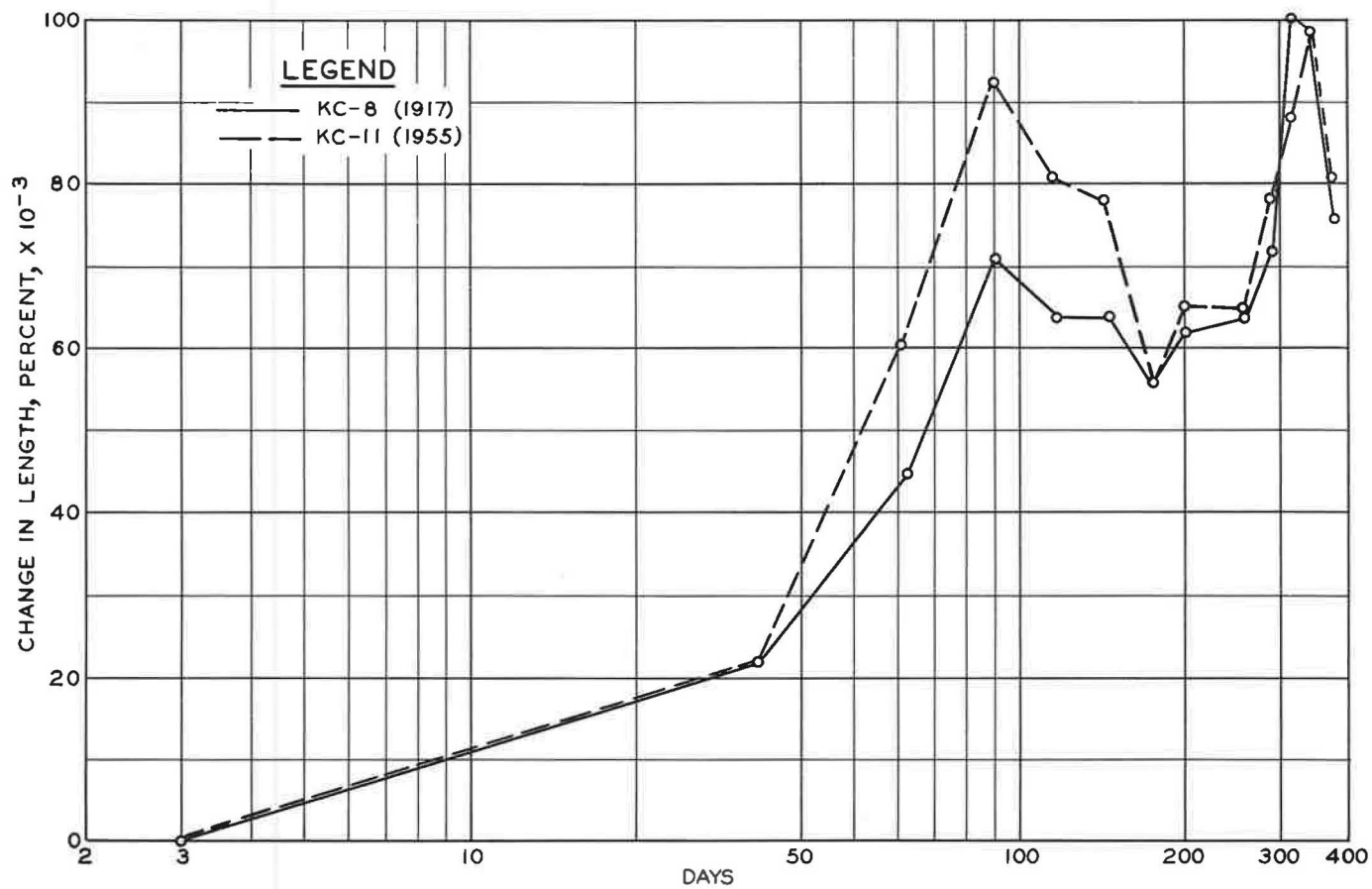
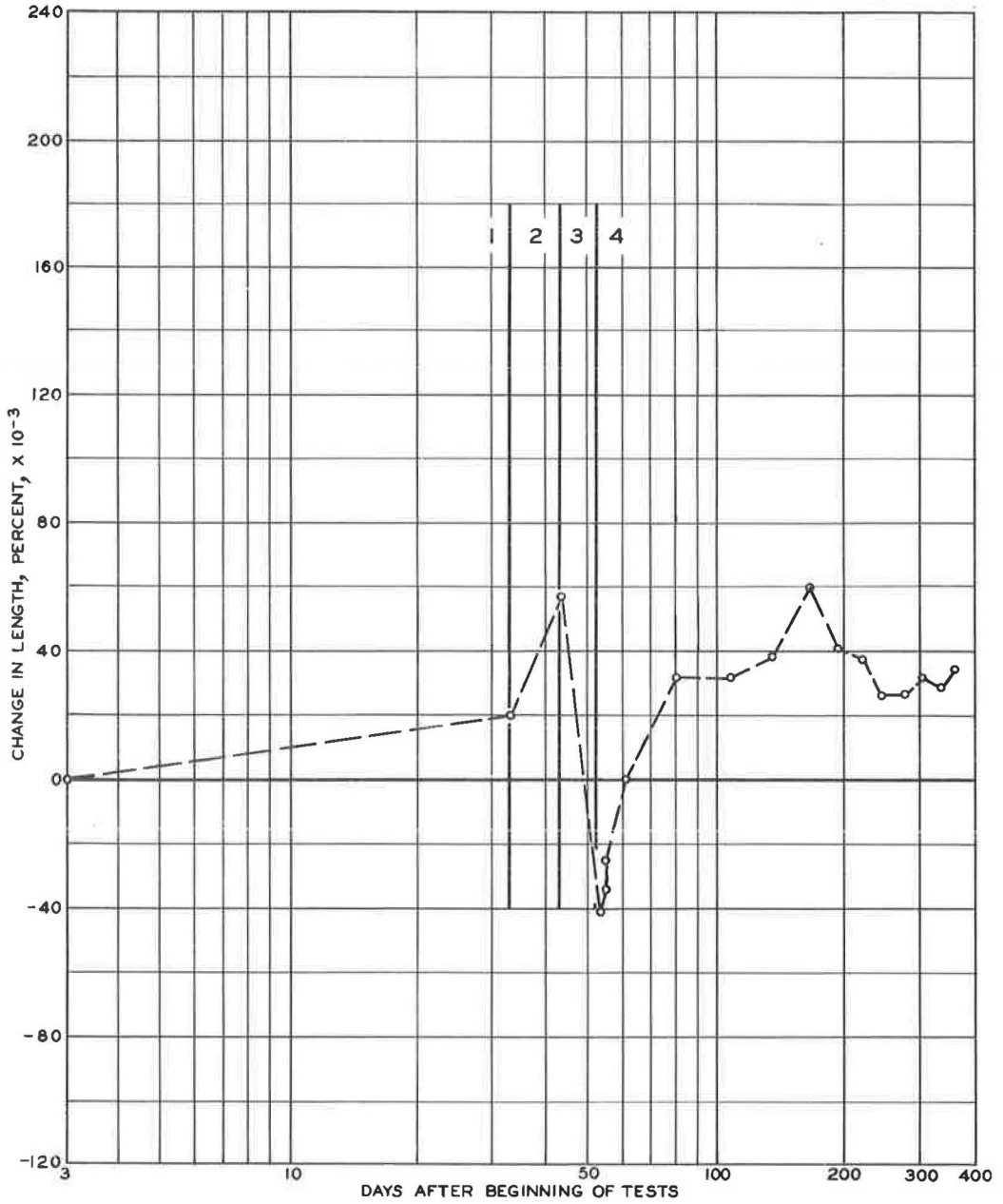


Figure 2. Expansion, during storage over water at 25 ± 2 C, of sawed concrete prisms from two structures at Fort Riley, Kan.



LEGEND

— — — KC-1 (1924)

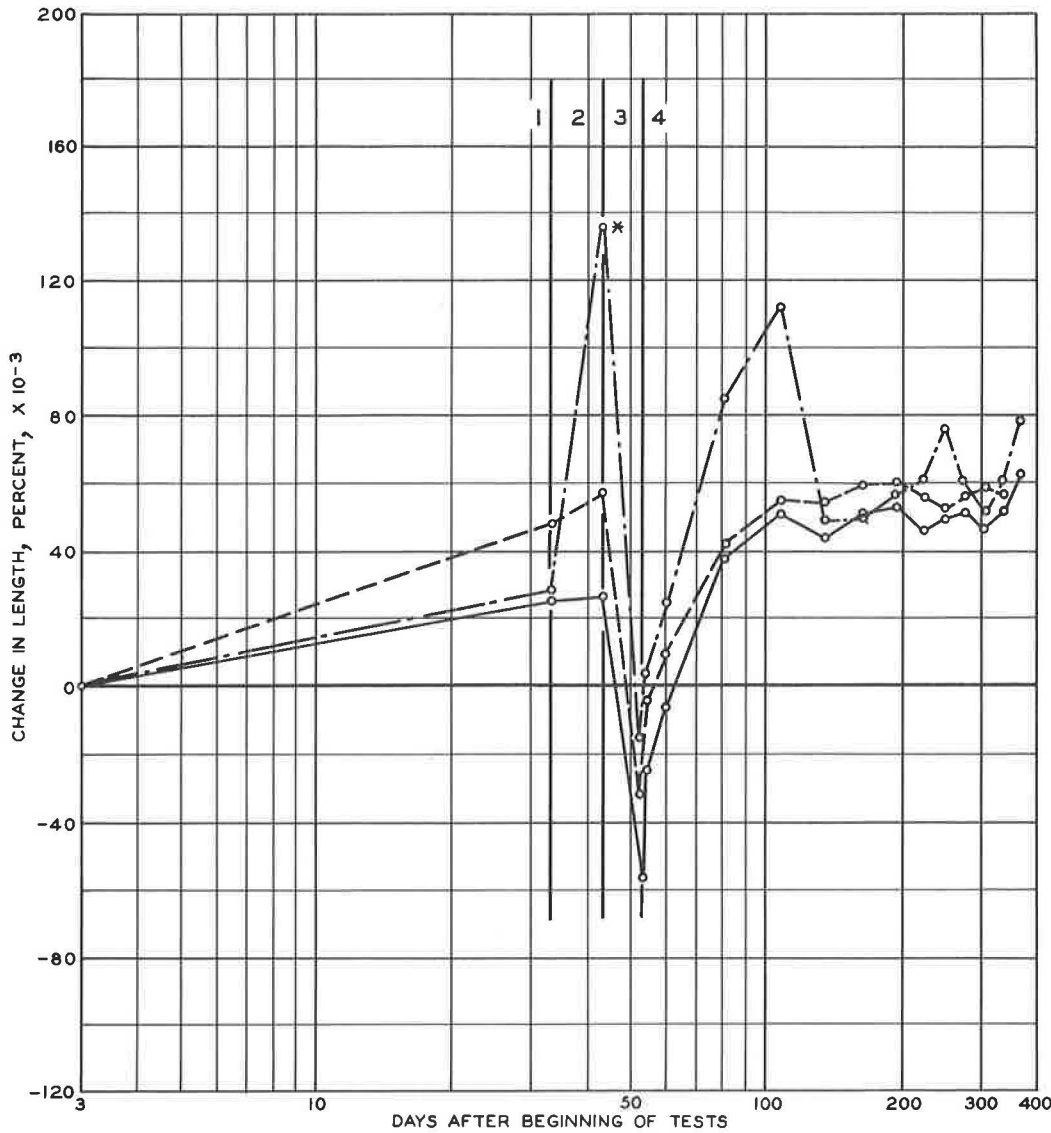
1=33 DAYS IN WATER AT $\approx 23^{\circ}$ C

2=7 DAYS IN WATER AT 55° C

3=7 DAYS IN AIR AT 55° C

4= IN WATER AT $\approx 23^{\circ}$ C

Figure 3. Effect of Conrow cycle on sawed concrete prisms from a structure at Scandia, Kan.



