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Alkali-Aggregate Phase of Chemical Reactivity in Concrete

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● THE action of potassium and sodium oxides on certain types of aggregate continues to be one of the primary topics in most publications concerning concrete reactions. The reality of this action has been recognized by a majority of the cement-research chemists; however, the theories explaining this action seem, in most cases, to be inadequate. This, among other reasons, has caused many investigators to treat this as a secondary reaction, or merely a vague possibility.

Many structural failures attributed to alkali-aggregate reaction may be the result of other chemical or physical action. Even when it is evident that alkali action is present, it is usually too late to prevent serious damage. A thorough knowledge of the individual concrete components, including the chemical analysis of the cement, water, and aggregate plus the petrographic analysis of the aggregate should certainly be required before designing the concrete mix. Several faulty structures in Alabama contain cements with high magnesia contents, as well as high alkali. In practically all instances, records of these structures contain little or no information concerning the petrographic or chemical content of the individual components. Many aggregates containing high sodium and potassium release the corresponding hydroxides by reaction with lime from hydrated cement. Some of the zeolites contain as much as 16 percent sodium oxide.

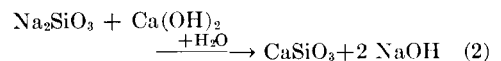
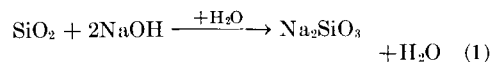
For alkali-aggregate reaction to progress, at least five major factors must exist: (1) sufficient alkali to react with the silica; (2) silica that is reactive with rather low concentrations

of alkali; (3) water available in amounts necessary to continue the reactions; (4) lime free to react with the alkali silicates, releasing the alkali back to solution, or enough alkali present to injure the concrete without regeneration; and (5) enough force to rupture the concrete after the damage by the alkali. It is evident that the last two factors contain the main controversial issues.

There is sufficient reason to doubt that the comparatively small amounts of alkali, derived from portland cement, could destroy enough aggregate or produce enough alkali silicate to be of great concern without some process of reviving the alkali hydroxides so as to continue the cycle. There is also evidence that the osmosis theory, as applied to the alkali silicates, has little or no application to the affected concrete samples examined in this department.

ALKALI SILICA AND LIME

The basis for the following data and comments is shown very simply by the following equations:



The use of sodium and calcium metasilicate is for simplicity only. It will be noticed that the sodium and calcium silicates have a higher silica ratio when used with a hydrous form of silica in the following experiments, however, the reactions produce similar results.

In Equation 1, the action of sodium hydroxide on the silica produces sodium silicate and an extra molecule of water. The sodium silicate remains in solution and the water adds to the free water in the solution.

In Equation 2, after practically all of the sodium hydroxide has been converted to the silicate, lime from the hydrated cement enters the solution reacting with the sodium silicate releasing two molecules of sodium hydroxide back to solution. This hydroxide forces the lime out of solution and reacts with more silica.

It is easy to see how this reaction can continue until one of the following conditions is encountered: (1) all of the reactive silica is consumed; (2) the hydroxide is exhausted by flowing to the surface and leaching; (3) the hydrated lime has been exhausted by action on the reactive silica and the alkali silicate in solution; and (4) water is prevented from entering the reaction.

To proceed with chemical research adequate to prove this theory, it was necessary to produce a silica that would react very readily with low and medium concentrations of sodium hydroxide. This silica was produced by reacting sodium tetrasilicate (technical grade) with hydrochloric acid and washing the silica, by decantation, with hot distilled water until clear of all chlorides (as shown by silver-nitrate solution). The silica was dried over a steam bath and then in an oven at 110 C. The moisture and molecular water content are very near the same as that of some practically pure opal from Nevada, as shown in Table 1.

The next preliminary step was to determine the product formed when this silica was dissolved in sodium hydroxide, filtered, and precipitated by a clear, saturated solution of calcium hydroxide. This dense white gel was filtered, dried, purified, and analyzed for silica and lime. The results shown in Table 2 are from five samples of CaO formed by this process using the special silica, and one using Nevada opal.

From these results, the average of 1.0 CaO to 1.2 SiO₂ of the special silica is very close to the 1.0 to 1.24 of the opal. When figured to an even number, the 1.0 CaO to 1.2 SiO₂ gives a ratio of 5.0 CaO to 6.0 SiO₂ or the compound Ca₅Si₆O₁₇. This compound is probably a combination of calcium metasilicate and calcium disilicate.

Using the sodium-silicate solution produced by the addition of sodium hydroxide to the special silica, solutions of calcium chloride and calcium sulphate were substituted for the original lime solution. The ratio of the calcium oxide to the silica in each of the resulting compound was 1 to 2, or calcium disilicate (Ca-Si₂O₅). The difference between the products formed by the lime and other two calcium compounds is probably due to the difference in ionization and solubility of the original calcium compounds.

