

# Evaluation of the Quick Chemical Test For Alkali Reactivity of Concrete Aggregate

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Since its publication in 1947, the quick chemical test for alkali reactivity of concrete aggregate has been used by many laboratories, and the procedure was accepted as a tentative standard by the American Society for Testing Materials in 1952 (Method C 289). The significance and reliability of the test are evaluated in the light of our experience and that of others.

As was indicated in the original publication of the method, anomalous results can be obtained if certain rocks or minerals are present. Moreover, reproducibility of results commonly is not satisfactory, primarily because chemical equilibrium is not established between the sample and the solution. Hence, the concentration of silica in solution and the reduction effected in the alkalinity of the solution are influenced by all aspects of the procedure, both during and following the reaction period.

In order to elucidate these matters, the following factors were investigated: (1) presence in the aggregate of minerals effecting extraneous reduction of alkalinity, including dolomite, antigorite, and calcite; (2) effect of agitation during the reaction period; (3) preliminary acid treatment of samples to remove carbonates; (4) measurement of pH during titration to determine the reduction of alkalinity; (5) modification of filtering procedures; and (6) variation in volume and concentration of the NaOH solution.

The results are summarized and discussed. The findings do not justify modification of the test procedure at this time. However, it is recommended that a petrographic examination of the aggregate be performed as a guide to evaluation of the results of the chemical test.

● THIS REPORT covers experience with the procedure developed in 1945-47 by the Engineering Laboratories of the Bureau of Reclamation, United States Department of the Interior, to determine quickly the potential reactivity of an aggregate with alkalis released during the hydration of portland cement (1). The procedure later was modified in certain respects and adopted by the Corps of Engineers, United States Army (Method CRD-C 128-48, 49, 50, and 52) (2), and as a tentative method of test by the American Society for Testing Materials (Method C 289-52T and 54T) (3). The method is commonly called the "quick chemical test." It has been widely applied in the testing of aggregates in this country (4, 5, 6, 7, 8).

Experience has indicated problems with reproducibility of the method and, in some instances, with reliability of the results. These justify review of the test procedure, the significance of the data obtained by the test, and investigations by ourselves and others to improve its reproducibility and reliability.

## DEVELOPMENT OF THE METHOD

The original procedure of the chemical test was published in 1947 (1). Conclusions on the validity of the method were based upon application of the test to approximately 70 sands, gravels, rocks, and minerals whose deleterious or innocuous character has been established by mortar test; 22 of the materials were known from service records to be deleteriously alkali-reactive. It was shown that the results of the method could be used to subdivide the tested materials correctly into those which are deleteriously alkali-reactive and those which are not according to a mortar bar test similar to ASTM Method C 227 (3) and available service records. Additional data on results of the tests

were published subsequently, at which time the criteria indicating deleterious degrees of alkali reactivity were modified slightly (4).

The test involves crushing and washing of the sample of the aggregate so as to obtain a specimen in the No. 50-100 size range; 25 grams of the prepared aggregate are placed in a specially designed reaction vessel with 25 milliliters of 1-N NaOH solution. The vessel is sealed and stored at 80 deg + 1 deg for 24 hours, whereupon the residual liquid is filtered off with minimal agitation of the solids. The filtrate is analyzed for dissolved silica, and the reduction effected in the alkalinity (basicity) of the solution is determined by titration. The potentially deleterious or innocuous character of the aggregate is established by plotting the determined values of silica concentration ( $S_C$ ) in millimoles per liter as the abscissa against the reduction of alkalinity ( $R_C$ ) and noting whether the point so located lies to the left or the right of a line found empirically to separate equivalent data points representing aggregates whose degree of reactivity was established in the original work.

Review of the data indicated that not only was the potentially deleterious or innocuous character of the aggregate established, but also that correlations could be established between the chemical quantities determined and the rate and magnitude of the expansion of the mortar bars. Thus, it was found that the proportion of the deleteriously reactive type giving the maximum mortar expansion (the so-called "pessimism" proportion) and the rate of mortar expansion correlated inversely with the reduction in alkalinity established in the chemical test. Other important relationships were established also.