LEGEND

- KC-4 (1949)
- KC-5 (1949)
- · - KC-6 (1947)
- 1=33 DAYS IN H_2O AT $\approx 23^\circ C$
- 2=7 DAYS IN H_2O AT $55^\circ C$
- 3=7 DAYS IN AIR AT $55^\circ C$
- 4=IN H_2O AT $\approx 23^\circ C$

NOTE: * BALL BEARING FELL OUT AND WAS REPLACED, LATER MEASUREMENTS MAY BE MEANINGLESS.

Figure 4. Effect of Conrow cycle on sawed concrete prisms from Harlan County Dam, Neb.

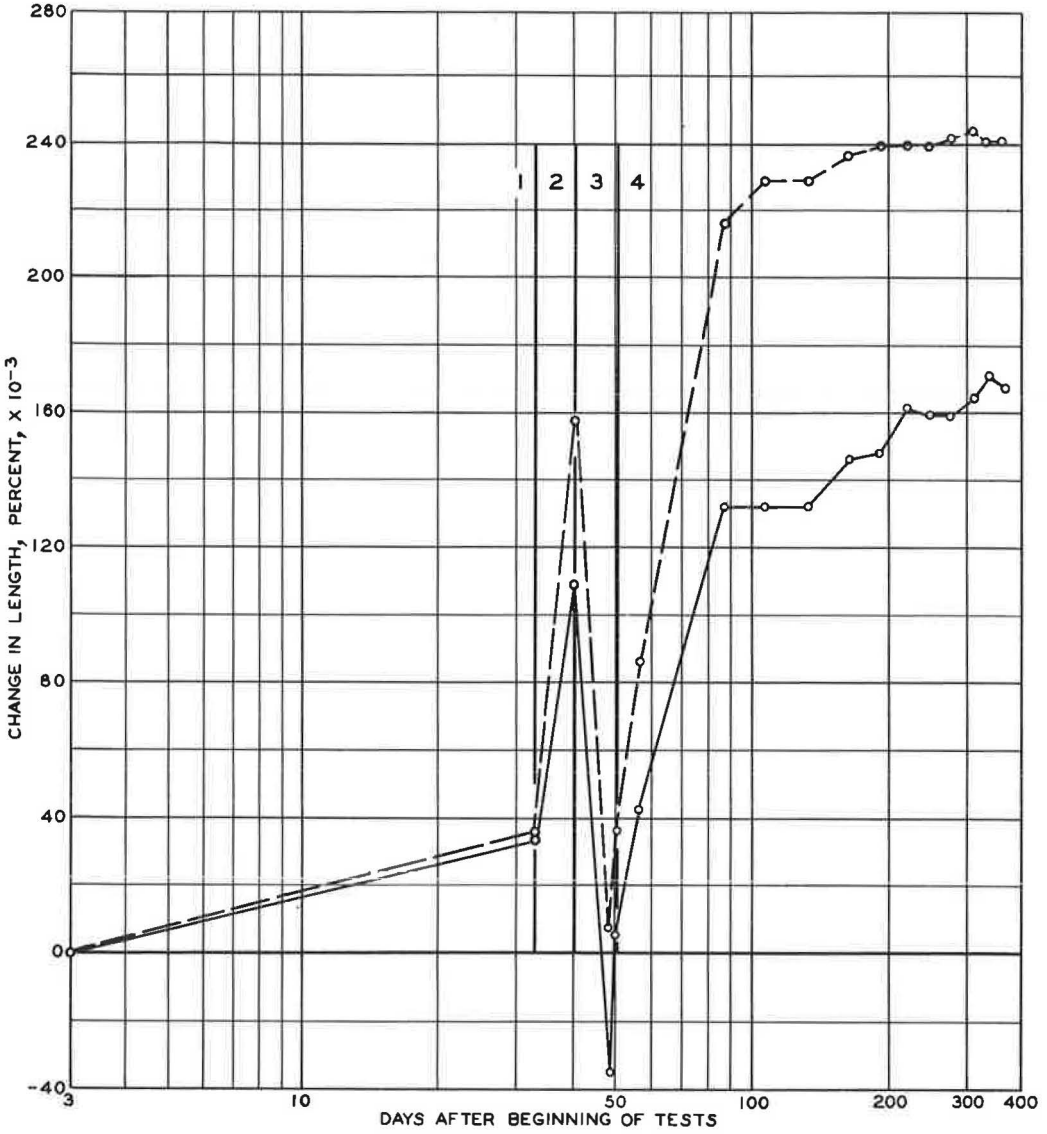


Figure 5. Effect of Conrow cycle on sawed concrete prisms from two structures at Fort Riley, Kan.

TABLE 8
COMPOSITION OF CARBONATE COARSE AGGREGATES IN EIGHT CONCRETE CORES

Specimen	Variety	Approximate Percent of Coarse Aggregate	Constituents Identified by X-ray
KC-1	Very pale orange (5YR 7/2) to pale yellowish-brown (10YR 7/2) fine-grained occasionally fossiliferous limestone, with slight tendency to form rims	75	Almost all calcite, minor chert, traces of kaolin-group clay and feldspar. (Chert is chalcedonic.)
	Moderate yellowish-brown to dark yellowish-brown (10YR 5/4 to 10YR 4/2) thin-bedded fossiliferous limestone with shale partings; fossils are coarse calcite and matrix is fine grained. Rims fairly prominent	15	Calcite major; chert minor; ferroan dolomite minor; kaolin-group clay; clay-mica, feldspar, pyrite in traces. (Chert is chalcedonic.)
	Pale yellowish-brown to dark yellowish-orange (10YR 6/2—10YR 6/6) limestone, a more weathered softer variety of that described just above. Rims fairly prominent	10	Constituents and proportions like those of previous variety
KC-4 and KC-5	Light olive-gray (5Y 6/1) ranging to medium light gray (N6) fine-grained limestone makes up almost all of the aggregate. Rims were common on etched surfaces. Traces of shaly and fossiliferous varieties were seen; no X-ray examinations of these were made.	97+	Major calcite; quartz very minor or traces; traces of clay-mica and other clay; no dolomite. Pattern of limestone from permanent sample previously tested was almost identical.
KC-6	Pale yellowish-brown (10YR 6/2) to light olive-gray (5Y 6/1) fine-grained dense limestone, some with faint rims	65	Major calcite; chert very minor to trace; dolomite, trace; traces of feldspar, clay-mica, chlorite, kaolin-group clay (?), pyrite
	Light gray (N7) fine-grained calcareous dolomitic sandstones to sandy limestones, which looked very much alike but showed the range in composition noted.	20	Major to moderate amounts of calcite and disseminated chert in all, with dolomite ranging from major to very minor; traces of clay-mica, feldspar, pyrite, chlorite, kaolin-group clay
	Somewhat weathered pale yellowish-orange shaly limestone (10YR 8/6)	5	Major calcite; moderate to minor chert; minor dolomite, very minor feldspar; clay-mica, very minor; traces of chlorite
	Light gray (N7) to medium light gray (N6) chert	10	Chert with very minor calcite, traces of dolomite and clay-mica
KC-7	Pale yellowish-brown (10YR 6/2) to yellowish-gray (5Y 8/1) dense fine-grained limestone, forming rims less soluble than interiors of pieces	50	Major calcite, minor chert, very minor dolomite; trace clay-mica
	Yellowish-gray (5Y 8/1) to light olive-gray (5Y 6/1) calcareous dolomitic cherts to cherty calcitic dolomites	30	All contain calcite, dolomite, quartz, in amounts ranging from moderate to major from piece to piece, with traces of feldspar, clay-mica, clays
	Pale yellowish-orange (10YR 8/6) to grayish-orange (10YR 7/4) weathered limestones and dolomites	15	Not examined
	Light gray (N7) chert, like that in KC-6 aggregate	5	Not examined
KC-8	Pale yellowish-orange (10YR 8/6) to grayish-orange (10YR 7/4) fine-grained fossiliferous limestone, not forming rims	65	Calcite and very minor quartz
	Very light gray (N8) to yellowish-gray chert (5Y 8/1), chalcedonic	25	Chert predominant, minor or very minor calcite, occasional traces of dolomite
	Light olive-gray (5Y 6/1) limestone	5	Major calcite, moderate chert, very minor clay-mica, traces of feldspar, kaolin or chlorite
	Medium dark gray (N4) fine-grained limestone	3	Major calcite, minor chert, clay-mica; traces of chlorite, feldspar, pyrite
KC-9	Very pale orange (10YR 8/2) soft fine-grained fossiliferous limestone, some pieces having reddish-brown rims in the mortar adjacent to them	70	Calcite, traces of quartz, possible trace of gypsum
	Grayish-orange (10YR 7/4) porous, fossiliferous limestone; fossils darker than matrix and sometimes leached. No rims observed.	15	Calcite, very minor chert, traces of mica
	Light gray (N7) to medium gray (N5) chalcedonic chert	15	Chert with traces of calcite, dolomite
KC-11	Yellowish-gray (5Y 8/1) very fine-grained earthy limestone	50	Calcite, very minor quartz, traces of feldspar, clay-mica
	Light olive-gray (5Y 6/1) limestone, otherwise like the the previous variety	30	Like the above
	Yellowish-gray (5Y 8/1) to dark yellowish-orange (10YR 6/6) vuggy limestone; vugs probably represent leached fossils. A few contained limonite.	10	Calcite, very minor quartz, traces of clay and mica
	Moderate yellowish-brown (10YR 5/4) weathered thin-bedded limestone, in elongated pieces with beds a few millimeters thick. The distribution and amount of insoluble residue varied from piece to piece.	10	Major calcite; very minor quartz, very minor clay-mica with some possible mixed layering with a 14-A clay, traces of feldspar, possible trace of dolomite

