A STUDY OF CEMENT-AGGREGATE REACTION AS AFFECTED BY TYPE OF EXPOSURE, ALKALI CONTENT AND PARTICLE SIZE OF AGGREGATE

by

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TABLE OF CONTENTS

INTRODUCTION

Certain types of deterioration of concrete have been found to be a result of chemical reaction between the alkali in cement and mineral constituents in the aggregates. Part of the evidence was a gel like substance, a by-product of the reaction, identified as sodium silicate. According to Hanson (3), the gel will produce osmotic pressure and cause the expansion of the concrete.

Many methods of test have been used to determine the reaction between cement and aggregate. From results of various tests it is known that different amounts of alkali content in cement and different types of aggregate will cause different expansion. It has also been found that smaller particle sizes of aggregate, which has larger surface area, would accelerate the chemical reaction and cause more expansion. Opal and chert have definitely proven to be highly reactive minerals. In general cements with high alkali contents give larger expansion than do cements with low alkali contents. But in Kansas, Arizona, and Washington some concretes have shown a contrary reaction, in which concrete made with sand containing a high percent of chert and cements with high alkali contents gave negligible expansion. So it is suggested to study the reaction between cement and aggregates in these areas.

There are many test methods used for determining cement-aggregate reaction. Four exposures, which seemed representative of weathering conditions, were chosen for this study as an attempt to determine a rapid and accurate means for detecting cement-aggregate reaction.

In order to study the cement-aggregate reaction as affected by particle size of aggregate and the alkali content of cement, 264-1"x 1"x 10" mortar bars have been made. One hundred and ninety two bars were made with Kaw River sand and 72 bars with Republican River sand. Both are reactive aggregates and have a bad service in Kansas. These sands were sieved into different sizes and mortar bars were made with each size of aggregate under the proportion of 1:2.25. Penn-Dixie cement which has a low alkali (0.132 percent) content was used in all mixes. Anhydrous sodium carbonate was added to the mixing water as a means of increasing the alkali content of this cement. A study was also made of the effect of sodium carbonate upon the modulus of elasticity and cement-aggregate reaction with the different exposures. Methods of mixing, molding and determining the amount of mixing water are based on "Proposed tentative method of test for determining the potential reactivity of cement-aggregate combinations", proposed A.S.T.M. standard.

REVIEW OF LITERATURE

Stanton (7) found cement-aggregate reaction to be the reaction of the alkali in the cement with the chert and shale in certain fine aggregates. The reaction of the soluble silicate with the alkali, as stated by Hanson (3), is:

$$4\ SiO_2 + 2\ NaOH \rightarrow Na_2Si_4O_9 + H_2O$$

or $$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H_2O$$

Catalyst is not required for this reaction. Hanson also stated that Na_2SiO_3 is a gel-like material and acted as a semi-permeable membrance. Silicate ions in solution of alkali silicate tend to associate into complex ions. The gel-like material would act as a semi-permeable membrance and permit water and ions of the alkali hydroxide to diffuse through it, but it would not permit the diffusion of silicate ions. Under these conditions any alkali silicate formed on the surface of aggregate particle would tend to draw solution from the cement paste and form a pocket of liquid within the specimen which would exert hydrostatic pressure against the confining paste and cause the expansion of the concrete.

Regarding the relation between alkali content and expansion, Stanton (7) found that some sands in combination with a cement having a sodium oxide equivalent of 1 percent, always showed excessive expansion in a few months. Stanton et al. (8) also stated that subsequent tests indicated that the alkali content should not exceed 0.6 percent. However, some investigators have reported that abnormal expansion does not always occur with high alkali contents. C. H. Scholer et al. (6) stated that the cement having the poorest record was one having a lower alkali content compared to some cements with good service records. Meissner (5) stated that mortars made with high alkali cement and Platte River sand gave negligible expansion. Tremper (9) stated that in one section of Cortright Creek Bridge of Washington, the same reaction was shown as that found by Meissner.

Regarding the relation between the particle size of aggregate and expansion, Carlson and Stanton (1) found that certain sizes of fine aggregate are more reactive than others. Investigations indicated that the 30 to 80 mesh size was the most reactive. In his test 5 percent of different mesh sizes of siliceous magnesian limestone was substituted for an equivalent percent of the neutral Russian River sand in a 1:2 mortar mix and the expansion for these various sizes are shown below. (Data are based on the result at 48 months.)

Size of particles of reactive admixture	-80	80-30	30-10	10-3
Percent expansion in 48 months	0.003	0.810	0.552	0.536
Sonic E x 10^{-6}	4.27	2.58	3.10	2.41
M. R. p.s.i.	1297	567	581	466

Kammer and Carlson (4) emphasized the necessity for the development of an accelerated test procedure, which at the same time would not be too severe but would truly represent weathering exposures in the field. Stanton et al. (8) stated that undoubtedly temperature accelerates the reaction, however, it would be desirable to hold the temperature down to not over 130° F. to 140° F. California data (1) showed how the temperature affected the expansion of concrete:

	Without NaOH		With NaOH	
Storage temperature	70° F.	130° F.	70° F.	130° F.
Percent expansion	0.017	0.067	0.064	0.146

Four exposures have been chosen for the study of cement-aggregate reaction and will be explained in detail in the section of testing.

CONCRETE MATERIALS

Aggregates

Kaw River sand and Republican River sand were used as aggregates. In order to test the relation between aggregate size and expansion, aggregates were separated into different sizes as follows:

Sieve No. 4	0.1850 in.
Sieve No. 8	0.0937 in.
Sieve No. 16	0.0469 in.
Sieve No. 30	0.0232 in.
Sieve No. 50	0.0117 in.
Sieve No.100	0.0059 in.

The percent of absorption is 0.55. Mortar bars were made by each size of aggregate mentioned above. The proportion of mix, according to ASTM Standard, is 1:2.25.

Cement

The cement used for this test is from Penn-Dixie Co., Georgia. The chemical composition of the cement is shown as follows:*

	Percent
Silicon Dioxide	22.23
Aluminum Oxide	5.72
Ferric Oxide	2.14
Calcium Oxide	64.96
Magnesium Oxide	1.18
Sulphur Trioxide	2.27
Ignition Loss	1.54
Sodium Oxide	0.02
Potassium Oxide	0.17

Alkali Content

The equivalent alkali content of the Penn-Dixie cement is 0.132 percent. In different mixes, four alkali contents have been used: 0.132 percent, 0.60 percent, 1.0 percent, and 1.5 percent. Anhydrous sodium carbonate was used as the additional alkali in the cement. Calculation for the amount of sodium carbonate added in the mix is shown in the Appendix.

Mixing Water

The amount of mixing water is determined by the Flow Test** and expressed as percentage by weight of the cement. The percent of flow is between 100 and 115 and is calculated by the formula:

$$\text{Flow percent} = \frac{\text{Spread diameter} - 4}{4} \times 100.$$

* Cement Test Report No. 68946, Material Lab. of State Highway Commission of Kansas, 9-15-1950.