TABLE 1
WATER CONTENT AND RATIO IN
HYDROUS SILICA

Loss at 110 C. (Moisture)	Loss (110 C.- 1,100 C.)	Molecular ratio SiO ₂ to H ₂ O
Special silica, 2.61%.....	8.63%	3:1
Opal, 2.67%.....	5.50	5:1

TABLE 2
LIME-SILICA RATIO IN SPECIAL
CALCIUM SILICATE

Sample	CaO	SiO ₂	Ratio CaO to SiO ₂
	<i>gms.</i>	<i>gms.</i>	
1 (Special SiO ₂).....	0.1564	0.1915	1:1.155
2 (Special SiO ₂).....	.1722	.2224	1:1.231
3 (Special SiO ₂).....	.0901	.0690	1:1.219
4 (Special SiO ₂).....	.1871	.2461	1:1.229
5 (Special SiO ₂).....	.1891	.2422	1:1.194
Average.....			1:1.20
6 (Nevada Opal).....	.2125	.2823	1:1.240

PROGRESSIVE CHEMICAL REACTIONS

To support this alkali-silica-lime theory, several weeks were necessary to design and test a chemical procedure that would show some of the progressive steps in this reaction cycle. This procedure is too long to include here; however, the following results and explanations should be sufficient.

The following amounts of alkali, lime, and silica were placed in each of four stainless steel Parr bombs:

Bomb	Na ₂ O (Gm. in 20 ML. H ₂ O) and Percent of Solution		CaO	SiO ₂
	<i>gm.</i>	%	<i>gm.</i>	<i>gm.</i>
1	0.10	0.5	0.30	0.50
2	0.14	0.7	0.30	0.50
3	0.20	1.0	0.30	0.50
4	0.30	1.5	0.30	0.50

The bombs were closed and the contents mixed (by shaking). These were allowed to

stand for 3 weeks at room temperature and agitated by shaking vigorously for 2 min. each day for the first week.

A second set of four bombs, Nos. 1A through 4A, was prepared with the same ingredients and amounts contained in the first set. These received the same treatment as the first set, except the time of reaction was 8 weeks. At the end of the reaction for each set, the bombs were opened and the analysis made on the contents of each bomb. The results are shown in Table 3.

It is evident, from the results in Table 3, that the reaction did not go to completion in the 3-week period, as shown by the free lime

1A through 4A, an average of 0.2935 grams of lime was recovered from the original 0.3 grams. It is very evident that all of the lime was consumed, as no free lime is left in either the filtrate or residue.

During the formation of calcium silicate from sodium and potassium silicate, it is evident that the calcium-silicate gel will include the water-soluble silicates and partially dehydrate them. In other words, the formation of the calcium-silicate gel will remove alkali silicates from solution in the form of a viscous gel. A clear example of this is contained in a glass bottle on the desk in this laboratory. Approximately 0.25 grams of calcium chloride

TABLE 3
LIME-SILICA-ALKALI PROGRESSIVE CHEMICAL REACTIONS

Bomb No.	Filtrate			Residue			
	Na ₂ O	5Na ₂ O·6SiO ₂	CaO	Ca ₃ Si ₆ O ₁₇ (5CaO·6SiO ₂)	5Na ₂ O·6SiO ₂	Free SiO ₂	Free CaO
Set No. I, Results After 3 Weeks							
1	0.0310	0.0000	0.0069	0.5757	0.1492	0.0631	0.0401
2	0.0520	0.0000	0.0043	0.5719	0.1903	0.0677	0.0450
3	0.0810	0.0000	0.0031	0.5646	0.2573	0.0231	0.0488
4	0.1540	0.0123	0.0005	0.5845	0.2897	0.0050	0.0435
Set No. II, Results After 8 Weeks							
1A	0.0267	0.0022	0.0000	0.6727	0.1563	0.0364	0.000
2A	0.0440	0.0000	0.0000	0.6709	0.2076	0.0110	0.000
3A	0.0887	0.0011	0.0000	0.6706	0.2270	0.0002	0.000
4A	0.1934	0.0575	0.0000	0.6688	0.1730	0.0000	0.000

remaining in the filtrate and residue. Also, no sodium silicate was found in the filtrate with the exception of Bomb 4, which contained the highest alkali. From this reaction, it seems that the high alkali goes through the reaction faster than the lower concentrations.

It is also apparent that the results from the 8-week period indicate that the reaction did go to completion, since there is no free lime in either the filtrate or residue. In bombs 3A and 4A, virtually all of the silica has been consumed by the combination of the 5CaO·6SiO₂ and 5Na₂O·6SiO₂. Since the amount of alkali remaining in the filtrate is low in Bombs 1A and 2A, the action on the silica has been retarded, although all of the lime has been consumed.

It is difficult to keep lime from absorbing water, even in the short period during cooling and weighing. Small amounts are also lost during long chemical manipulation. In Bombs

was placed in a large gelatin capsule and dropped to the bottom of a solution of sodium silicate. When the capsule dissolved, calcium silicate was found occupying the bottom, or Number 1, layer. The second layer contained a mixture of calcium-silicate and sodium-silicate gels. The third layer appeared to contain only sodium-silicate gel while the fourth, or top layer, occupying about one fourth the total volume, contained only solution.