widest at the coarse aggregate-mortar interface, dwindling into the surrounding mortar (Fig. 6). X-ray examination of the dark shells and discolored mortar did not show any brucite ($\text{Mg}(\text{OH})_2$) and little dolomite was present in the interiors of the rimmed coarse aggregate. A slice of the concrete etched with hydrochloric acid by the procedure of Lemish et al. (8) revealed thin rims, just inside the surfaces of some coarse aggregate particles, less soluble than the surfaces or the interiors (Fig. 7). Two counts of one sawed surface were made at low magnification to determine whether there was any association between the rim phenomena and any evidence of distress. Results of the first count of a 6- by 6½-in. sawed surface parallel to the axis of the core are given in Table 9 and results of the second count are given in Table 10. Chi square, calculated as 49.586 with 2 degrees of freedom, corresponds to a probability less than 0.01 of this degree of association between size and rims arising by chance, showing that rims were more abundant on larger pieces of coarse aggregate. Qualitatively, rims were also more abundant on two darker lithologic varieties which together amounted to one-quarter of the whole coarse aggregate. Rims were least abundant on the commonest lithologic variety in the aggregate (Table 8).

Thin sections of the concrete contained a few highly carbonated areas of mortar, usually partially rimming a coarse aggregate particle and projecting as a short lobe into the mortar. The limestone coarse aggregate ranged from fairly pure and very fine grained to highly fossiliferous and shaly limestone particles, some of which contained coarser-grained recrystallized calcite, and cherty areas. The fine aggregate was coarse natural sand composed of quartz, feldspar, and rock fragments, with occasional chert and cryptocrystalline and glassy rock particles. Most of the sand grains were in the No. 16 to 50 sieve size range. Corroded or partially unhydrated cement grains were abundant. Calcium hydroxide was present both in the paste and at fine aggregate-paste contacts. Chert, and cryptocrystalline and glassy rocks—the poten-



Figure 6. KC-1, sawed surface, three-quarter size. Note dark rims around most of limestone coarse aggregate particles and darker staining of mortar around large limestone particle in lower right corner.



Figure 7. KC-1, sawed surface, three-quarter size, etched with 3N hydrochloric acid. Limestone coarse aggregate particles were etched more than mortar surface itself, and are therefore in negative relief. Note Lemish rim located just inside large limestone particle in lower left center.

tially reactive constituents of the aggregate—showed no signs of having reacted with the alkalis in the cement.

One surface of the prism stored over water (Table 6, Fig. 1) was part of the original surface of the pavement; several white gel spots formed on it. A small gel-filled crack was noted next to a limestone coarse aggregate particle on another surface. No gel appeared on the prism subjected to the Conrow cycle (Table 7, Fig. 3). The gel spots formed on the first prism substantiated the presence in the concrete of ingredients capable of alkali-silica reaction in environments favoring the reaction.

Cores KC-4 and -5, Administration Building, Harlan County Dam, Neb.—Two horizontal cores were drilled from the outside of the north and south walls of the Administration Building at Harlan County Dam, Harlan County, from concrete placed in 1949. The concrete materials were (a) type IA cement; (b) crushed limestone coarse aggregate, Pixley Mine, Independence, Mo.; and (c) Kansas River sand, Stewart Sand and Materials Company plant, Turner, Kan. Chemical analyses of cements from this source, made by the National Bureau of Standards during 1949, indicated total alkali contents, expressed as Na_2O , as high as 0.68 percent. The alkali content of the cement used in the structure is not known.

A sample of limestone (KAN-4 G-6(E-H)) from Pixley Mine, examined at the WES in 1948 (18), was soft limestone of nonuniform texture, with bulk specific gravity in the $\frac{3}{4}$ -in. to No. 4 size of 2.63; absorption, 1.1 percent, and durability factor with manufactured limestone sand from the same source, 58; with natural fine aggregate from Georgetown, Miss., 30. KC-4 was drilled across a vertical crack below a window outside of the patterned area adjoining the window on the west (Fig. 8). The core arrived as an intact half, from which a deformed reinforcing bar protruded, and several smaller pieces from the other side of the crack. The crack surface was partly

TABLE 9

Aggregate Type	No. of Particles
Limestone coarse aggregate:	
Without rim ¹	38
With rim in rock	20
With lobe or partial rim in mortar	7
With rim in rock, and lobe or partial rim in mortar	32
With crack in rock	2
Chert with adjoining gel pocket	1
Miscellaneous coarse sand grains with evidence of alkali-silica reaction	1
Total	101

¹Most of the unrimmed particles were very pale orange, fine-grained, high-calcite limestone with minor chert and traces of kaolin-group clay and feldspar.

TABLE 10

Maximum Dimension of Particle (in.)	Rim	No Rim	Total
Up to 1/4	8	44	52
1/4 to 1/2	28	14	42
1/2 to 3	20	0	20
Total	56	58	114

coated with secondary calcium carbonate. KC-5 was an intact core of reinforced concrete. Both cores appeared to have entrained air contents lower than normal with scattered irregular voids up to 1/4 in. in diameter. Dark rims on limestone coarse aggregate were common in both cores. The coarse aggregate was 1-in. maximum size limestone, light olive-gray to medium light gray and fine grained, with about 3 percent shaly and fossiliferous pieces; the particles larger than 1/2-in. maximum diameter had long axes of the exposed sections usually twice as long as the short axes, but the smaller particles were more blocky. In both cores dark rims were conspicuous just inside the peripheries of many of the coarse aggregate particles, more or less concentric with their outer edges. Several relations between the solubilities of different zones appear in Figures 9, 10 and 11. Some coarse aggregate particles show no rims after etching; in others, the center is slightly less soluble than the rim. Many particles in KC-4 (Fig. 9) showed the periphery most deeply etched, the next zone concentric to it narrow, irregular, and the least soluble region of the particle; and the central region more soluble than the intermediate zone but less sol-

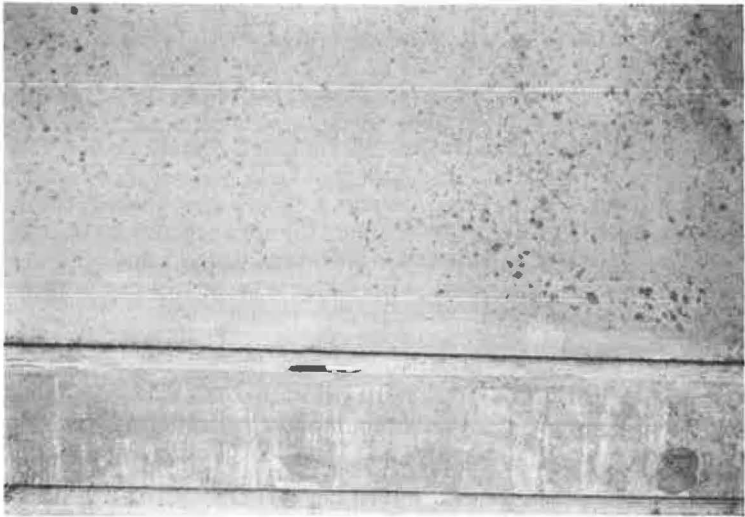


Figure 8. North wall of administration building, Harlan County Dam, Harlan County, Neb., showing mottling of concrete. The ball-point pen is 5 1/8 in. long. KC-4 was drilled to left of field shown.

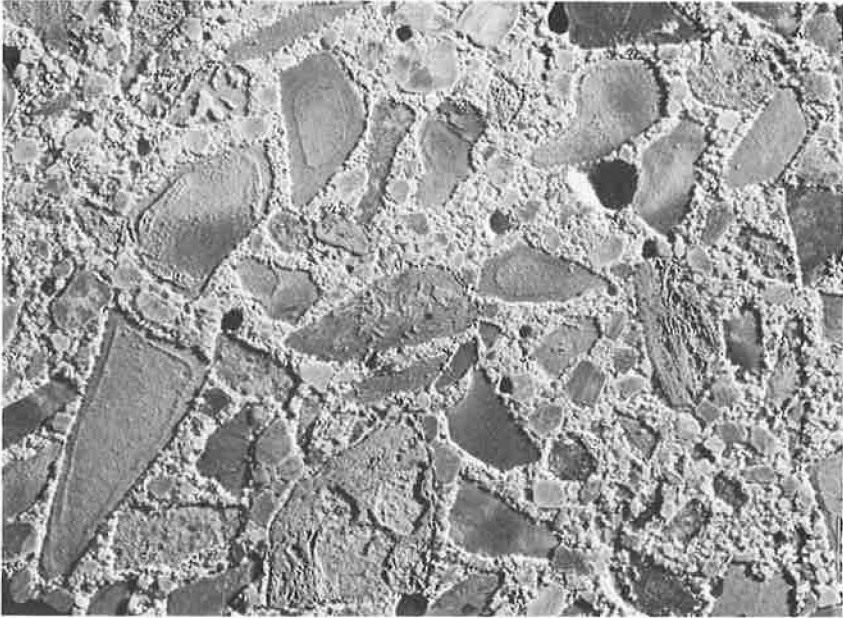


Figure 9. KC-4, sawed surface, $\times 1\frac{1}{2}$, etched in 3N hydrochloric acid. Limestone particles were etched deeper than rest of surface and are therefore at lower elevations than rest of surface. An excellent example of the Lemish rims that developed on many of these particles is shown in the large, wedge-shaped particle in lower left. Others are present.