**"Standard method of test for flow of Portland cement by use of the flow table" ASSHO Designation T 120-42, p. 290.

MIXING AND MOLDING THE PRISM

Mixing was done in a bowl by continuous stirring, squeezing, and kneading with one hand protected by a rubber glove. The materials for a batch were introduced into the bowl in the following sequence:

1. Place the anhydrous sodium carbonate into the bowl.

2. Add water into the bowl and stir with hand protected by rubber glove till the sodium carbonate is completely dissolved in water.

3. Add the cement into water and mix for 30 seconds.

4. Add approximately one-half of the aggregate and mix for 30 seconds.

5. Add the remainder of the aggregate and mix for 1 1/2 minutes.

Immediately following mixing, the mold was filled in two layers, each layer being compacted with the tamper. The mortar was worked into the corners, around the reference points, and along the surface of the mold with tamper until a homogeneous specimen was obtained. After the top layer has been compacted, the mortar was cut off flush with the top of the mold and the surface smoothed with a few strokes of the trowel.

SPECIMEN PREPARATION

A total of 264 beams were made for the Kaw River and Republican sand. Sand was separated into different sizes: Sieves

No. 4, 8, 16, 30, 50, and 100. Four batches containing different alkali (0.132 percent, 0.6 percent, 1.0 percent, and 1.5 percent) were made of one size of aggregate. Eight beams from each batch were separated into four parts (2 in each part) and tested under four different exposures.

Water-cement ratio was determined by the flow table test and the result is shown as follows:

Batch		W/C Gal/Sack
Sieve No. 4	A	4.89
	B	4.89
	C	4.89
	D	4.98
Sieve No. 8	A	4.98
	B	4.98
	C	4.98
	D	5.08
Sieve No. 16	A	5.08
	B	5.08
	C	5.08
	D	5.17
Sieve No. 30	A	5.08
	B	5.08
	C	5.08
	D	5.17
Sieve No. 50	A	6.02
	B	6.02
	C	6.11
	D	6.58
Sieve No.100	A	7.61
	B	7.61
	C	7.80
	D	7.80

The proportion of the mixes were 1:2.25. Twelve hundred grams of cement and 2700 grams of aggregate were used for one batch.

The weights of Na_2CO_3 for different batches are shown as following. Calculations are in the Appendix.

Batch A	(0.132 percent)	0 gm
Batch B	(0.60 percent)	9.6 gm
Batch C	(1.00 percent)	17.81 gm
Batch D	(1.50 percent)	28.07 gm

Molds were thinly covered with mineral oil, after this operation the stainless metal reference points were set, care being taken to keep them clean and free of oil.

Temperature of mixing water, moist closet and room in which specimens were measured, was 70° F.

Relative humidity of the moist room was 90 percent.

The beams, immediately after molding, were stored in the moist room. Curing days and methods of exposure will be described in the Testing section.

TESTING

Four types of exposures, which were considered such as could occur in nature exposure at a much slower rate, were chosen for this study. Exposure I* (Sealed Container) was recommended by the ASTM and others and was considered as the standard method for

* "Proposed Tentative Method of Test for Determining the Potential Alkali Reactivity of Cement-Aggregate Combinations", ASTM.

cement-aggregate reaction test. Exposures II and III (Wet and dry; spray) were recommended by C. H. Scholer.* Exposure IV** (Heat then 70° F. water) was recommended by A. D. Conrow. Details of these exposures are given as follows:

Exposure I

1. After the mold had been filled, it was immediately placed in the moist closet. Specimens remained in the moist closet for 24 ± 2 hours.

2. At 24 ± 2 hours after molding, the specimens were removed from the molds and measured for length, weight, and sonic. The specimens were protected against loss of moisture prior to the reading for initial length. The specimens were then stood on end in a metal container maintained at 37.8 ± 1.7° C. (100 ± 3° F.). The specimens in the container were not in contact with the water in the container. When length measurements were to be made at subsequent periods, the metal container holding the specimens was removed from the 100 ± 3° F. storage and placed in a room at a temperature of 73.4 ± 3° F. for at least 16 hours prior to measuring the specimens. When measurements were made, the specimens, comparator and reference bar were at the temperature of 23 ± 1.7° C. (73.4 ± 3° F.). After measurement the specimens were replaced in

* "A Study of Special Concrete Problems in Kansas, Nebraska, Iowa and Western Missouri", by C. H. Scholer, Kansas State College, Feb. 1949.

** "Cement-aggregate-Reaction Expansion of Concrete Containing Kaw River Sand-Gravel as Aggregate when Made with a Representative Range of Portland Cements Manufactured in the Central United States Region", by A. D. Conrow, Ash Grove Lime and Portland Cement Co., Chanute, Kansas.

the metal container, in inverted position, and the container returned to the 100 ± 3° F. temperature storage. The difference in length of the specimens, when removed from the molds at one day and at any subsequent periods, were calculated to the nearest 0.01 percent of the effective gage length and reported as the expansion of the specimen at that period. The average of the expansion of the two specimens of a given cement-aggregate combination were reported as the expansion of the combination at a given period.

Exposure II. Preliminary Curing and Measurements

1. Cured in mold in moist room for 20 to 24 hours.

2. Removed from mold and read sonic and length at 70° F.

3. Cured in moist room for 6 days and read sonic and length at 70° F.

4. Placed in laboratory air for 21 days, read sonic and length at 70° F.

5. Placed in water for 2 days and read sonic and length at 70° F.

Subsequent treatment: Placed in 130° F. dry oven for 8 hours then 16 hours in 70° F. water bath daily except Sunday and holidays at which times beams were remained in 70° F. water. Took sonic and length measurement with beams as near 70° F. as possible. Subsequent readings were made at ages of 60, 90, 120, and 180 days.

Exposure III. Preliminary Curing and Measurements were the Same as with Exposure II

Subsequent treatment: Placed beams vertically in the spray tank. Alternated water of 70° F. and 130° F. were sprayed continuously on beams with 32 cycles in a day. Test will be ended when beams have subjected to 2000 cycles.*

Exposure IV. Preliminary Curing and Measurements

1. Cured in mold in moist room for 20 to 24 hours.

2. Removed from mold and read sonic and length at 70° F.

3. Placed in 70 F. water for 20 to 24 hours and read sonic and length at 70° F. Then returned to 70° F. water bath until 28 days of age.

Subsequent treatment:

1. Placed in oven at 130° F. for 7 days.

2. Cooled to 70° F. in 70° F. water bath for 20 to 24 hours.

3. Placed in 130° F. drying oven for 7 days.

4. Cooled to 70° F. dry for 20 to 24 hours.

5. Placed in 70° F. water bath indefinitely pending developments.

Took sonic and length measurements with beams as near 70° F. as practical.

A non-destructive method for determining the Modulus of

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* The proposed exposure is for 3"x 4"x 16" concrete beams. When this exposure was subjected to 1"x 1"x 10" beams, very small expansion was shown. So test was carried on after 2000 cycles.

Elasticity of concrete* was by taking flexural resonant frequencies from the sonic machine. The equation for computing the Modulus of Elasticity by this method is:

$E = CWN^2$ Where:

W = Weight of the specimen

N = Resonant frequency

C = A factor which depends upon the shape and size of the specimen, the mode of the vibration, and Poisson's ratio. For 1"x 1"x 11" prism, C = 3.693.

Beams were soaked in a constant temperature tank of 70° F. for 20 ± 4 hours prior to the measurement of the length.