The presence of sodium and potassium silicates occluded in a mass of hydrated calcium silicate makes the purification of the calcium silicate difficult. It seems best to dehydrate the whole mass at 105 C and remove the sodium or potassium silicate with the minimum amount of hot distilled water. Even then, small amounts of calcium silicates are dissolved. Cold water removes alkali silicates from this mixture very slowly.

CONCRETE GEL

An interesting example of alkali reactivity is shown in the analysis of gel obtained from the Lone Star Cement Corporation's test road. This road is located in the plant area of the Birmingham, Alabama, plant. The concrete cores were donated by M. A. Swayze, director of research for the Lone Star Cement Corporation, and Harry Williams, chief chemist of the Birmingham plant. The aggregate used in this section of concrete road was the Montgomery Roquemore type containing an average of 5 percent hydrous silica. The cement was Type 1 containing 1.03 percent K_2O and 0.29 percent Na_2O . Production of this type of cement has been discontinued. Other sections

Since the molecular ratio of lime to the acid soluble silica is the same in both cases and is closer to $1CaO$ to $2SiO_2$ than any other reasonable combination, the compound is assumed to be $CaO \cdot 2SiO_2$ or calcium disilicate. This compound does not require all of the acid-soluble silica; therefore, 4.53 percent SiO_2 is left from the Lone Star sample and 5.33 percent from the Alabama sample.

As potassium precedes sodium in the electromotive series and the K_2O content is higher than the Na_2O content, it seems reasonable that the remaining acid-soluble silica reacted with the K_2O as follows:

TABLE 4
ANALYSIS OF CONCRETE GEL FROM TEST ROAD

	Lone Star	Alabama
	%	%
Insoluble residue (sand).....	27.80	25.54
Acid soluble silica (SiO_2).....	34.20	37.46
Iron and aluminum oxides (Al_2O_3) (Fe_2O_3).....	0.76	1.89
Calcium oxide (lime) (CaO).....	13.85	15.00
Magnesium oxide (MgO).....	0.22	0.44
Sulphur trioxide (SO_3).....	0.09	0.16
Moisture (loss at 105 C.).....	4.66	11.84
Loss (105-1000 C.).....	8.84	--
Sodium oxide (Na_2O).....	2.40	3.48
Potassium oxide (K_2O).....	7.30	6.96

	Na_2O Total	K_2O Total	SiO_2 Remain- ing	$K_2Si_2O_7$	K_2O Used	K_2O Remain- ing
	%	%	%	%	%	%
Lone Star.....	2.40	7.30	4.53	8.08	3.55	3.75
Alabama.....	3.48	6.96	5.33	9.51	4.18	2.78

This, of course, leaves potassium and sodium as oxides free in the following amounts:

	Na_2O	K_2O
	%	%
Lone Star.....	2.40	3.75
Alabama.....	3.48	2.78
Average.....	2.94	3.27

of this road made from cements with low alkali contents remain in good condition.

The two analyses shown in Table 4 were made from the gel obtained from two cores of the same section of test road. The one listed as Lone Star was made by the Hudson Research Laboratory of the Lone Star Corporation and the other by the chemical section of the Alabama Highway Department Laboratory. Considering that the samples were obtained from two different cores, the results agree quite well.

To appreciate the full meaning of the results from the gel analyses, it is necessary to compare the ratio of the calcium oxide to the acid-soluble silica, as shown below:

	CaO	Acid Soluble SiO_2	Mol Ratio CaO to SiO_2	$CaSi_2O_7$ Calcium disilicate	SiO_2 re-quired	SiO_2 remain-ing
	%	%		%	%	%
Lone Star	13.85	34.20	1:2.31	43.52	29.67	4.53
Alabama	15.00	37.46	1:2.33	47.13	32.13	5.33

To be sure of the existence of the free alkali, enough gel was extracted from another core from the same section of test road to analyze for water-soluble sodium and potassium oxides and accompanying water-soluble silica, acid-soluble sodium and potassium oxides, and acid-soluble silica. In order to dissolve as little of the combined water-soluble silica as possible and still get the free alkali oxides, the sample was ground to pass the 100-mesh sieve, transferred to a No. 40 Whatman filter and washed with cold distilled water until the total volume of filtrate was 100 ml. After analyzing the filtrate and residue, the following results were obtained:

	Na_2O	K_2O	SiO_2
	%	%	%
Water soluble.....	2.60	1.80	0.44
Acid soluble.....	0.68	3.48	34.98
Total.....	3.28	5.28	35.42

This analysis shows only 0.44 percent of the silica was dissolved from the alkali silicates, also, that 2.60 percent of a total 3.28 percent Na_2O was water soluble while 1.80 percent of the total 5.28 percent K_2O was water soluble. This, of course, leaves the acid-soluble 3.48-percent K_2O combined as potassium silicate. This 3.48-percent K_2O is equivalent to 7.918 percent of $\text{K}_2\text{Si}_2\text{O}_5$, which compares favorably with the 8.08-percent $\text{K}_2\text{Si}_2\text{O}_5$ figured from the gel analysis of the Lone Star Research Laboratory.

Substituting the calcium disilicate, potassium disilicate and the free oxides of sodium and potassium in the original analyses of the Lone Star and Alabama Laboratories, gives the results shown in Table 5.