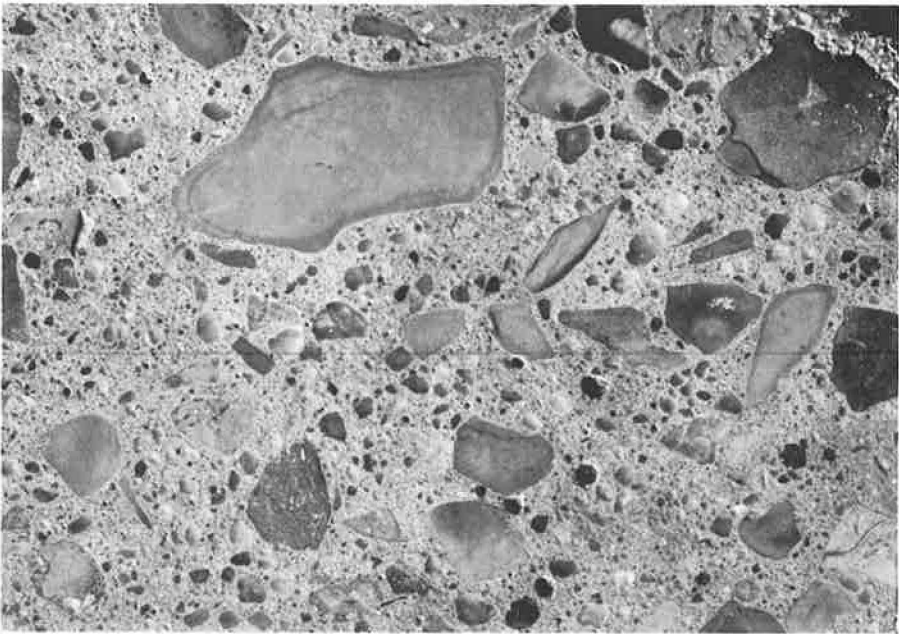


Figure 10. KC-5, sawed surface, $\times 1\frac{1}{2}$. Concrete in KC-4 and -5 was made from same aggregate and cement combinations; therefore, limestone particles in both exhibit the same type of rims. Compare with Figures 9 and 11.

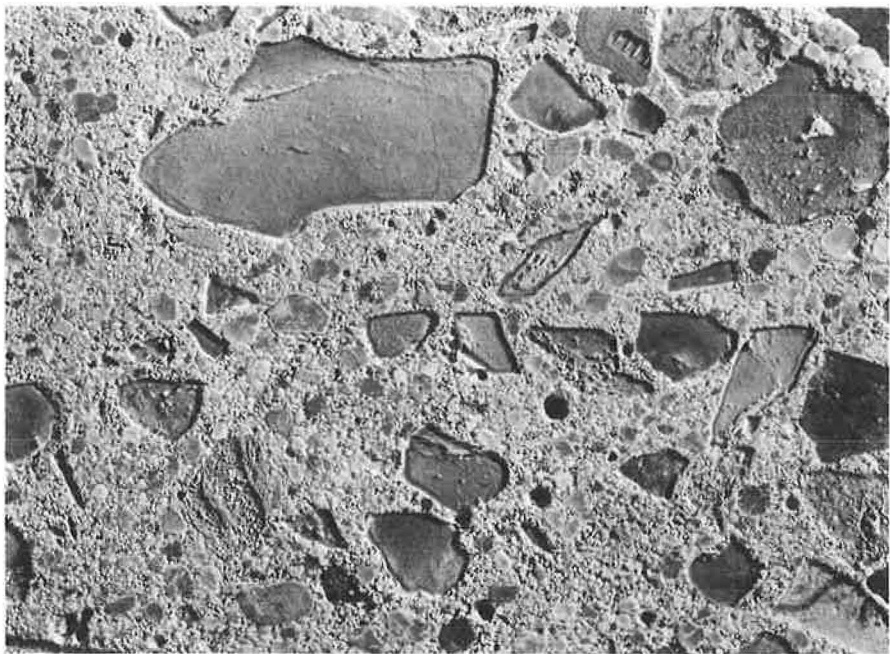


Figure 11. KC-5, sawed surface, $\times 1\frac{1}{2}$, etched with 3N hydrochloric acid (same surface as Fig. 10). Note that particles in this photograph displaying Lemish rims are, in most cases, same particles that had dark surface rims in Figure 10.

uble than the outer rim. Coarse aggregate particles were counted on sawed slices from both cores to determine the amount and type of rimming present (Table 11). There was no apparent relation between rimming and particle size. Quartz silt appeared in the limestone as an impurity, recognized in thin sections and by X-ray diffraction, but neither chert nor cherty limestone was found. No dolomite was detectable in the X-ray patterns of the limestone (Table 8). The limestone represented in the 1948 sample contained 2.45 percent insoluble residue, principally quartz, with minor pyrite, and very minor plagioclase, clay-mica, chlorite, and possible kaolin.

X-ray examination of cement paste adjoining a limestone coarse aggregate particle contained substantially more monocarboaluminate than a paste sample farther away from coarse aggregate.

Thin sections of concrete from both cores showed abundant calcium hydroxide in the paste and around many aggregate grains, and substantial carbonation of the mortar at the cement paste-aggregate borders of several of the limestone coarse aggregate particles. The carbonation was heaviest at the paste-aggregate contacts, and usually thinned and faded out a short distance away from the contacts. Calcium hydroxide was generally absent in areas of carbonated paste and at paste-fine aggregate contacts in carbonated areas, but was present on the sides of the particles that were outside the carbonated areas. The resulting texture of the paste was unusual.

TABLE 11

Constituent	Percentage	
	KC-4	KC-5
Limestone:		
No rims or cracks	78	69
With internal rims	17	25
With external rims	2	3
With internal cracks	—	1
With border cracks	—	1
Other (large natural aggregate)	3	1
Total	100	100

Stereomicroscope examination of mounted thin section blanks of these two cores showed an unusual number of microfractures in the cement paste, particularly in the blanks from KC-4, by comparison with blanks of KC-6. The fine aggregate contained a few particles regarded as potentially alkali-silica reactive, but no signs of alkali-silica reaction were observed. Rims of the type present in some of the limestone particles on the sawed surfaces were not recognized in the thin sections. No differences in the limestone particles from the interiors to the borders could be seen, whereas in particles on the sawed surfaces there was a color difference and a difference in solubility in dilute hydrochloric acid just inside the borders of rimmed particles. Most of the limestone particles were fine grained and slightly fossiliferous, with occasional coarser-grained particles, and coarser-grained areas in the finer-grained particles.

No signs of alkali-silica reaction gel were found on the prisms stored at high humidity or those subjected to a Conrow cycle (Tables 6, 7; Figs. 1, 4). The comparison between the behavior of the prism from KC-4 and that from KC-5 in storage at high humidity (Fig. 1) indicated that KC-4 represented concrete that had probably exhibited some of its reactive potential in the structure. The pattern on the outer surface on the north wall of the building (Fig. 8) may represent the result of such expansion. The south wall of the building was not patterned like the north wall; KC-5, from the south wall, retained its expansive potential and exhibited it in the higher expansion it developed and retained in storage over water.

Core KC-6, Garage, Harlan County Dam, Neb.—A horizontal core was drilled from the west wall of the garage building at Harlan County Dam, from concrete placed in 1947 that contained (a) crushed limestone coarse aggregate from the Loring quarries, Bonner Springs, Kan., (b) Republican River sand from the More Sand Company, Junction City, Kan., and (c) type II cement of unknown alkali content. Two samples of type II cement from this mill, analyzed by the National Bureau of Standards during 1947 for projects where low alkali cement was required, had total alkali contents, expressed as Na_2O , between 0.50 and 0.60 percent.

The concrete was well consolidated with slightly higher entrained air content than core KC-4 or -5. Larger entrapped air voids were also numerous; no cracks were observed. The core contained one deformed reinforcing steel bar. No alkali-silica reaction gel was found on the core as received, or after it had been soaked in water for several days.

The crushed stone coarse aggregate consisted of several varieties of limestone, cherty limestone, and chert, graded to 1-in. maximum size. Coarse aggregate particles exposed on sawed surfaces were more blocky with fewer tabular and elongated particles than in cores KC-4 and -5. Light olive-gray and yellowish-brown fine-grained limestone particles made up about 65 percent of the coarse aggregate. A very few of the limestone particles showed rims when sawed surfaces were etched in 3N hydrochloric acid (Figs. 12 and 13).

Light gray, very fine-grained porous particles ranging in composition from calcareous dolomitic sandstone to sandy limestones made up about 20 percent of the coarse aggregate (Table 8). Narrow dark reaction rims located at the aggregate-mortar contacts surrounded most of these particles. The rims were destroyed when the slabs were etched, although the particles were only slightly etched. The etched particles looked porous and spongy (Fig. 13) because the calcite was dissolved out leaving an open network of disseminated chert. Light and medium gray hard dense chert particles with indices of refraction below 1.544 made up about 10 percent of the coarse aggregate. Rims at the mortar-aggregate contact on about one-half of the chert particles were destroyed during etching, although the chert was practically unaffected. The remainder of the coarse aggregate was weathered and shaly limestone.

A count was made on a slice of this core, in which the coarse aggregate particles were classified according to lithology and presence or absence of rims (Table 12). The results given in Table 12 demonstrate that the limestone did not form recognizable rims, but the cherty limestone and chert particles did. The ratio of rimmed to unrimmed particles of cherty limestone was larger than 8 to 1, and the ratio of rimmed to unrimmed particles of chert was 2 to 1. Although no alkali-silica gel was found in this core, the dark rims in the mortar adjoining the cherty limestone and cherty particles

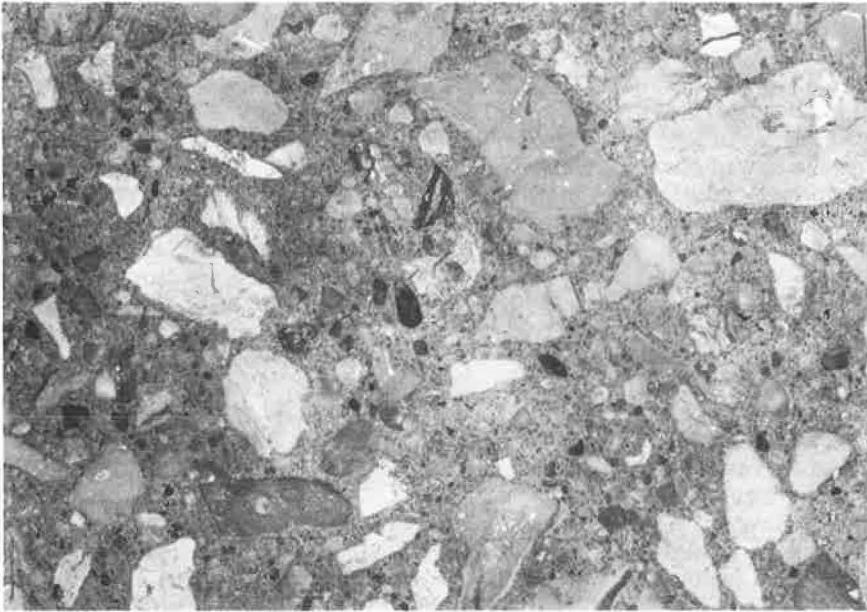


Figure 12. KC-6, sawed surface, $\times 1\frac{1}{2}$. Narrow rims are present in paste at paste-aggregate contacts of most of lighter coarse aggregate particles, although rims are not readily apparent from this photograph.