Length comparator, accurated to 0.0001", was used to measure the change of length. The percent of expansion was expressed as $\frac{\text{growth of length}}{10} \times 100$ or growth of length x 10.

RESULTS

The percent of expansion, Modulus of Elasticity, maximum shrinkage of the concrete at different ages are tabulated in the following tables.

In order to express the relation between exposures, alkali contents in cement, particle sizes of aggregate and the expansion, part of the data in the tables were selected and plotted into curves and blocks.

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* Gerald Pickett, "Equations for computing elastic constants from flexural and torsional resonant frequencies of vibration of prisms and cylinders", Research Laboratory of the Portland Cement Association, Bulletin 7, Sept. 1945.

Table 1. Percent of expansion of beams under Exposure I. (Kaw River sand)

		Age in days				
		60	90	120	150	180
K-4	A	-.001	-.001	-.003	-.005	-.004
	B	.002	.003	-.001	.000	.001
	C	.006	.007	.007	.008	.011
	D	.011	.015	.017	.021	.031
K-8	A	.008	.005	.002	.001	.000
	B	.006	.000	-.002	-.001	.001
	C	.006	.014	.017	.021	.028
	D	.009	.018	.025	.034	.038
K-16	A	.003	-.001	-.001	-.003	-.004
	B	.004	.002	.003	.002	.004
	C	.006	.006	.006	.007	.010
	D	.013	.020	.029	.030	.034
K-30	A	.002	.000	-.003	-.003	.002
	B	.004	.001	.002	.001	.004
	C	.007	.002	.004	.004	.005
	D	.005	.007	.006	.008	.011
K-50	A	.009	.004	.003	.006	.007
	B	.006	-.002	-.004	-.001	.002
	C	.002	-.005	-.006	-.001	.000
	D	.003	-.002	-.002	.003	.002
K-100	A	.009	.005	.007	-.001	.003
	B	.007	.001	.004	.005	.003
	C	-.006	-.003	.001	-.002	-.001
	D	-.002	-.001	-.002	.002	.000

Table 2. Percent of expansion of beams under Exposure II. (Kaw River sand)

		Age in days				
		60	90	120	150	180
K-4	A	.024	.036	.047	.126	.206
	B	.020	.030	.036	.110	.195
	C	.028	.042	.046	.113	.159
	D	.038	.040	-	-	-
K-8	A	.021	.021	.027	.105	.197
	B	.020	.022	.036	.122	.202
	C	.023	.026	.038	.099	.151
	D	.025	.032	.034	.068	.092
K-16	A	.008	.007	.010	.053	.094
	B	.012	.011	.011	.038	.056
	C	.015	.013	.011	.032	.041
	D	.024	.024	.017	.032	.040
K-30	A	.010	.005	.007	.016	.029
	B	.006	.004	.006	.013	.023
	C	.008	.008	.008	.014	.021
	D	.011	.005	.002	.010	.018
K-50	A	.009	.006	-.003	.006	.013
	B	.007	.003	-.003	.004	.011
	C	.004	-.001	-.004	.006	.009
	D	.010	.006	.000	.010	.010
K-100	A	.008	.003	.003	.003	.009
	B	.004	.003	.003	.007	.007
	C	.012	.005	.008	.010	.015
	D	.000	.001	-.006	.000	-.002

Table 3. Percent of expansion of beams under Exposure III. (Kaw River sand)

		Age in days				
		60	90	120	150	180
K-4	A	.021	.026	.032	.038	.039
	B	.024	.036	.049	.073	.085
	C	.029	.030	.032	.037	.040
	D	.031	.030	.033	.036	.040
K-8	A	.026	.030	.034	.043	.046
	B	.021	.022	.026	.031	.041
	C	.025	.029	.032	.036	.036
	D	.026	.033	.032	.037	.033
K-16	A	.017	.016	.019	.023	.022
	B	.019	.023	.028	.027	.032
	C	.020	.020	.024	.022	.026
	D	.030	.035	.037	.036	.039
K-30	A	.020	.019	.020	.020	.025
	B	.014	.015	.018	.017	.023
	C	.017	.020	.023	.022	.025
	D	.023	.026	.025	.028	.038
K-50	A	.023	.020	.022	.025	.029
	B	.015	.011	.013	.018	.021
	C	.018	.015	.016	.020	.025
	D	.016	.013	.017	.020	.025
K-100	A	.018	.016	.020	.020	.023
	B	.022	.020	.023	.024	.027
	C	.020	.018	.023	.021	.024
	D	.009	.012	.012	.018	.017

Table 4. Percent of expansion of beams under Exposure IV. (Kaw River sand)

		Age in days				
		60	90	120	150	180
K-4	A	.066	.119	.140	.155	.165
	B	.064	.099	.112	.126	.131
	C	.044	.060	.065	.071	.076
	D	.060	.064	.069	.074	.075
K-8	A	.107	.227	.283	.315	.338
	B	.086	.154	.189	.212	.229
	C	.067	.092	.101	.108	.112
	D	.067	.074	.076	.078	.078
K-16	A	.051	.162	.281	.338	.379
	B	.056	.183	.277	.331	.369
	C	.037	.060	.076	.087	.095
	D	.043	.064	.075	.079	.087
K-30	A	.022	.097	.234	.324	.369
	B	.022	.072	.132	.180	.227
	C	.022	.032	.037	.041	.046
	D	.020	.020	.015	.017	.021
K-50	A	-.003	-.003	-.003	.000	.004
	B	-.003	-.001	-.001	.003	.005
	C	.008	.006	.006	.011	.013
	D	.004	.001	.001	.005	.007
K-100	A	-.005	-.006	-.001	-.005	-.002
	B	-.006	-.008	-.004	-.005	-.113
	C	-.003	-.005	-.001	.000	.000
	D	-.004	-.112	-.001	.004	.002

Table 5. Percent of expansion of beams under Exposure I. (Republican River sand)

		Age in days				
		60	90	120	150	180
R-16	B	.005	.006	.003	.007	.010
	C	.033	.035	.035	.037	.040
	D	.016	.024	.025	.029	.031
R-30	B	.010	.006	.009	.006	.012
	C	.029	.023	.023	.017	.021
	D	.002	.006	.011	.010	.008
R-50	B	-.008	-.003	-.003	.000	.000
	C	.003	.004			
	D	.008	.006			

Table 6. Percent of expansion of beams under Exposure II. (Republican River sand)

		Age in days				
		60	90	120	150	180
R-16	B	.016	.020	.021	.042	.059
	C	.018	.020	.017	.038	.051
	D	.024	.030	.032	.055	.072
R-30	B	.011	.003	.009	.009	.017
	C	.011	-.001	.008	.010	.015
	D	.002	.003	.004	.009	.008
R-50	B	.001	.007	.003	.010	.010
	C	.005	.008			
	C	.008	.012			

Table 7. Percent of expansion of beams under Exposure III. (Republican River sand)

		Age in days				
		60	90	120	150	180
R-16	B	.023	.026	.024	.022	.032
	C	.024	.037	.036	.044	.045
	D	.051	.056	.054	.057	.063
R-30	B	.029	.026	.032	.028	.032
	C	.017	.019	.026	.023	.032
	D	.026	.027	.030	.033	.032
R-50	B	.011	.017	.021	.023	.026
	C	.025	.030			
	D	.027	.033			

Table 8. Percent of expansion of beams under Exposure IV. (Republican River sand)

		Age in days				
		60	90	120	150	180
R-16	B	.041	.105	.171	.234	.277
	C	.041	.063	.068	.085	.095
	D	.051	.061	.061	.065	.066
R-30	B	.024	.065	.189	.291	.383
	C	.023	.042	.070	.092	.123
	D	.037	.046	.043	.047	.049
R-50	B	.004	.008	.009	.012	.014
	C	.008	.012			
	D	.008	.014			

Table 9. Sonic modulus of elasticity of concrete (Kaw River sand).