TABLE 5
CONCRETE-GEL ANALYSIS SUBSTITUTING
CALCIUM AND POTASSIUM DISILICATES

	Lone Star	Alabama	Average
	%	%	%
Insol residue (sand).....	27.80	25.54	26.67
Fe_2O_3 and Al_2O_3	0.76	1.89	1.33
$\text{Ca}_2\text{Si}_2\text{O}_5$	43.52	47.13	45.33
$\text{K}_2\text{Si}_2\text{O}_5$	8.08	9.51	8.80
MgO	0.22	0.44	0.33
SO_3	0.09	0.16	0.13
Na_2O	2.40	3.48	2.94
K_2O	3.75	2.78	3.27
Moisture (105 C.).....	4.66	11.84	8.25
Loss (1000 C.).....	8.84	—	—

MORTAR BARS

It seems that no test on concrete is considered complete without showing a long line of results obtained from the expansion of mortar bars. To be consistent with this idea, a special set of mortar bars was constructed on July 19, 1948. These bars were designed to duplicate the approximate 20-percent-chert content of the Roquemore large aggregate by substituting 20 percent of Aliceville chert. The remaining 80-percent aggregate was quartz sand.

Roquemore large aggregate, actually, contains an average of 22.03 percent chert, 64.00 percent quartzite, 11.00 percent quartz, and 2.87 percent shale. As mentioned before, it contains an average of 5 percent hydrous silica that is practically all contained in the 22 percent chert. Solid particles of hydrous silica are rarely, if ever, found; but voids filled with hydrous silica appear frequently in the chert particles.

The Aliceville large aggregate contains an average of 97.50 percent chert and 2.50 percent quartzite. The chert is practically all chalcedony with little or no hydrous material. The Columbus, Mississippi, large aggregate is the same type as the Aliceville aggregate. This aggregate has a very good service record regardless of the brand of cement used.

The cements used in the mortar bars were two brands from this area. Cement A contained 0.21 percent Na_2O , and 0.96 percent K_2O . Cement B contained 0.16 percent Na_2O , and 0.20 percent K_2O . Since the Na_2O contents of both cements were very near the same, sodium hydroxide was added to the mixing water in bars containing both types of cement, equivalent to 1.8 percent Na_2O .

TABLE 6
EXPANSION OF MORTAR BARS
Aggregate: 20% Chert, 80% Quartz Sand
Mix: 25% Cement, 75% Aggregate

Bar No.	Cement	Percent Expansion						
		Na_2O	K_2O	3	7	37	43	46
				Mo.	Mo.	Mo.	Mo.	Mo.
1	A	0.21	0.96	0.014	0.014	0.015	0.017	0.017
2	A	0.21	0.96	0.009	0.009	0.012	0.017	0.018
3	A+	2.10	0.96	0.014	0.065	0.242	0.244	0.245
4	A+	2.10	0.96	0.021	0.038	0.193	0.193	0.194
5	A+	2.10	0.96	0.010	0.030	0.184	0.185	0.185
6	B+	1.96	0.20	0.015	0.019	0.051	0.052	0.052
7	B+	1.96	0.20	0.010	0.018	0.068	0.070	0.070
8	B+	1.96	0.20	0.010	0.013	0.067	0.067	0.068
9	B+	1.96	0.20	0.011	0.017	0.071	0.072	0.072
10	B	.16	0.20	0.005	0.011	0.012	0.013	0.013
11	B	.16	0.20	0.008	0.010	0.013	0.013	0.013

This brought the total Na_2O content in bars made from Cement A to 2.10 percent, and those made from Cement B to 1.96 percent. The cements in these bars are designated by A+ and B+. Cement was added in the amount equivalent to 25 percent of the dry weight of each bar. The water-cement ratio was 0.5.

The results from the expansion of the mortar bars are shown in Table 6. Although intermittent expansion measurements were taken, the main idea was to obtain the maximum expansion of each bar and the time required to attain it.

From the results contained in Table 6, it is apparent that both brands of cement, without the addition of sodium hydroxide, caused very little expansion. Also, Cement A+ shows excessive expansion, while Cement B+ shows less than half the expansion of A+. It

seems that the difference of 0.76 percent K_2O contained in Cement A+ was responsible for the abnormal expansion. It is also evident, that for all practical purposes, the bars had attained the maximum expansion in 43 months.

On June 24, 1952, Bars 1, 3, 4, 6, and 10 were removed from the containers for chemical analysis. Bars 3, 4, and 6 had wet spots on the outer surfaces when first removed from the containers. This was much more pronounced on Bars 3 and 4.

In a research article by H. E. Vivian, of the Commonwealth Scientific Research Organization of Australia, the wet spots on the faces of mortar bars, processed in a similar manner, were referred to as alkali-silica gel. However, when the solution from the wet spots came in contact with the flesh, during handling the bars, the characteristic slick feeling of alkali hydroxide was very noticeable. To find just what the spots contained, Bar 3 was soaked approximately 2 min. in 400 ml. of boiling distilled water. The solution was filtered through a No. 41 Whatman filter paper, acidified, evaporated to a volume of 100 ml., and analyzed for sodium and potassium hydroxides and silica. The following results show that both the hydroxides and the silicates were present but the hydroxides or carbonates were present in a much larger amount.