Figure 13. KC-6, sawed surface, $\times 1\frac{1}{2}$, etched with 3N hydrochloric acid. Light colored, spongy-textured, cherty particles were more resistant to acid attack and are therefore in relief above etched concrete surface. Limestone particles, being less resistant, are in negative relief.

TABLE 12

Constituent	Without Rim		With Rim		Total Observed
	Calculated Theoretical ¹	Observed	Calculated Theoretical ¹	Observed	
Limestone	117.71	143	33.29	2	145
Cherty limestone	30.05	4	8.95	35	39
Chert	9.24	4	2.76	8	12
Total		151		45	196

¹ Assuming observed rims distributed uniformly among coarse aggregate particles without regard to type.

Note: N = 196.

Degrees of freedom = 2.

Chi square = 149.480.

Probability of chance occurrence = < 0.01.

are considered a result of reaction between alkalis in the cement and the fine-grained chalcedonic chert in the porous particles. The chalcedonic chert is believed to have acted as a pozzolan in the concrete, using up the available alkalis and thus preventing later expansions caused by alkali-silica or alkali-carbonate reaction.

Thin sections from selected areas of the concrete showed little carbonation of the paste, and no reaction by potentially reactive chert and volcanic rock particles in the sand. Calcium hydroxide crystals were abundant in the paste and partially surrounding fine and most coarse aggregate particles. There was less $\text{Ca}(\text{OH})_2$ at the mortar-aggregate contacts of the very fine-grained coarse aggregate particles. Disseminated chert in these particles was generally masked by high birefringence of the calcite. The areas selected for thin sectioning contained several coarse aggregate particles with definite reaction rims, but the rims could be distinguished in thin section only by a general absence of calcium hydroxide in the areas where the rims should have been.

No gel was found on the surfaces of prisms stored at high humidity (Figs. 1 and 4).

Core KC-7, Swimming Pool, Fort Riley, Kan.—A horizontal core was drilled from the wall of the officers' club swimming pool, from concrete placed in 1945 that contained 1-in. maximum size limestone coarse aggregate of unknown source, and Republican River sand from the More Sand Company, Junction City. The type and source of the cement are unknown.

The concrete was not air entrained; it contained two reinforcing steel bars at right angles to each other. The concrete appeared to have a fairly high water-cement ratio, was oversanded, and contained occasional large entrapped air voids. Many of the coarse aggregate particles, and a few of the large sand grains that resembled opaline siltstones, were bordered by narrow rims that ranged from pale to fairly dark. One void partly filled with alkali-silica gel was observed on a sawed surface. No new gel formed on the core surfaces during the several days that it was soaked in water.

The coarse aggregate in KC-7 resembled that in KC-6 and contained the same lithologic varieties in different proportions. Possibly both aggregates came from one formation. KC-7 contained fewer limestone particles readily etched with hydrochloric acid and fewer chert particles, but more calcareous and dolomitic particles with high chert contents and slightly different colors (Table 8; Figs. 12, 13, 14, and 15).

The results of a count of coarse aggregate particles exposed on an unetched slice of this core, in which the particles were classified by lithology and by the presence or absence of rims are given in Table 13. The calculated value of Chi square, 0.237, showed no association between either variety of aggregate and rimming, the reverse of what a similar calculation showed for the aggregate in KC-6. Most of the unrimmed particles were less than $\frac{1}{4}$ in. in apparent diameter. When sawed surfaces of this core were etched with hydrochloric acid, the rims around the cherty limestone particles were destroyed, as in KC-6.

The etched surfaces of the rimmed limestone particles contained thin rims, at or just inside the aggregate-mortar interfaces (Fig. 15) that were less soluble than the interiors of the particles. Why the limestone particles in KC-7 had rims and those in KC-6 did not is not known. The possibilities include:

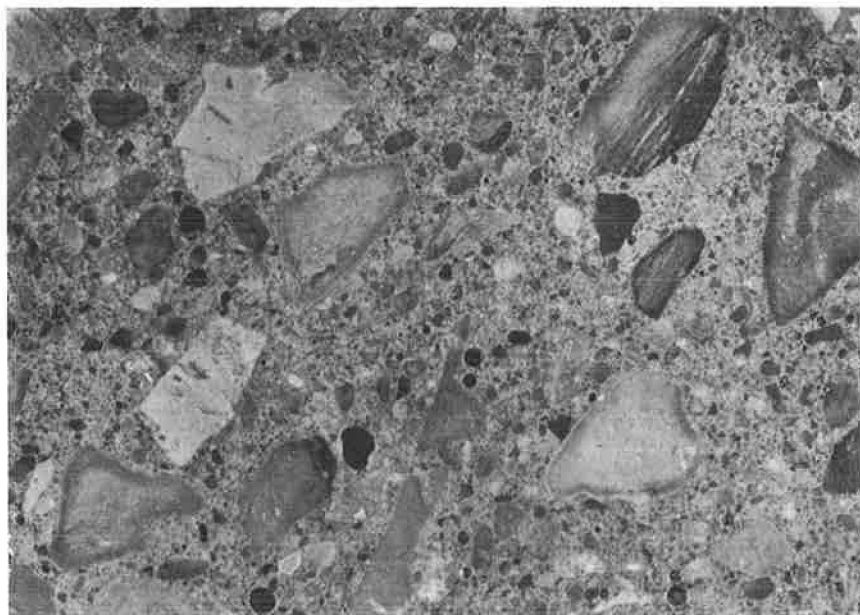


Figure 14. KC-7, sawed surface, $\times 11\frac{1}{2}$. Lighter colored coarse aggregate particles with rims in mortar immediately surrounding particles are composed of chert and cherty limestone. Darker particles with internal rims are composed of fairly pure limestone.



Figure 15. KC-7, sawed surface, $\times 11\frac{1}{2}$, etched with 3N hydrochloric acid. Rims that were present in mortar surrounding cherty particles were destroyed by the acid etch. Rims are present in two limestone particles in upper part of photograph.

TABLE 13

Constituent	Without Rim		With Rim		Total Observed
	Calculated Theoretical	Observed	Calculated Theoretical	Observed	
Limestone	26.38	26	28.62	29	55
Cherty limestone	20.62	21	22.38	22	43
Total		47		51	98

Note: $N = 98$; degrees of freedom = 1.

1. The alkali content of the cement in KC-6 was relatively lower, in terms of providing alkali to react with cherty limestone, chert, and limestone in the aggregate.

2. The assumption that the two aggregates came from the same formation is wrong, and the comparison between them—which tacitly assumes that they had similar permeability and porosity and similarly reactive chert—is unfounded.

3. Apparently the concrete proportions did differ, and KC-6 contained more and better graded coarse aggregate per unit volume than KC-7; KC-7 apparently had a higher water-cement ratio.

4. The aggregate in KC-6 contained a larger proportion of chert particles than that in KC-7; Table 8 shows 10 percent in KC-6 and 5 percent in KC-7. Both estimates were based on inadequate samples of the same size and should not be accepted as true for the structures, although they are of the right order of magnitude for the cores. Unless the insoluble residue in every piece of calcareous dolomitic sandstone to sandy limestone, all containing chert, that amounted to 20 percent of the coarse aggregate in KC-6, and the insoluble residue in every piece of the calcareous dolomitic chert to cherty calcitic dolomite that amounted to 30 percent of the coarse aggregate in KC-7, were examined, it would not be possible to decide which aggregate contained more total chert. No conclusive evidence of a real difference in total chert content was obtained, although it appeared that KC-6 contained more.

5. The environments of the two concretes were different. KC-6 came from the outer wall of a building above ground. KC-7 came from the wall of a swimming pool, probably below ground, and may have had a better opportunity of becoming saturated, from water in the soil or by failure of the swimming pool liner.

The two concretes may have behaved differently for reasons other than those listed; items 4 through 5 are partly supported by observation or history. It seems unlikely that the two years of age difference between the two concretes was very significant.

Thin sections of areas containing heavily rimmed coarse aggregate particles showed that alkali-silica reaction had occurred between coarse aggregate and paste. Around several cherty limestone particles it was difficult to distinguish between aggregate and mortar, because the mortar bordering the aggregate was heavily carbonated, and dark, dense looking rims of varying widths occupied the vague boundary areas. The interiors of the cherty limestone particles contained porous, cracked, torn areas of types previously associated with and apparently characteristic of reactive aggregate in concrete in which alkali-silica reaction has taken place. Such areas are believed to result from the rock weakening by alkaline solutions and removal of dissolved silica by diffusion or migration. The dark denser rims are a result of deposition of alkali-silica gel in the mortar immediately surrounding the reacted particles. The mortar in the dense rims was heavily carbonated, but the paste as a whole was not. Some alkali-carbonate reaction may have occurred. Calcium hydroxide crystals were abundant in the paste, and around fine aggregate particles located away from the carbonated areas, but were depleted around the reacted cherty limestone particles and perhaps masked in the carbonated paste. Calcium hydroxide crystals were present adjacent to several of the unreacted limestone particles. The potentially reactive constituents present in the fine aggregate were largely unreacted.

Core KC-8, Enlisted Men's Swimming Pool, Fort Riley, Kan.—A vertical core was taken from a World War I sewage plant later converted into an enlisted men's swimming

TABLE 14

Condition	Limestone		Calcareous Chert		Total Observed
	Expected	Observed	Expected	Observed	
No definite rims, no cracks	132.34	152	19.66	0	152
Internal rim with or without internal crack	25.25	3	3.75	26 ¹	29
Vague peripheral rim or crack in mortar	17.41	20 ²	2.59	0	20
Total		175		26	201

¹ 15 of 26 particles had interior cracks.

² 8 of 20 particles had cracks in mortar.

Note: N = 201; degrees of freedom = 2; Chi square = 177.18. Probability of chance occurrence = < 0.01.

pool at Camp Funsten, Fort Riley. The concrete, placed in 1918, was well consolidated, and only slightly oversanded; no reinforcing steel was exposed in this core. The coarse aggregate was limestone of 1-in. maximum size of unknown source; the fine aggregate came presumably from the Kansas or Republican River near Junction City, and the cement from an unknown source.