Exposure		I		II		III		IV	
		Age in days							
		30	180	30	180	30	180	30	180
K-4	A	4.00	4.79	4.00	4.00	4.06	4.66	4.94	5.00
	B	4.14	4.58	4.07	3.61	3.80	5.50	4.21	5.00
	C	4.76	5.12	3.91	4.00	4.14	5.65	5.54	5.72
	D	4.27	4.49	2.89	-	3.79	4.74	5.00	5.25
K-8	A	4.50	5.23	4.48	4.17	4.51	5.53	5.14	5.06
	B	4.72	5.35	4.37	4.04	4.38	5.45	4.90	5.18
	C	4.69	4.92	4.35	4.26	4.14	5.02	5.01	5.18
	D	4.70	4.67	4.80	4.09	3.90	5.16	4.60	4.98
K-16	A	4.90	5.23	4.70	4.74	4.60	5.37	4.60	4.64
	B	5.10	5.12	4.40	4.89	4.80	5.63	4.80	4.82
	C	4.80	4.76	4.55	4.81	4.70	5.51	4.65	4.86
	D	4.99	4.89	4.45	4.94	4.20	4.97	4.85	5.19
K-30	A	4.95	4.86	4.10	4.69	4.35	4.39	4.90	4.64
	B	4.90	5.27	4.70	4.92	4.30	5.08	4.80	4.67
	C	4.70	4.98	4.20	4.76	4.30	5.18	4.60	4.69
	D	4.00	4.32	3.70	4.34	3.75	4.68	4.00	4.11
K-50	A	4.40	4.49	3.70	4.51	3.80	4.92	4.30	4.59
	B	4.00	4.42	3.50	4.12	4.10	4.61	3.95	4.24
	C	3.95	4.29	3.45	4.45	3.65	4.52	4.00	4.46
	D	3.50	3.99	3.10	4.17	3.05	4.23	3.60	4.09
K-100	A	3.10	3.25	3.10	3.42	3.00	3.27	3.30	3.39
	B	3.20	3.14	2.80	3.20	2.50	3.33	3.20	3.32
	C	3.25	3.47	2.80	3.35	2.70	3.42	3.65	3.36
	D	3.00	3.22	2.40	3.06	2.20	3.03	2.90	3.35

Table 10. Maximum shrinkage of concrete beams under Exposure IV.

Alkali	0.132	0.60	1.0	1.5
	percent			
K-4	.058	.056	.050	.053
K-8	.058	.054	.053	.052
K-16	.067	.065	.055	.058
K-30	.070	.070	.057	.051
K-50	.061	.074	.062	.054
K-100	.068	.058	.046	.048

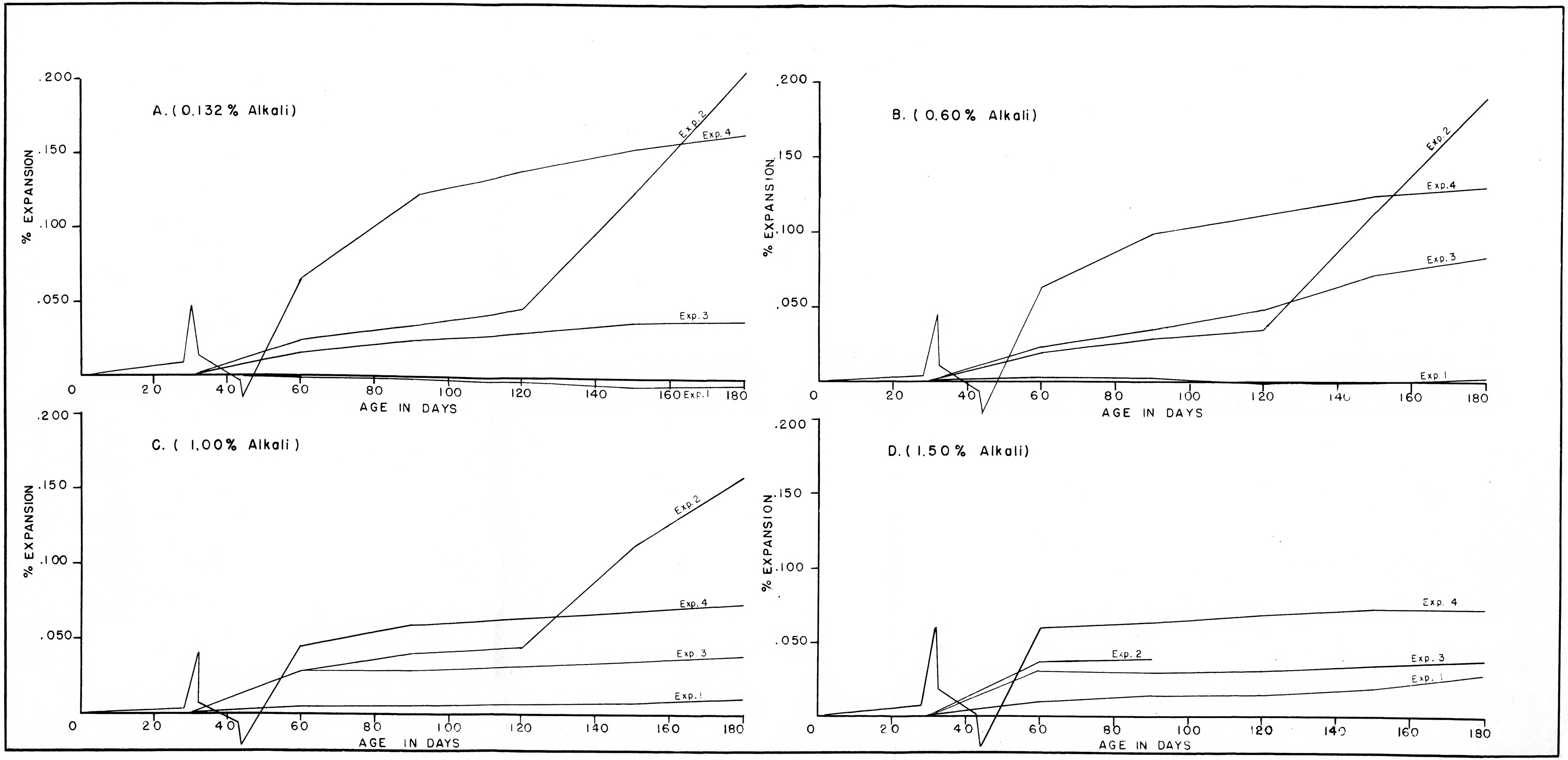

Fig. 1. Relation between alkali cotent, type of exposure and expansion. (Concrete was made with Kaw-River sand, sieve No.4.)