	Na_2O	K_2O	SiO_2
Bar 3.....	0.0590	0.0240	0.0195

This bar was the only one tested that contained more than a trace of water-soluble silica.

Bars 1, 4, 6, and 10 were dried, ground to pass the 100-mesh sieve, and analyzed. The results are shown in Table 7.

Comparing the results from the analysis, it is evident that the acid-soluble silica increases with the alkali content of the cement. Since Bars 1 and 10 were made with the plain cement and showed no appreciable expansion, it is not surprising that the acid-soluble silica is very near the same percent. However, Cement A contains the highest alkali of the two, and consequently the highest acid-soluble silica.

The results from Bars 4 and 6 show acid-soluble silica in line with the total expansion

of the bars and the alkali content of the cement. Cement A+ contained 2.10 percent Na_2O and 0.96 K_2O and produced 8.94 percent acid-soluble silica with an expansion of 0.194 percent in Bar 4. Cement B+ contained 1.96 percent Na_2O and 0.20 K_2O , and produced 7.47 percent acid-soluble silica with an expansion of 0.052 percent in Bar 6.

On further examination of these results, it is evident that the magnesia content is higher in bars made with Type A and A+ cement than those made with Type B and B+ cement. This is due, of course, to the difference between the magnesia contents of the two cements.

TABLE 7
CHEMICAL ANALYSIS OF MORTAR BARS

Type Cement Used	A	A+	B+	B
Bar Number.....	1	4	6	10
	%	%	%	%
Moisture (to 105 C.).....	2.90	4.32	3.76	3.75
Loss (105-1000 C.).....	5.49	5.19	5.67	5.34
Insoluble residue (sand).....	66.68	64.62	65.29	66.72
Acid soluble SiO_2	6.95	8.64	7.47	6.60
Al_2O_3	1.04	1.00	.86	0.81
Fe_2O_3	1.36	1.80	1.28	1.32
CaO	13.81	13.29	14.00	14.06
MgO	0.72	0.70	0.51	0.52
Na_2O	0.05	0.33	0.30	0.03
K_2O	0.23	0.20	0.05	0.08
Water soluble Na_2O	0.05	0.33	0.30	0.04
Water soluble K_2O	0.14	0.14	0.04	0.05
Water soluble SiO_2	0.00	0.00	0.00	0.00

Type A contained 3.86 percent MgO and Type B contained 2.80 percent. Since there is, apparently, very little sodium or potassium silicate present in the bars, it is doubtful that the expansion can be attributed to osmosis. Most of the original alkali content was present in each bar.

POZZOLANS

By adding predetermined amounts of extra-fine reactive silica to high-alkali concrete mixes, it is possible to decrease the expansion due to chemical action. There are several benefits derived from this operation under controlled conditions. Many publications contain discussions on the good and bad points of pozzolans, so this discussion will be confined to chemical action as related to the original subject matter.

To begin, it seems reasonable to expect a good pozzolan to be very reactive with lime. It should also possess a high silica content with a minimum of impurities. The impurities in pozzolans add impurities to the concrete

mix and often cause undesirable physical and chemical effects.

One of the best prospective pozzolans found in this locality is tripolite. This is a very fine, hard silica with only very small amounts of impurities. Its solubility in lime ranks above that of calcined opal and slightly under diatomite. It is much more compact or dense than diatomite and possesses a much higher solubility in lime without calcining.

Since it is possible to tie up effective amounts of free lime in concrete mixes by using special reactive silica, the trouble caused by releasing the sodium and potassium hydroxides from their respective silicates should be greatly reduced. Most of the cements from this locality have a rather low water-soluble-alkali content. It has been proven experimentally that the combined alkali in cement is released as water-soluble alkali in from 60 to 90 days after hydration. With only part of the sodium or potassium hydroxide in solution during part of this period, the maximum concentration of lime should be present. If this lime is allowed sufficient reactive silica, much of it will be exhausted before all of the combined alkali is released.

When the combined alkali is released and reacts with the silica forming the alkali silicates, the reaction should continue until the alkali-hydroxide concentration is low enough to allow the lime back into solution. The lime will then react with the alkali silicates and the reactive silica, further reducing the lime content. It is probable that the effective supply of lime is exhausted before the alkali reaction cycle is allowed to progress far.

CONCLUSIONS

The progressive reaction of the alkali and aggregate in concrete depends on lime to liberate the alkali from the alkali silicates before continuing the cycle. Proof of this reaction cycle can be conducted chemically in comparatively short periods; however, very careful chemical manipulation is necessary. Results from the analysis of the concrete gel are in accordance with progressive-reaction theory.

The analysis of the mortar bars disclosed little or no alkali silicates. The presence of free alkali, near the original percent, dispelled the possibility that the alkali silicates had escaped. The acid-soluble silica in the mortar

bars varied directly with the alkali content and total expansion. The cement showing the highest expansion in the mortar bars contained the highest magnesia as well as the highest alkali content.