Examination of the core, as received, revealed dark rims around cherty coarse aggregate particles and around a few opal-bonded siltstone particles in the fine aggregate. Several of the chert particles were traversed by fine cracks which ran out into the mortar a short distance. No alkali-silica reaction gel was found. After the core had been sliced, soaked in water for several weeks, and the slices dried under gentle heat, several white gel spots were present on the sawed surfaces and in the fine cracks in some cherty particles.

The composition of carbonate coarse aggregate exposed on sawed surfaces of this core is shown in Table 8. The results of a count made on a sawed surface of this core, in which the particles were classified by lithology and the presence or absence of rims and cracks, are given in Table 14. The calculations indicate that: (a) the calcareous chert was associated with interior rims and cracks but the limestone was not, and (b) the limestone was associated with vague peripheral rims and cracks in the adjoining mortar but the calcareous chert was not. The rims and cracks in the cherty particles appeared typical of alkali-silica reaction, and as in KC-6, the evidence summarized here indicated alkali-silica reaction with the cherty coarse aggregate in the concrete.

Sawed and etched surfaces of slices of the core are shown in Figures 16 and 17. Figure 16, the unetched surface, shows the dark internal rims associated with the cherty particles, and shows less clearly vague rims in the mortar surrounding some of the limestone particles. Hydrochloric acid etching destroyed the rims in the chert completely. The mortar bordering the cherty particles was not etched as deeply as mortar in other areas, probably indicating that the mortar around the alkali-silica reactive particles was enriched with alkali-silica gel. The rims that developed on etched surfaces of some limestone particles in KC-1, -4, -5, and -7 were not present on limestone particles in this core; the etched surfaces of the particles were generally smooth and evenly etched.

Most of the area of thin sections from this core was heavily carbonated, but the carbonation was not areally associated with any other recognized feature. Calcium hydroxide was fairly abundant, especially at interfaces between sand grains and paste. No rims were seen in thin section on any of the limestone particles, and only very faint rimming was seen on a few of the cherty particles. Evidence of alkali-silica reaction appeared as cracks in some of the cherty particles and depletion of calcium hydroxide in the adjacent mortar. Small fossils and spherulitic nodules gave the chert a texture which made reacted chert difficult to distinguish from unreacted. The potentially reactive fine aggregate particles had not reacted. Evidence of alkali-silica reaction was much more apparent on sawed slices of this core under low magnification than in thin

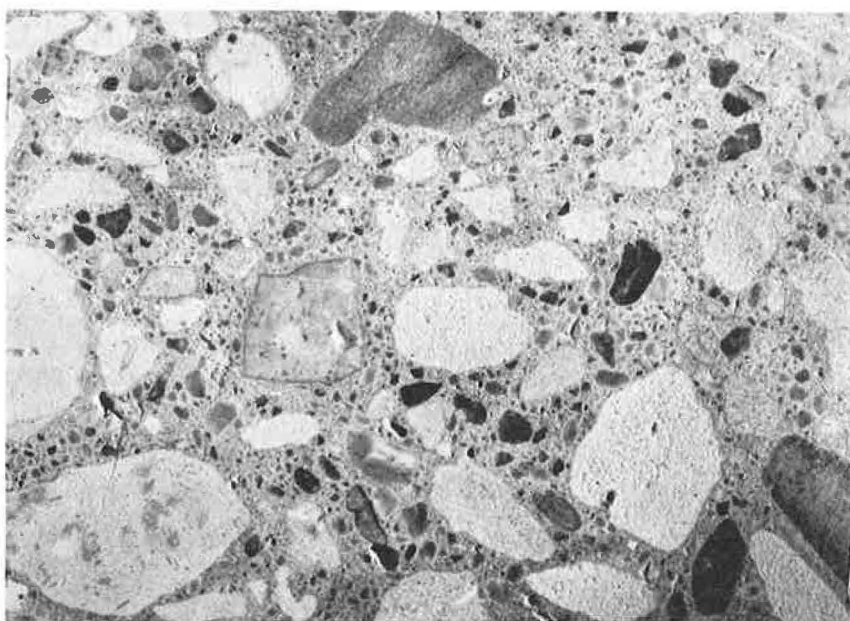


Figure 16. KC-8, sawed surface, $\times 1\frac{1}{2}$. Particles with dark, narrow reactions rims are composed of chalcedonic chert. Rest of particles, some of which are surrounded by vague rims, are of limestone composition.

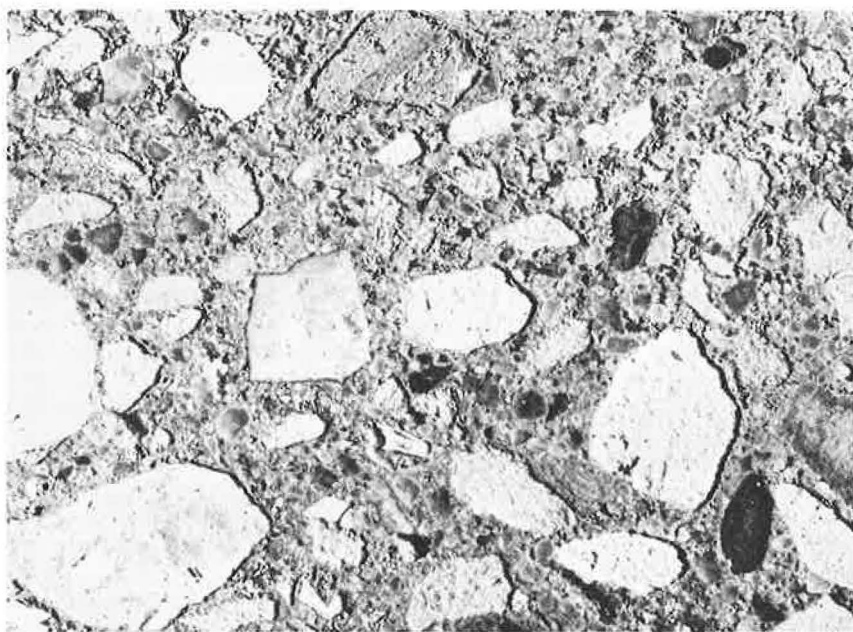


Figure 17. KC-8, sawed surface, $\times 1\frac{1}{2}$, etched with 3N hydrochloric acid. This is same surface as shown in Figure 18. Limestone particles were heavily etched by acid, whereas the chert particle, located just to left of center, was unaffected.

sections made from the same or adjacent areas of the concrete. No gel or secondary calcite was found on the prism stored at high humidity (Fig. 2); some white gel was found on the surfaces and in mortar adjoining some of the lighter gray calcareous chert particles in the prism subjected to the Conrow cycle (Fig. 5).

Core KC-9, Bridge over Clark's Creek, Geary County, Kan.—A horizontal core was taken from the right abutment of the Geary County highway bridge over Clark's Creek, from reinforced concrete placed in 1926, that contained $2\frac{1}{2}$ -in. maximum size crusher-run limestone, probably from the Cottonwood formation, natural sand from the Republican River at Clay Center, and cement of unknown source.

Examination of the core as received, and of slices sawed from it, indicated that little reaction had taken place. No gel or obviously reacted particles were found. The chert particles were not conspicuously rimmed as in core KC-8; some of the larger limestone particles were partially rimmed by darker reddish-brown mortar borders that blended within short distances into the normal gray mortar of the rest of the core. The discolorations in the mortar were somewhat like those around some of the limestone particles in KC-1, but those in KC-9 were not as conspicuous. At low magnification a few hairline cracks were observed on sawed surfaces; the cracks appeared to originate in large coarse aggregate particles, and extended out into the mortar, running around and through other coarse aggregate particles, before fading out. The cracks were not lined with reaction products. They are believed to have been present in the concrete core before sawing. The coarse aggregate ranged from about $2\frac{1}{2}$ -in. maximum size down into sand sizes, with most of the larger particles larger than $1\frac{1}{2}$ in. About one-half of a surface sawed normal to the length of the core contained four or five coarse aggregate particles (Figs. 18 and 19). Hydrochloric acid etching destroyed rims in the mortar surrounding the limestone particles, and revealed rims similar to those in KC-1, -4, -5, and -7 on several of the limestone particles (Fig. 19).

The results of a count made on a sawed surface in which the particles were classified by lithology and the presence or absence of rims or cracks are given in Table 15. The calculations indicated that rims and cracks were associated with the cherty particles and not with the limestone. These rims and cracks were attributed to a reaction between alkalis in the cement and soluble silica present in the chert.

The mortar in thin sections from selected areas of this concrete core was only slightly carbonated, with abundant large unhydrated cement grains containing clusters of alite and belite crystals. Apparently the cement used was coarser than modern cements. Calcium hydroxide was abundant in the paste and at the paste-aggregate contacts of siliceous fine aggregate and some limestone coarse aggregate particles.

Several chert particles were either wholly or partially surrounded by dark gel-soaked rims produced by alkali-silica reaction. One such particle was bordered by a short narrow gel-filled crack along the contact between the particle and paste. Most of the reacted chert particles contained short cracks which originated in the particles and stopped at the aggregate-paste contact or extended a short distance into the paste. Calcium hydroxide was absent in the gel-soaked rims and along the inner sides of paste-aggregate contacts of fine aggregate particles in or near the rims, but was present along the opposite sides of such particles, away from the rims. The reddish-brown mortar borders around some limestone particles were seen in the thin sections as highly carbonated areas in which no calcium hydroxide was present. The narrow carbonate rims usually had one or more lobes or tongues extending out into the mortar. These rims were probably the result of an alkali-carbonate reaction.

Several longer old cracks in the mortar of some thin sections were bordered by highly carbonated paste. The potentially reactive fine aggregate particles, present in very minor amounts, had not reacted.

Core KC-11, Boiler Plant, Fort Riley, Kan.—A horizontal core was drilled from the north wall of the Fort Riley hospital boiler-plant compressor room. The reinforced concrete placed in 1955 contained 1-in. maximum size limestone from the Towanda formation, quarried near Milford; Republican River sand from the More Sand Company, Junction City; and type I or IA portland cement. Mill certificates during the construction period indicated that the cement had (a) alkali contents, expressed as Na_2O , ranging between 0.46 and 0.51 percent; (b) MgO , between 2.85 and 3.08 percent; and (c) auto-



Figure 18. KC-9, sawed surface, three-quarter size. Reddish-brown carbonated rims associated with some of the limestone particles are illustrated by dark mortar rim around large limestone particle in lower right. Others are present but are less distinct. Dark particle in upper extreme right is chalcedonic chert.