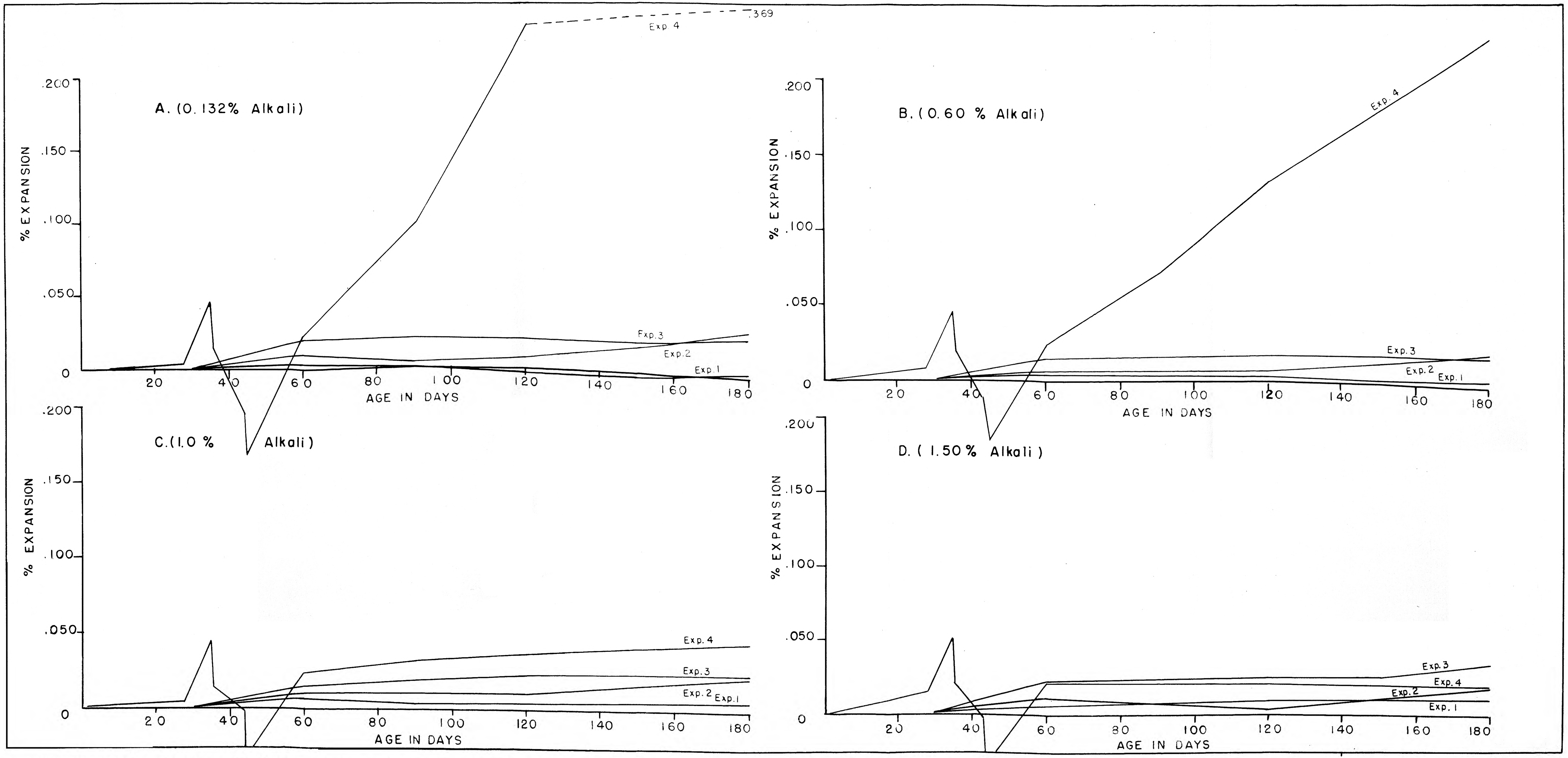

Fig. 2. Relation between alkali, content, type of exposure and expansion. (Concrete was made with Kaw-River sand, sieve No.30)

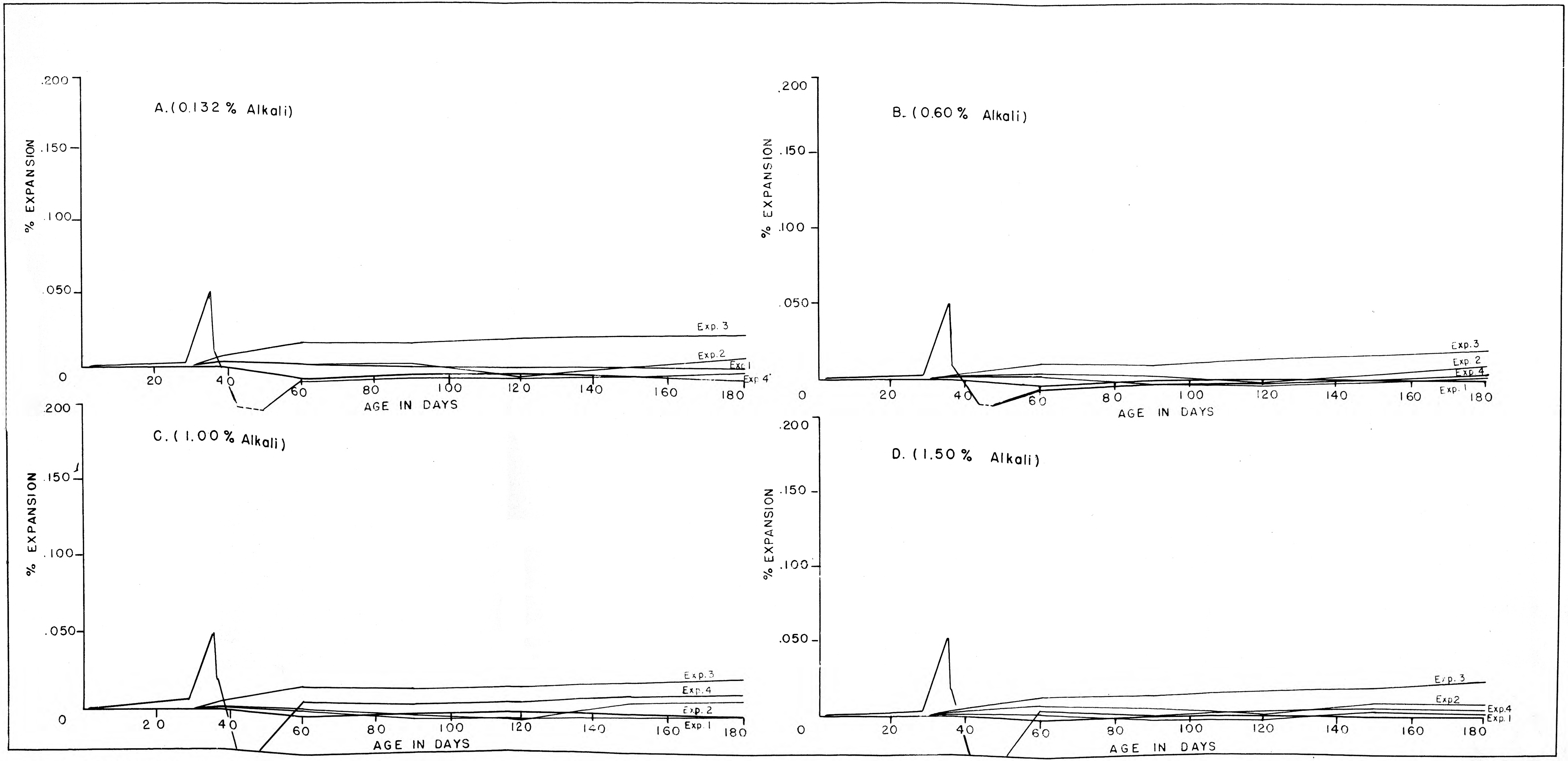

Fig.3. Relation between alkali content, type of exposure and expansion (Concrete was made with Kaw-River sand, sieve No. 50)