DISCUSSION

W. J. HALSTEAD AND B. CHAIKEN, *Chemists, Physical Research Branch, Bureau of Public Roads*—Hester and Smith have used two simple formulas as the basis for discussing the alkali-aggregate reactions which occur in concrete and which cause expansions. It is recognized that this is a simplified approach and normally such a presentation would be desirable. In this case, however, it is believed that it fails to emphasize properly the complicated phenomena associated with such reactions.

There is some disagreement among investigators as to the theoretical explanation of the causes of expansion resulting from the alkali-aggregate reaction, but it is generally agreed that simple chemical equations are not adequate to explain the phenomena which occur. It has been shown that the amount of water; temperature; particle size; amount of the reactive portion of the aggregate; degree of availability of the alkali; ratio of reactive aggregate to available alkali; and other factors all have effects on expansion. Evidence points to the fact that the chemical constitution of the products of the reactions are less important than the manner in which these reactions occur and the conditions within the concrete after their occurrence.

It is generally known that, except for very special cases, the reactions between alkali hydroxide and silica form gel or sol systems of colloidal and ionic silica rather than a simple compound of alkali silicate. The properties of the systems formed vary considerably depending upon the ratio of the alkali to silica present and also on the amount of water available. Once formed, such systems are not stable but vary with the conditions surrounding them. Under one set of conditions a system may be a rigid gel capable of withstanding (or exerting) considerable pressure without deformation, while under other circumstances it may be a plastic gel which yields slowly under pressure, or may even be converted to a sol state ranging in characteristics from that of a viscous liquid to that of a fluid solution.

The reaction between calcium hydroxide and an alkali-silicate system also varies considerably, the composition of the products formed being dependent on the concentration of the solution and the ratio of alkali to silica. A dilute alkali-silicate system contains a high proportion of ionic silica which reacts quantitatively with calcium-hydroxide solutions to precipitate calcium silicates. On the other hand, a more-highly concentrated system contains a greater proportion of colloidal silica which does not react quantitatively but forms indefinite adsorption complexes with calcium hydroxide. These latter products vary considerably in calcium to silica ratio and also contain various amounts of alkali.

Hester and Smith did not discuss the mechanism of the expansion reaction according to their hypothesis, but it must be recognized that in order for expansion to occur as a result of a reaction there must be a condition which develops internal pressures. Hansen's theory (1), relative to the alkali-aggregate reaction, stated that the cement paste surrounding a particle of reactive silica acted as the confining medium which permitted the passage of alkali solution and water into the reaction center but blocked the exit of the viscous, complex alkali-silicate gel. He compared this action to that of an osmotic cell. In more recent work conducted in Australia by Vivian (2), the development of pressure was attributed to the swelling action of the reacted particle or gel itself as it absorbed solution and water. It is of interest to note that Hansen himself did not state that a true semipermeable membrane existed but likened the action to that of the osmotic cell. Thus the basic concept advanced by both men is the same: There is a one-way passage of water or solution into a confined space which results in the development of internal pressures.

The data presented in the paper under discussion do not conflict with this concept but, rather, tend to support it. For example, analyses of concrete-gel products containing about 15 percent of calcium oxide and about 10 percent of sodium and potassium oxides were reported. The total alkali content of the cement used in this concrete was reported to be about 1.3 percent. If we assume that the mortar contained one part of cement to two parts of sand, its alkali content would

be about 0.4 percent. Thus, the localized concentration of alkalis within the reaction product makes it evident that there has been a movement of solution containing these constituents toward reaction centers and that these alkalis are held to a considerable extent rather than recycled on a quantitative basis. Others have reported gel products containing low percentages of calcium and high concentrations of alkalis (chiefly sodium) in the range of 25 percent. In the Bureau of Public Roads Laboratory, gel products containing essentially the same composition as those reported by Hester and Smith, as well as those containing chiefly sodium and silicon, have often been found. It is quite possible that the high-calcium gels are developed either after the absorption of water or solution by the alkali-silicate gel has reduced its viscosity to the point that allows the liquid to migrate and come in contact with additional lime solution or after the alkali concentration of the surrounding solution in the mortar paste has decreased to a point which allows an increasing amount of calcium hydroxide in solution.

If a definite chemical reaction with calcium hydroxide occurred, it is true that alkali hydroxide would be formed. However, it is believed that, under the conditions prevailing in a mortar or concrete, the alkali-silicate systems first formed will contain considerable colloidal or polymerized silicic acid and also free alkali hydroxide. Therefore, the reaction with calcium hydroxide would involve to a great extent an adsorption phenomena which would not actually regenerate additional free alkali. Free alkali would be present in both situations, but only a small part of this, if any, would be free to be recycled throughout the concrete, because of the enmeshment which normally exists in any gel product.

This belief is supported by the relatively large amounts of alkali found in gel products, even when considerable calcium is also present, and also by the fact pointed out by the authors themselves that alkalis associated with calcium silicate products are very difficult to remove, even when washed with considerable quantities of water. In addition, if recycling were an effective force, it would be reasonable to expect the same amount of reactive constituent in different mortar bars or concrete would ultimately produce approximately the

same expansions regardless of the alkali content. The difference would be chiefly in the rate of expansion. Observed laboratory results do not confirm this but, rather, show increasing expansion with increasing alkali content up to the point of optimum ratio of alkalies to reactive aggregate.