Figure 19. KC-9, sawed surface, $\times \frac{1}{2}$, etched with 3N hydrochloric acid. Large limestone particle in center contains a shell of less soluble material along two sides of particle, a slight distance inside aggregate-mortar contact. Chert particles were unaffected by acid.

TABLE 15

Constituent	No Rim, No Cracks		With Internal or External Rim, With or Without Cracks ¹		Total Observed
	Expected	Observed	Expected	Observed	
Limestone	114.26	123	14.74	6	129
Chert	9.74	1	1.26	10	11
Total		124		16	140

¹ External rims in mortar around 5 limestones; cracks in 3 cherts; no cracks in limestone.

Note: N = 140; degrees of freedom = 1; Chi square = 66.22; probability of chance occurrence = < 0.01.

clave expansions of about 0.095 percent. The concrete was well consolidated and in good physical condition. The entrained air content was rather low; few entrapped air voids were observed on sawed surfaces; no rimmed or reacted coarse aggregate particles were noted; and only one reacted opaline siltstone particle was seen on a sawed surface.

The finished surface of the core, representing the outer surface of the wall, was mottled light gray and olive-gray (Fig. 20). The mottling was caused by variations in bond between the wood-formed surface and a cement paste rendering put on to improve the appearance of the wall. Part of the rendering adhered and part did not adhere to



Figure 20. KC-11, finished wall surface, three-quarter size. Mottled appearance of surface is due to poor bond between wood-formed surface and rubbed on cement paste. Light areas are rubbed cement still adhering to original surface. Impression of wood form is apparent. Irregular dark lines are penciled traces of fine shrinkage cracks.

the concrete, producing the mottled appearance. Several thin very shallow shrinkage cracks were observed in the mortar and rubbed cement paste when the surface was viewed at low magnification ($\times 10$).

Crushed limestone aggregate from the Shandy quarry, 0.8 miles west of Milford, in the Towanda formation, the source used in the boiler plant of the Fort Riley hospital, was tested in 1956 by the Missouri River Division Laboratory, with the following results: specific gravity, 2.51; absorption, 1.9 percent; durability factor with Georgetown, Miss. sand, 57, and with Big Blue River sand, 50. The petrographic examination found 74 percent dense limestone, 24 percent porous limestone, and 2 percent shaly limestone. Additional tests of limestone from this source in 1958, 1959, and 1960 indicated that the quality of the aggregate was similar.

The apparent proportions of the three varieties of limestone (Table 8) in this core agree fairly well with the composition reported by the MRD Laboratory. The small amount of quartz identified by X-ray diffraction and seen in thin sections was present as detrital quartz grains and not as chalcedonic chert. The results of a count on a sawed surface of the core are given in Table 16.

Unetched and etched sawed surfaces of KC-11 are shown in Figures 21 and 22. The etched surfaces of most of the coarse aggregate particles were smooth and even. The vuggy particles were more irregular and pocked because of holes left by previously

TABLE 16

Constituent	Percent
Limestone, no rims, no cracks ¹	91
Limestone, with vague external rims	2
Limestone, with internal cracks ²	2
Other (large fine aggregate)	5
Total	100

¹9% of particles were vuggy.

²Cracks were probably produced before aggregate was used in concrete.

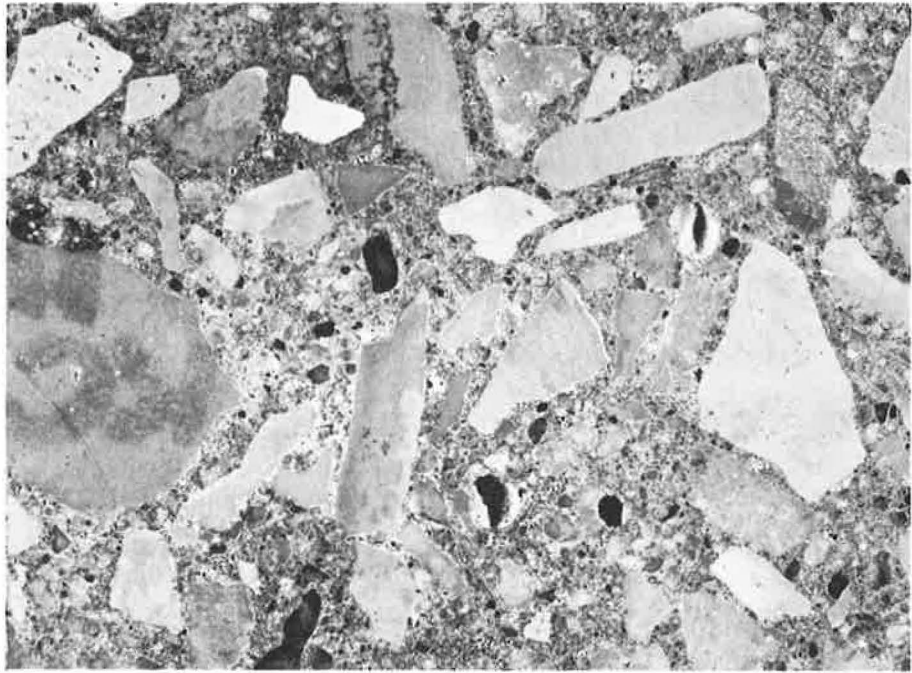


Figure 21. KC-11, sawed surface, $\times 1\frac{1}{2}$. No coarse aggregate particles are rimmed. One rimmed opaline siltstone particle is located just beneath tabular limestone particle in upper right. Dark areas in large air voids are shadows caused by crosslighting.



Figure 22. KC-11, sawed surface, $\times 1\frac{1}{2}$, etched with 3N hydrochloric acid. Acid made a smooth, even etch on most particles. Pocked appearance of some particles is due to dissolved-out fossils. All coarse aggregate particles are in negative relief.

leached fossils. None of the etched particles showed rims of any kind. The limestone aggregate in this structure had been almost totally unaffected by any of the types of reactions known to occur between cement paste and carbonate aggregate particles when the core was taken. The prism cut from the core and stored at high humidity for 19 months had developed fairly conspicuous rims between 12 months and 19 months of storage; no rims were found when the prism was sliced. (The expansion at the time when the prism was sawed was 0.067 percent, while the maximum attained has been 0.098 percent.) The rims were interpreted as a leaching phenomenon, because they were confined to the outer surface of the prism.

X-ray diffraction examination of paste concentrates from the prism stored at high humidity showed that additional high-sulfate calcium sulfoaluminate, and calcium monosulfoaluminate had formed; the failure to find increased calcium monocarboaluminate was surprising.

Thin sections of this concrete were characterized by abundant calcium hydroxide in the paste, at the contacts between paste and aggregate particles, and lining many of the entrained air voids. Virtually no secondary carbonation of the mortar had developed. The limestone coarse aggregate particles had not developed carbonate rims. Almost all the potentially reactive fine aggregate particles—chert and glassy volcanic rocks—were unreacted. The thin sections of this concrete at the age of six years indicated that normal hydration had taken place, producing a normal texture, degree of hydration, and appearance of the concrete.

One large gel exudation was found on the surface of the prism subjected to the Conrow test after it had been soaked in water only three days. The exudation continued to grow, and several small gel pockets formed on the surface and in surface air voids during the ten months that the prism was measured. No gel deposits or rims were observed on the surfaces of the prism stored at high humidity during the first ten months of storage;

the rims observed at 19 months have already been described. The prism from KC-11 developed the second highest expansion in storage over water and higher expansion in the Conrow cycle than any of the other concretes tested.

CONCLUSIONS

Cores from seven structures in Kansas and Nebraska, representing concrete that ranged in age from 6 to 43 years at the time of examination, all contained carbonate coarse aggregate and natural fine aggregate, and all showed evidence of a chemical reaction or of more than one chemical reaction, exclusive of those found in normal hydration of cement.

All of the fine aggregates contained the reactive constituents typical of natural aggregates in northeastern Kansas—opal in the form of calcareous opal or opal-bonded siltstone, chert, and glassy volcanic rocks. In large measure, these minor reactive constituents of the sands had not reacted or had reacted only to a minor degree. In all seven cases, the constituents showing most reaction were constituents of the coarse aggregates.

Two sawed prisms were prepared from each of six cores representing five of the structures; ball bearings were cemented to each end of each prism as reference points. One prism from each core was stored over water at high relative humidity; the other was subjected to a cycle like that in the Conrow test (ASTM Designation: C 342), but with slightly greater fluctuations in the temperature of the storage room than allowed by the method.

The length-change tests were made because field examination of some of these structures had not shown any unequivocal evidence of expansion, although it was known that all of the sands contained alkali-silica reactive constituents. Inasmuch as the structures are located in areas where the average precipitation ranged from 21 to 32 in. per year, it seemed desirable to investigate the question, whether the concretes had significant expansive potential if moisture were supplied. Prisms sawed from the cores offered the only available test specimens, because the aggregate and cement sources for several of the concretes were not known.

Although the meaning of the length changes developed by the concrete prisms is not entirely clear, because the alkali contents of the cements are not known, the following points are clear (Tables 6 and 7):

1. All of the concretes expanded more than 0.05 percent by 88 days of storage at high relative humidity.

2. Three of them thereafter either shrank or at least slowed the rate of length gain substantially, but three continued to grow, and reached length changes of 0.098 or 0.099 at 340 days or one year.

3. One of the three was KC-8, 43-year-old concrete, which, because of the amount of perceptible alkali-silica reaction that it exhibited in the as-received condition, was believed to have reacted as much as it was likely to before the prism was placed in high humidity. The other prism sawed from the same core reached an expansion of 0.168 percent in the Conrow cycle.

4. The other two concretes that expanded the most were KC-5, from the only structure in the group that is known to have shown any outward peculiarity of its concrete (Fig. 8). KC-4, from the same structure, but from the mottled wall of that structure, showed considerably less expansion, suggesting that this concrete had used more of its expansive and reactive potential at the time when the core was taken.

5. KC-11, from the youngest structure in the group, expanded to the maximum degree found both in storage at high relative humidity and in the Conrow cycle. This concrete contained the aggregate combination that had been approved for use in the concrete in Milford Dam.