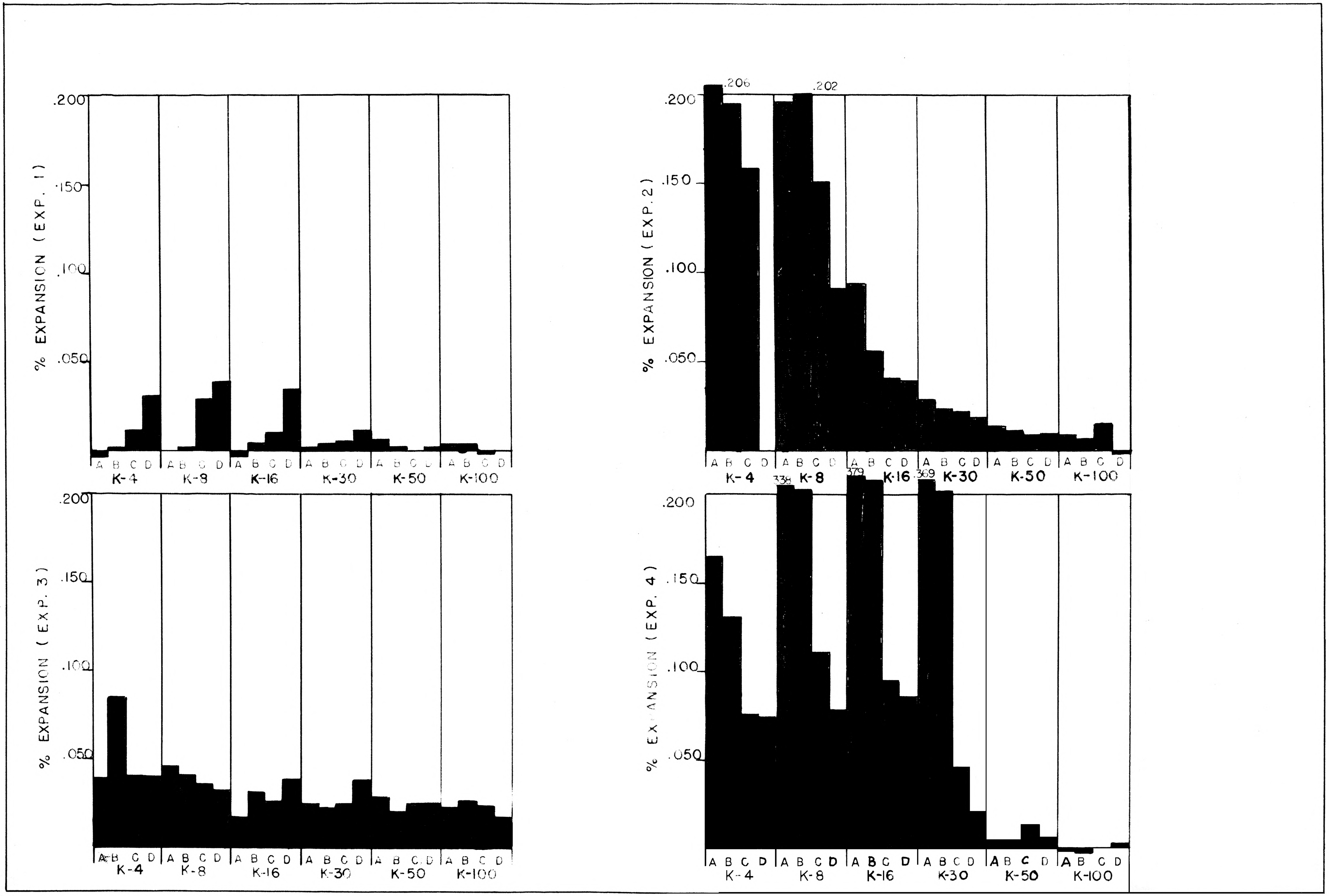

Fig. 4. Percent of expansion of concrete made with Kaw-River sand at 180 days age.