Laboratory results also show that, with bars made from the same cement and increasing amounts of reactive aggregate, the amount of expansion reaches a maximum and then begins to decrease. It is believed that this phenomenon cannot be accounted for in terms of an effective recycling of the alkalies. Also, under the conditions of an effective recycling process, it would be expected that once all the reactive constituent had been exhausted (as evidenced by no further expansion) all gel products would contain a large amount of calcium. Observations in the Public Roads Laboratory indicate that this is not true; gel products very low in lime content continue to exist.

The data presented by Hester and Smith show reactions of lime, silica, alkali, and water which are of fundamental interest. However, as Kalousek (3) showed in his studies of similar systems, the ratio of calcium to silica in the products formed varies for different concentrations of sodium. It was also shown that where a gellike precipitate was obtained it also contained some alkali. It is believed that these properties have not been adequately considered by the authors in their analysis of the data they obtained. They have used the ratio of calcium to silica found under one set of conditions as the basis for estimating the amounts of definite compounds under other sets of conditions. Such calculations are not in accordance with known chemical behavior and have little significance when applied to data obtained from concrete or mortar bars.

One of the conclusions drawn by the authors is that mortar bars containing reactive aggregate and alkali showed little or no alkali silicate. It is believed that the tests upon which this conclusion is based may have been misleading. In these tests, one of the bars was immersed for some time in boiling water, following which the solution was filtered and the filtrate examined for dissolved silica. Under these conditions it would normally be expected that some calcium hydroxide would be dissolved from the bar as

well as any soluble silicates. In the extremely high dilutions present, the dissolved calcium hydroxide would quantitatively precipitate any soluble silicate, and dissolved silicate would not appear in the filtrate. It is probable that this reaction would take place mostly within the pore spaces or on the surface of the bar, and there would be no visual evidence of a precipitate other than a possible whitening of some areas.

In conclusion, it is reemphasized that the amount of chemical reaction which occurs in a concrete is not necessarily directly related to the amount of expansion which takes place. Expansion results from a combination of a number of factors, each of which has a variable influence depending on the conditions existing in a particular instance. The regeneration of free alkali as a result of a secondary reaction between alkali-silicate gels and lime may have some effect on the ultimate expansion resulting from the alkali-aggregate reaction. However, it is believed that this phenomenon is not as directly related to expansions as suggested by Hester and Smith nor would the occurrence of such a reaction invalidate in any way present theories concerning the development of internal pressures.

REFERENCES

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3. KALOUSEK, G. L., "Studies of Portions of the Quaternary System Soda-Lime-Silica-Water at 25 C." *Research Paper No. 1580*, *Journal of Research, National Bureau of Standards*, Vol. 32, No. 6, June, 1944.

J. A. HESTER, *Closure*—The discussion of this paper by Halstead and Chaiken seems to be largely the result of misinterpretation, which often results when one tries to draw conclusions based on experimental work accomplished by others. In this case, as in many others, the authors have experimental data not published in the original paper. These

experiments were conducted to support the published experimental data and to help in drawing the final conclusions. Although some of these data have been furnished to other investigators, it seems at least a part of it will have to be included here.

It is regrettable that Halstead and Chaiken were so concerned over the two simple illustrative chemical equations appearing in the third paragraph of the original paper. It seems that during discussions with many different cement research chemists, the explanation contained in the same paragraph with the equations was sufficient.

Since there was no discussion of the expansion process in the original paper, it was possible to eliminate the possible combinations and physical reactions of the alkali silicates. There is no doubt, however, that during dehydration the alkali silicates will reduce from a solution to various stages of gel and finally to a dry crystalline form. During the viscous gel stage, this mass will absorb excess alkali or other chemicals present. Chemical analysis of this gel would naturally show a higher sodium or potassium ratio in respect to the silica present. However, when enough water is available the gel will revert to partial solution and finally to solution. At this time it is natural for included alkali to be released and continue reacting with the silica until the alkali hydroxide content is low enough to allow lime into the solution.

It is easy to see why gels of different composition are obtained from different samples of concrete. It seems to only be a matter of what stage of reaction was present in the concrete at the time the sample was obtained. There is no time table to account for the actual stage of reaction present in concrete. The amount of alkali present, availability of water, and many other factors influence the speed of reaction. Samples of gel obtained from open cracks and soft sections of concrete that have been exposed to rain or other sources of water frequently contain calcium silicate with little or no alkali present. A few samples of this type have been examined in this laboratory.

There seems no reason to doubt that viscous alkali silica gels deposited in voids in concrete or the seams in the aggregate cause internal pressure when absorbing water. This can certainly happen during stages in the reaction

cycle. It is necessary to realize that the alkali reaction takes plenty of time, even under the most-favorable conditions.