The major difficulty in the examination of these seven concrete cores, which all showed evidence of chemical reaction, lay in distinguishing which reactions were present in each concrete, and which should be regarded as significant in the performance of the concrete. Four of the structures—those represented by KC-1, -4, -5, and -6,

TABLE 17
CONCRETES FROM STRUCTURES IN KANSAS AND NEBRASKA

Characteristic	Specimen KC-8	Specimen KC-1	Specimen KC-9	Specimen KC-7	Specimen KC-6	Specimen KC-4, -5	Specimen KC-11
Age (yr)	43	37	34	16	14	12	6
Rainfall at site (in./yr)	32	26	32	32	21	21	32
Type of structure	Swimming pool wall	Pavement	Bridge abutment	Swimming-pool wall	Bldg. wall above grade	Bldg. wall above grade	Bldg. wall above grade
Chert in coarse aggregate	25+% chalcidonic	Minor in all varieties	15+% chalcidonic	Moderate to major chert in 30% of total, the variety ranging from calcareous dolomitic chert to cherty calcareous dolomite; minor chert in limestone making 50% of total; 5% chert.	10% chalcidonic chert; moderate chert in 20% of total ranging from calcareous dolomitic sandstone to sandy limestone; very minor to traces in the 65% of fine-grained limestone.	Not detected	Not detected
Dolomite in coarse aggregate	Traces in the 25% of chert	Minor in two varieties that total 25%	Trace in the 15% of chert	Very minor in the 50% of fine-grained limestone; moderate to major in the 30% of the total containing most of the chert.	Major to very minor in the 20% ranging from sandstone to sandy limestone; minor to traces in the rest.	Not detected	Not detected
Estimated or determined insoluble residue	Low in 68% of aggregate.	Medium	Low in 85% of aggregate.	Low in 65% of the aggregate.	Low in 70% of the aggregate.	2.45%, qtz, ¹ pyrite, feldspar, clays.	Low
Expansion of prisms stored at high humidity at 1 yr	0.098 at 340 days	0.063	Not tested	Not tested	0.067	KC-4: 0.066% KC-5: 0.099%	0.098% at 340 days
Expansion of prisms exposed to Conrow cycle at 1 yr	0.168%	0.034%	Not tested	Not tested	0.057% at 333 days ²	KC-4: 0.079% KC-5: 0.061%	0.241
Monocarboaluminate in mortar concentrate: passing No. 100 sieve retained on No. 100 sieve	Minor ² Trace ²	Trace ³ Not detected	Minor ² Minor ²	Minor ² Trace	Minor Trace	KC-4 KC-5 Minor Minor-Trace Trace	Minor-Trace
Carbonation of mortar	Widespread, patchy; no association with other features detected.	Carbonated rims and lobes projecting into mortar, around two varieties of limestone making 25% of total.	Some widespread carbonation; some rimming limestone as in KC-1.	As in KC-1.	Negligible; association with other features not detected.	Along cracks in KC-4; as in KC-1 in both cores.	Absent
Alkali-silica reaction with coarse aggregate	Rims on calcareous chert; internal cracks in most of the rimmed chert.	Evidence not clear.	Rims on chert and internal cracks most of the rimmed chert.	Rims on the cherty calcareous dolomite ranging to calcareous dolomitic chert.	Rims on the cherty limestone and chert.	Evidence not clear in either core; no alkali-silica reactive constituent.	Not with the coarse aggregate; no alkali-silica reactive constituent.
Alkali-carbonate reaction with coarse aggregate	Vague rims in mortar surrounding some calcitic limestone.	Rims and lobes in mortar surrounding two dolomitic varieties making 25% of total.	Rims bordering some calcitic limestone.	Etched surfaces (in Fig. 15) shows one particle with periphery less soluble than interior.	Not recognized.	Conspicuous and fairly common in calcitic limestone.	Not recognized in the core; formed on outer surface of prism stored at high humidity.
Coarse aggregate constituents involved in reaction	Calcareous chert; calcitic limestone to a minor extent.	Large pieces of dolomitic clayey-cherty limestone.	Chert; calcitic limestone to a minor extent.	Calcareous dolomitic chert to cherty calcareous dolomite; limestone.	Cherty limestone and chert.	Fine-grained calcitic limestone.	Fine-grained calcitic limestone (in prism stored at high humidity.
Major reaction	Alkali-silica	A carbonate reaction involving the varieties containing minor dolomite.	Alkali-silica	Alkali-silica and alkali-carbonate reactions.	Alkali-silica	Alkali-carbonate with calcitic limestone.	Alkali-carbonate with calcitic limestone.
Minor reaction	Alkali-carbonate with calcitic limestone.	Very minor alkali-silica reaction with fine aggregate.	Alkali-carbonate with calcitic limestone.	The two above appear virtually equal.	None recognized.	None recognized.	None recognized.

¹Determined on 153.6 g of sample acquired in 1948.

²Reference point fell out, invalidating next reading.

³High in calcium sulfoaluminate among these concretes.

had been inspected by the senior author; the only one in which the concrete looked odd was the administration building at Harlan County Dam, represented by cores KC-4 and KC-5. All four structures were presented as examples of concrete in good condition. The other three structures were not described as showing evidence of improper behavior by the concrete, but on the other hand none was located on a poorly drained subgrade and all were exposed to less than average annual precipitation. When rims were found on the surfaces of KC-1, -4, and -5, it was necessary to discover how many of the concretes showed evidence of alkali-carbonate reaction, as well as or instead of the alkali-silica reaction with fine aggregate, that had been regarded as probable.

Because of the indications of alkali-carbonate reaction, the composition of the coarse aggregate was investigated in detail and evidence of rim formation and of dedolomitization was sought. Tests of association, between composition of individual pieces of coarse aggregate and various phenomena of rimming and cracking that were found, served in some cases to distinguish those lithologic varieties that were related to reaction from those that were not, and permitted conclusions on which reaction was the more important in concrete in which more than one was detected.

The concretes may be sorted into four groups; evidence other than the calculations of Chi square that assisted in the sorting is summarized in Table 17.

1. Reaction principally involving dolomitic limestone. KC-1 contained two varieties of aggregate in which dolomite was a minor constituent; chert was a minor constituent of all varieties. Rims within coarse aggregate particles, visible on unetched surfaces as well as on etched ones, and staining and carbonation of the mortar around the coarse aggregate, were associated with the two limestone varieties containing dolomite, and not with the major variety that did not contain dolomite. The mortar from this concrete was low in calcium monocarboaluminate as compared to the rest of the concretes, and high, by comparison, in high-sulfate calcium sulfoaluminate. Brucite was not detected in the rims on the coarse aggregate or in the surrounding paste. The existence of alkali-silica reaction in the cherty dolomitic limestone cannot be demonstrated, although evidence of minor alkali-silica reaction with some of the fine aggregate was seen.

2. Carbonate reactions with calcitic limestone. KC-4 and -5, and KC-11, each contained coarse aggregates in which dolomite was a trace constituent at the most, and in which chert was not detected. The insoluble residue in aggregate from the source of that used in KC-4 and KC-5, represented by a sample taken one year earlier than the concrete was placed, was 2.45 percent, mostly quartz silt; the insoluble residue in the coarse aggregate in KC-11 was as low or lower. KC-5 and KC-11 prisms expanded in storage at high humidity to 0.099 and 0.098 percent at one year. KC-4 did not expand beyond 0.066 percent at one year, but came from the side of the building on which the concrete was visibly affected. KC-4 and KC-5 manifested rims on etched surfaces which were more soluble than the interior of the particles; it is unlikely that the removal of so small a quantity of insoluble residue as this coarse aggregate contained would produce so apparent a difference in solubility.

3. Alkali-carbonate and alkali-silica reactions equal. The coarse aggregate of KC-7 contained both chert and dolomite in one variety of rock ranging from calcareous dolomitic chert to cherty calcareous dolomite; it also contained 5 percent of chert particles, and minor chert in the limestone. No association between lithology and rims was recognized, because all varieties of aggregate showed some kind of rim in about one-half of the particles, and cherty regions in the coarse aggregate were cracked and torn in thin sections in the manner characteristic of alkali-silica reacted chert. The type or types of carbonate reactions are not known.

4. Major alkali-silica reaction, alkali-carbonate reaction minor or absent. KC-8 coarse aggregate contained 25 percent chalcedonic chert; dolomite was present in traces in the chert but was not found in the limestone; KC-9 coarse aggregate contained 15 percent of chalcedonic chert with traces of dolomite but no other dolomite; KC-6 coarse aggregate contained 10 percent chalcedonic chert and moderate amounts of chert in 20 percent of the aggregate that ranged from calcareous dolomitic sandstone to sandy limestone. KC-8 showed reaction with the chert, accompanied by some crack-

ing, and minor development of rimming in mortar around calcitic limestone; KC-9 showed rims on the chert and minor development of rims in the mortar; KC-6 showed conspicuously more rimming of limestone containing disseminated chert than of chert, and negligible rimming of limestone. No reaction other than alkali-silica reaction was established in the case of KC-6. The structure from which this core came, appeared to be in good physical condition; apparently the alkali-silica reaction was not harmful, and was in fact concluded to be beneficial, by comparison with the condition of KC-4 from the adjoining building.

DISCUSSION

The first part of this paper describes an instance in which alkali-silica reaction and the alkali-carbonate reaction, dedolomitization, were found to have occurred in the same laboratory specimens, but the alkali-silica reaction was apparently confined to opaline montmorillonitic shale and the dedolomitization reaction was confined to dolomitic limestones, and was manifested in the development of brucite in the mortar surrounding the dolomitic limestone particles.

The second part describes seven more complicated situations involving field concretes that all contained fine aggregates capable of some alkali-silica reaction, and carbonate coarse aggregates with and without dolomite, and with and without chalcedonic chert. None of the concretes was in great distress. The concrete from the structure that showed visible peculiarities of the concrete contained a quite pure calcitic limestone with no more than traces of dolomite and no chert; it was concluded that a reaction affecting the calcitic limestone was the only recognized cause of the distress. Prisms from this concrete and from another structure made from a similar limestone expanded 0.10 percent in one year of storage at high humidity. In one case, the particles of coarse aggregate showing the most evidence of reaction were those of two varieties containing dolomite; the calcitic limestone was not affected. The dolomitic varieties also were clayey and cherty. Alkali-silica and alkali-carbonate reactions were of apparently equal importance in one structure; the types of alkali-carbonate reaction are not known. Alkali-silica reaction predominated over alkali-carbonate reaction with calcitic limestone in two cases; in a third, the major alkali-silica reaction was not accompanied by alkali-carbonate reaction.

The principal difficulties in reaching any conclusions with regard to the concretes discussed in the second part of the paper lie, first, in recognizing that so many different reactions and combinations of reactions were represented in so small a group of concretes that had been expected to be comparable in many respects, and in developing evidence that would permit conclusions about the relative importance of reactions when more than one was involved.

The second part demonstrates that the question of beneficial effects of the addition of carbonate coarse aggregates to the sands and sand-gravels of the Kansas-Nebraska area is a very complex one in which the chemical reactivity of the carbonate coarse aggregates may be of the greatest significance.

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