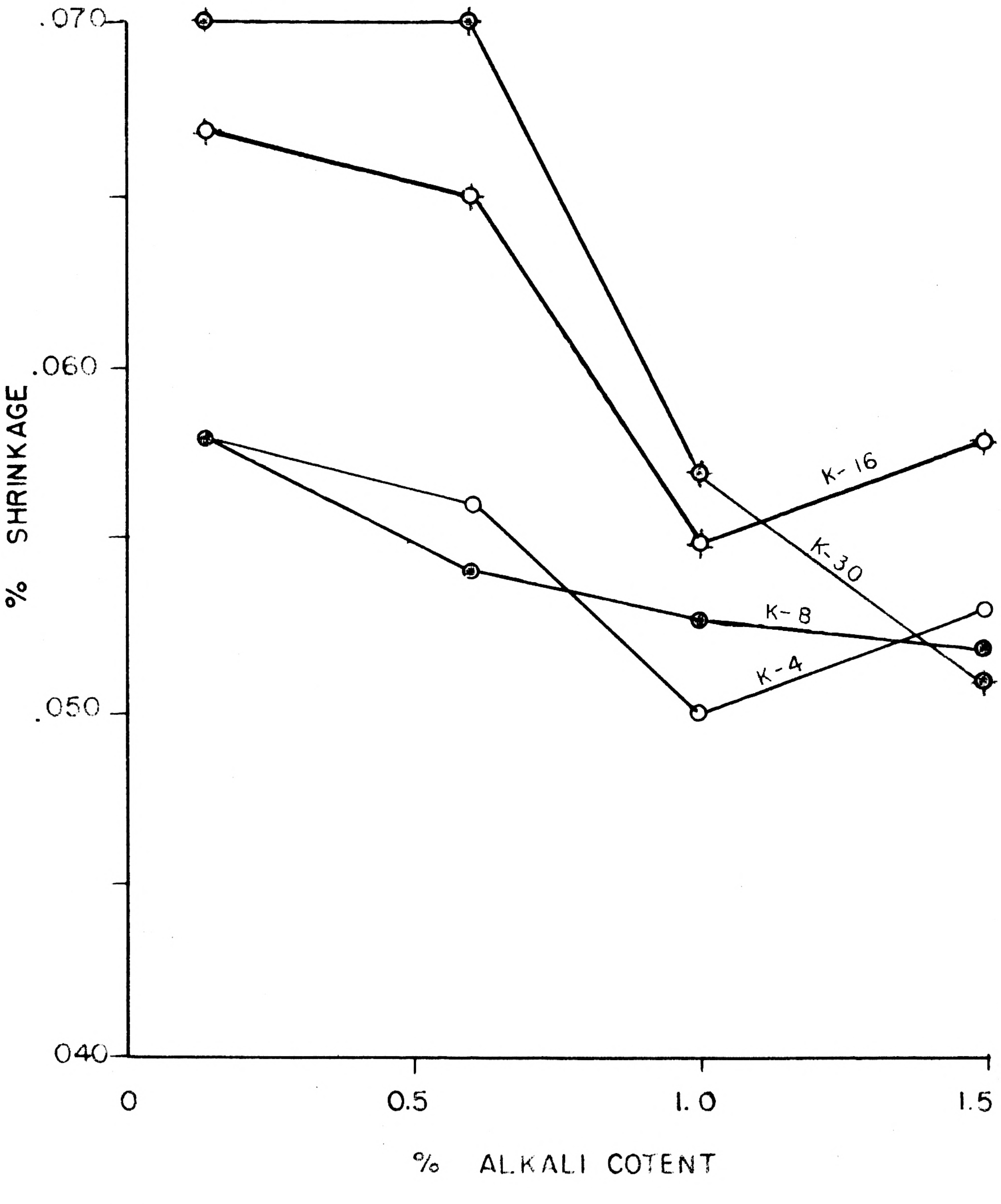

Fig. 5. Shrinkage due to change of temperature and water content.

DISCUSSION

Effect of the Various Exposures Upon the Expansion

Exposure I (Sealed container-100° F. with about 90 percent humidity). Cement and aggregate reaction under this exposure was very slow. In this exposure the beams were moist during the entire test. Although alkali ions could diffuse through the saturated gel and react with the soluble silica in the aggregate, this process was very slow as compared to the other exposures in which drying cycles occurred. The author believes that when drying occurs in concrete, small cracks develop in the gel and allow the alkali to enter and react with the silica of the sand.

At 180 days very little expansion had developed for any of the specimens in this exposure and there was not sufficient evidence to express the factors affecting the cement-aggregate reaction from this exposure.

Exposure II (Alternate wetting 70-80° F. and drying 130° F.). Concrete beams were subjected to a 130° F. oven drying for 12 hours and 70° F. soaking for 8 hours. In this exposure the author believes that during the drying process sodium silicate gel will shrink and crack and permit the alkali to react with the silica directly and thus accelerate the expansion.

It is a known fact that high temperatures will tend to accelerate the cement-aggregate reaction and the author believes that 130° F. was not too severe when used for cement-aggregate reaction tests. Records of mass concrete indicated that unless special cooling precaution is taken, the temperature in the interior of the mass may be expected to reach 130° F. and even higher. By studying Figs. 1, 2, and 3, the concrete beams under Exposure 2 gave satisfactory data showing the factors which affected the cement-aggregate reaction.

Exposure III (Alternate heating and cooling by a spray of water 70-130° F.). After 4000 cycles of this exposure, very little expansion occurred for any of the specimens. It should be pointed out that there is a similarity between Exposures 1 and 3, i.e., the specimens were moist during the entire test in both exposures. As already pointed out, very little expansion developed in Exposures 3 and 1. Since the specimens in these exposures were saturated at all times, it was more difficult for the sodium ions to diffuse through the gel and react with SiO_2, tending to retard the cement-aggregate reaction.

In the exposure where drying occurred, considerable expansion developed in many of the specimens. The author believes that this drying tends to crack the cement paste - which is a physical phenomena. Cement-aggregate reaction is probably a result of both physical and chemical action.

Exposure IV (7 days immersion in 130° F. water, then dried at 130° F.). The concrete beams were immersed in130° F. water for 7 days to accelerate the hydration and then oven-dried (130° F.) for 7 days to develop cracking around the sand particles. Because of the small cracks in the cement paste, the alkali could react with SiO_2 of the aggregate more easily - allowing cement-aggregate reaction to occur. Figures 1, 2, and 3 showed that the expansion was much slower after 120 days. The author believes that as these cracks become filled with the gel, the rate of the reaction is reduced.

Since the expansions for all specimens in Exposures I and III were quite low, the effect of size of aggregate and alkali content upon cement-aggregate reaction will be based upon Exposures II and IV.

Effect of the Particle Sizes of Aggregate Upon the Expansion

As shown in Fig. 4 (Exposure IV) the No. 30 size aggregate gave the largest expansion followed by the 16, 8, and 4 in that order. This degree of expansion for the various sizes of particles seems to be proportional to their surface areas; i.e., the larger surface area permits more chemical reaction between the alkali and SiO_2 of the aggregates.

However, sieves No. 50 and 100 gave negligible expansion and the author believes that these particle sizes were so small that it reacted as a pozzolanic material and the chemical reaction was completed before the hardening of the mortar paste.

Effect of the Various Alkali Contents Upon the Expansion

Figure 4 showed that the expansion of concrete beams decreased as more alkali salt (Na_2CO_3) was added into the mixture. Probably this could be explained by the following:

(1) Precipitation of Ca CO_3 isolated the aggregates. The possible chemical reactions between cement, aggregate and Na_2CO_3 are written in the following order:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (a)$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2\ NaOH \qquad (b)$$

As indicated in equation (b), more $CaCO_3$ will be precipitated when greater amounts of Na_2CO_3 are added into the mix. The precipitation will form an impermeable shell around the aggregate and thus isolate the particles of aggregates. It is believed that the alkali content within the shell is too small to cause progressive expansion.

Gaskin (2) treated some concrete mortar with carbon dioxide moist, 90 percent by volume, under normal atmospheric pressure and stated that the expansion was reduced by this treatment. Carbon dioxide, as he stated, would react with $Ca(OH)_2$ and form a non-reactive calsium carbonate which is similar to the author's theory of the $CaCO_3$ shell mentioned above.

(2) The reduction of $Ca(OH)_2$ retarted the cement-aggregate reaction. The cement-aggregate reaction may be expressed as follows during the mixing:

$$CaO + H_2O \rightarrow Ca\ (OH)_2$$

$$Na_2\ CO_3 + Ca\ (OH)_2 \rightarrow CaCO_3 + 2\ NaOH$$

After the mixing, the NaOH may react with SiO_2 in cement or aggregate and formed sodium silicate.

$$NaOH + SiO_2 \rightarrow NaHSiO_3$$

The progressive expansion of concrete is a result of the reaction between the $NaHSiO_3$ and $Ca(OH)_2$ where the sodium ions are released from the $NaHSiO_3$ and are combined with $(OH)^-$ from the $Ca(OH)_2$. This reaction between the Na^+ and $(OH)^-$ produces NaOH which becomes available for reaction with the silica of the sand.

$$NaHSiO_3 + Ca(OH)_2 \rightarrow CaSiO_3 + NaOH$$

As indicated above, a reduction of $Ca(OH)_2$ will reduce the progressive reaction. It was also mentioned before that adding Na_2CO_3 will reduce the amount of $Ca(OH)_2$.