It would seem to be hard to account for the long time required for concrete failure, if the initial formation of the colloidal alkali silicates and the subsequent physical action of this gel alone could account for the destruction. We have structures containing the same type of reactive aggregate, only containing cements of different alkali and magnesia contents, that require vastly different amounts of time under favorable conditions to produce definite pattern cracking. Some of our higher alkali cements produced definite cracking in 3 yr. while some of the very-low-alkali cements have required from 12 to 15 yr. to produce similar results. Unless the alkali-reaction cycle was a reality, it would seem to be hard to give a reasonable explanation of this difference in time.

Under the results from the second set of bombs contained in Table 3 of the paper, it is apparent that Bombs 1A and 2A have no lime left in either filtrate or residue; also, there is only 0.0267 gm. of sodium oxide in solution in 1A and 0.044 gm. in 2A. However, there remains 0.0364 gm. of free SiO_2 in 1A and 0.0110 gm. in 2A. In Bombs 3A and 4A, practically no free silica remains. It is evident that free alkali content of Bombs 1A and 2A is insufficient to dissolve the silica at the same rate that it occurred in Bombs 3A and 4A. Since there is no free lime left in Bombs 1A and 2A, no more alkali can be released from the existing alkali silicate. It is believed this is a reasonable explanation for the extra time necessary for the low-alkali cements to produce pattern cracking in some of our concrete structures.

If the 20 ml. of solution contained in each bomb in Table 3 seems to be an excessive amount, it will be well to recall a few lines from page 37 of the book, *Rock Family Minerals*, by Dake, Fleener, and Wilson (1938): "At the base of a chalk formation in Farnham, England, there is a bed of quartz that is actively acidic. If slaked lime is mixed with it in a paste and allowed to remain for a few weeks a silicate of lime is formed, the action of which may be promoted by the addition of 2 or 3 percent of sodium carbonate." It is clear that this passage was intended to show the acidic properties of some forms of quartz,

but the chemical reaction is very much the same as in the bomb experiment with the exception of the extra step in the conversion of the sodium carbonate to sodium hydroxide by a part of the lime present.

Extensive work with lime silicates in this laboratory has shown the silicates in question not nearly so complicated as it may seem. During the formation of calcium silicate gel from solutions of lime and alkali silicates, it is shown that alkali silicates are occluded in the mass. It is nearly impossible to form calcium silicate and exclude all the carbon dioxide during this formation, both from the alkali and from the lime. Even the alkali carbonate transfers the carbonate to the lime. This calcium carbonate is, of course, included in the calcium silicate gel, as well as any free lime forced out of solution by the final concentration of alkali. To obtain the true form of the calcium silicate, it is necessary to first filter and dry the gel at 100 C. to 110 C. After grinding the dried product, it is necessary to remove all alkali and alkali silicates and then determine the free lime and the calcium carbonate. After all this is accounted for, we find that the remaining compound follows definite molecular ratios of lime to silica. The lime inside concrete is, of course, protected from carbon dioxide from both air and water by the outer surface of lime; therefore, the calcium silicate can be formed inside concrete without inclusion of the carbonate, provided the concrete is not cracked or too porous.

It does not seem feasible to cover all points in this discussion; however, it does seem necessary that some conclusions advanced by Halstead and Chaiken, of the analysis of the mortar bars in the original paper, be cleared up. The extraction of the beads of alkali from mortar bar number three contained in the eighth paragraph under the heading *Mortar Bars* must stand as it is shown. After washing the beads from the outside of the bar, the solution had no precipitate of calcium silicate in the washings. This solution was next filtered and no calcium silicate remained on the filter, only a few grains of sand appeared to be present. The solution was then acidified by

pouring hydrochloric acid through the filter paper into the filtrate. After evaporation and on analysis of this filtrate no lime was present.

This experiment was checked by using Bar 7. The outside of the bar was washed with a stream of cold distilled water until a total of 100 ml. of solution was obtained. This was processed the same as Bar 3 and the results still showed no lime and this time only a mere trace of silica while the alkali content was approximately 10 percent of the amount shown in Bar 3.

The last item in Table 7 shows no water soluble silica present in the bars. This experiment was checked by substituting a 4-percent solution of sodium hydroxide for the extraction instead of water on one portion of the sample while an equal volume of water was added to an equal portion of the sample. After heating both portions for 3 min., 50 ml. of water was added to the first portion and 50 ml. of 4-percent hydroxide to the second portion; after stirring and heating again for 3 min., the samples were filtered and the filtrate analyzed. The maximum difference between the silica dissolved in the two portions was 0.1 percent in the bars containing the highest alkali. Further analysis showed the 4-percent NaOH was sufficiently strong to inhibit interference by lime.

Before closing, there are two separate expressions contained in the discussion that are not clear to the authors. At the last of Paragraph 2 appears the phrase: "Thus evidence points to the fact that the chemical constitution of the products of reaction are less important than the manner in which these reactions occur and the conditions within the concrete after their occurrence." The authors will not express their interpretation, as it must surely have a different meaning. It is also noticeable that the expression "it is general knowledge" appears at least in two places in the discussion.

It is admitted that the solution in concrete flow, however, the fact that gel is frequently found distributed through nonreactive sections of the concrete, makes it doubtful that the flow is confined to the reaction centers.