The author believes that the reduction in expansion of concrete by adding Na_2CO_3 is due to the decreasing of the $Ca(OH)_2$ content.

In order to prove that the admixture (Na_2CO_3) reduced the formation of a gel, a shrinkage test was made. Concrete beams from the Exposure IV were soaked in 130° F. water for 24 hours, then dried in a 130° F. oven for 24 hours, then put in a 70° F. lab. air for 24 hours. The shrinkage, following the initial 24 hour soaking, was determined by the length comparator. It is known that the shrinkage is due to the loss of moisture from the gel and that amount of shrinkage is proportional to the amount of gel presented. By studying Table 10 and Fig. 5, it was found that the shrinkage was reduced when the Na_2CO_3 increased. These results may prove that the admixture reduced the gel formation-reducing the cement-aggregate reaction. As shown in Fig. 4, the higher the Na_2CO_3 content the less the expansion.

The Research Laboratory of Lehigh Portland Cement Company tried 1 percent of lithium salt as an admixture which was also effective in reducing the amount of expansion.

(3) The effect of alkali content of the cement upon the modulus of elasticity:

Table 9 showed, in general, that the modulus of elasticity was increased when alkali was added to 1 percent.

CONCLUSION

It may be said that cement-aggregate reaction is a complex degree of physical and chemical reaction between the constituents of the cement pastes and aggregate. The factors affecting the physical and chemical activities are many and the author realizes that only several of these factors have been considered in this study. From the research data presented in this manuscript, the following conclusions are made in reference to the effect of aggregate size, alkali content, and exposure upon cement-aggregate reaction:

1. To determine the cement-aggregate reaction, it was found that Exposure II (Alternate wetting 70 -80° F. and drying 130° F.) and Exposure IV (7 days immersion in 130° F. water then dried at 130° F) gave satisfactory results. The expansion in Exposure I (Sealed container - 100° F. with about 90 percent humidity) and Exposure III (Alternate heating and cooling by a spray of water, 70 -130° F.) were small and no conclusions could be made at 180 of age.

2. As shown in Exposure IV, the No. 30 size aggregate gave the largest expansion followed by the No. 16, 8, and 4 in that

order. This degree of expansion for the various sizes of particles seems to be proportional to their surface areas. Sieves No. 50 and 100 reacted as pozzolanic materials and gave negligible expansion.

3. One percent of Na_2CO_3 (equivalent to 1 percent Na_2O) was effective in reducing the expansion of concrete. The reasons are: (1) Precipitated $CaCO_3$ formed an impermeable shell around the aggregate and thus isolated the particles of aggregate and (2) Decrease of $Ca(OH)_2$ content will reduce the progressive action.

4. Modulus of elasticity was slightly increased when alkali salt (Na_2CO_3) was added to equivalent 1 percent.

ACKNOWLEDGMENT

Indebtedness is acknowledged to Professor C. H. Scholer, Head of the Department of Applied Mechanics for guidance and encouragement during this study; to Mr. Gerald M. Smith of the Research Laboratory of the Department of Applied Mechanics for counsel and suggestions; to Mr. J. E. McCornell for counsel; and to the Material Testing Laboratory of the Kansas Highway Commission for technical assistance.

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APPENDIX

Calculation of Alkali Contents in Concrete

1. Equivalent alkali content of Penn-Dixie cement:

   Molecular wt. of $Na_2O = 2 \times 23 + 16 = 62$

   Molecular wt. of $K_2O = 2 \times 39.09 + 16 = 94.18$

   Equivalent alkali content by wt.:

   $Na_2O = 62/94.18 = 0.6583\ K_2O$

   Equivalent alkali content of Penn-Dixie cement =

   $0.02 + 0.6583 \times 0.17 = 0.13$ percent.

2. Amount of Na_2CO_3 added in different batches:

   Molecular wt. of $Na_2CO_3 = 2 \times 23 + 12 + 16 \times 3 = 106$

   Molecular wt. of $Na_2O = 62$

   No. of Na^+ in 1.71 gm (106/62) of Na_2CO_3 = No. of Na^+ in 1 gm of Na_2O.

   Batch A: (0.132 percent) No Na_2CO_3 was added.

   Batch B: (0.60 percent)

   0.6-0.132 = 0.468 (Wt. of Na_2O needed in 100 gm of cement to produce 0.6 percent alkali).

   0.468 x 1.71 = 0.8002 (Equivalent amount of Na_2CO_3 needed in 100 gm of cement).

   0.8002 x 12 = 9.6 gm (Na_2CO_3 needed in 1200 gm of cement).

   Batch C: (1.0 percent)

   1-0.132 = 0.868

   0.868 x 1.71 = 1.484

   12 x 1.484 = 17.81 gm (Na_2CO_3 needed in

1200 gm of cement).

Batch D: (1.5 percent)

1.5 - 0.132 = 1.368

1.368 x 1.71 = 2.339

12 x 2.339 = 28.07 gm (Na_2CO_3 needed in 1200 gm of cement.

A STUDY OF CEMENT-AGGREGATE REACTION AS AFFECTED BY TYPE OF EXPOSURE, ALKALI CONTENT AND PARTICLE SIZE OF AGGREGATE

by

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Evidences showed that certain types of the deterioration of concrete are due to the alkali reaction between cement and aggregate. The soda and potash of cement, reaction with an aggregate containing opal and chert, produces a gel-like substance called sodium silicate. According to Hanson, the gel will produce osmotic pressure and cause the expansion of the concrete.

From results of various tests it has been found that smaller particle sizes of aggregate, which have a larger surface area, would accelerate the chemical reaction and cause more expansion. In general, cement with high alkali content gives larger expansion than does cement with low alkali content. But in Kansas, Arizona and Washington some concrete has shown a contrary reaction, in which concrete made with sand, containing a high percentage of chert, and cement, with a high alkali content, gave negligible expansion. So it is suggested that a study of the reaction between cement and aggregate in these areas be continued.

There are many test methods used for determining cement-aggregate reaction. Four exposures, which seemed representative of weathering conditions, were chosen for this study as an attempt to determine a rapid and accurate means for detecting cement-aggregate reaction.

In this study 264-1"X1"X10" mortar bars were made with a low alkali cement and Kaw River and Republican River sands, both of which were reactive and have given bad service records in Kansas. Anhydrous sodium carbonate was added to the mixing water as a means of increasing the alkali content of cement.

From the research data it was found that Exposure II (Alternate wetting 70-80 F and drying 130 F) and Exposure IV (7 days immersion in 130 F water then dried at 130 F) gave satisfactory results.

Regarding the effect of aggregate size on the expansion of concrete, it was found that aggregate retained on the No. 30 sieve size gave the largest expansion, followed by Nos. 16, 8 and 4 respectively. This degree of expansion for the various sizes of particle seems to be proportional to their surface areas. Aggregate retained on sieves No.50 and 100 reacted as pozzolanic materials, and gave negligible expansion.

It was also found that one per cent of equivalent alkali (Na_2CO_3) was effective in reducing the expansion of the concrete. Modulus of elasticity was slightly increased when alkali (Na_2CO_3) was added to the equivalent of one per cent.