On the other hand, the original investigation demonstrated that certain rocks and minerals could effect an extraneous reduction in alkalinity, with resulting spurious increase in  $R_C$ . Carbonates of magnesium or ferrous iron cause difficulty in this way. It was shown that the tests indicated the deleterious degree of alkali reactivity when a quartz aggregate contained as little as 1 percent of opal, whereas a similar combination of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) was indicated to be innocuous. This effect results from precipitation of hydroxide as a hydroxide of magnesium or ferrous iron, and a consequent increase in  $R_C$  above the value produced as a result of alkali-silica reaction. The data point representing the aggregate thus is shifted upwardly and possibly across the boundary between innocuous and deleterious materials.

However, the data demonstrated that the valid and definite indication of deleteriousness would be obtained if the aggregate contained 2.5 percent of opal. Apparently the extraneous precipitation of hydroxide is halted or prevented in the presence of moderate or high proportions of silica in solution. If an aggregate contains 5 percent or more of opal, the values of  $S_C$  and  $R_C$  are similar whether the bulk of the aggregate is dolomite, quartz, or other minerals.

The published account of the test and its application created widespread interest throughout the country and it was introduced into testing procedures by numerous laboratories. In 1949, the Corps of Engineers included the procedure into their "Handbook for Concrete and Cement" as Method CRD-C 128 (2).

Available data and experience with the method were reviewed by Subcommittee II-b on Chemical Reactions of Aggregates in Concrete, ASTM Committee C-9 on Concrete and Concrete Aggregates, and in 1952 a tentative method of test covering the procedure was issued (ASTM Designation: C 289-52T, Tentative Method of Test for Potential Reactivity of Aggregates (Chemical Method) (3)). Many of the details of the tentative method were based upon work of the Corps of Engineers, United States Army (8). The tentative method included specific instructions and fixed several details of procedure not defined adequately in the original publication, but departed substantially from the original procedure only in the titration and calculation to determine the reduction of alkalinity ( $R_C$ ). As a result of extensive study and discussion, this change was rescinded in 1954 so that ASTM Method C 298-54T conforms closely with the original procedure.

#### STUDIES BY THE CORPS OF ENGINEERS

In May 1949, the Waterways Experiment Station, Corps of Engineers, United States Army developed an extensive program to investigate the quick chemical test (their Method CRD-C 128-49) (2) and the mortar bar test (their Method CRD-C 123) (2), particular-

ly to establish causes and means to control unsatisfactory reproducibility (8). The program concerning the chemical test comprised all of the Corps of Engineers Division Concrete Laboratories, seven in number, and the Petrographic Laboratory, Division of Engineering Laboratories, Bureau of Reclamation, Denver, Colorado. Portions of six aggregates were distributed to the participating laboratories both in original condition and after preparation of the material for test by the Waterways Experiment Station. Each was tested three times in triplicate in accordance with Method CRD-C 128-49.

Statistical analysis of the resulting data indicated that inadequate reproducibility was due to lack of proper detail in the specification of the procedure. Accordingly, the description of the method was modified extensively so as to specify more rigorously the equipment; techniques; and procedures; the statement of tolerances, such as in preparation of reagents; analytical procedures; preparation of the aggregate for testing; and filtration following the reaction period. The modified procedure was designated Method CRD-128-50.

Tests were repeated, employing only one aggregate (a chert gravel from Arkansas). In Phase I of this portion of the program, the aggregate was processed at the Waterways Experiment Station and distributed to the cooperating laboratories for testing. In Phase II, the natural gravel was submitted to each cooperating laboratory for processing. The finished sample for testing was then returned to the Waterways Experiment Station for performance of the chemical test. Results are summarized in Table 1.

Agreement among the laboratories is adequate, although three results in Phase I differ markedly from the others. Agreement among the laboratories was better in this series, involving only one aggregate, than in the previous series, involving six aggregates. The improvement observed is the result of the increased reproducibility of  $S_c$ . Reproducibility of  $R_c$  remained about the same for most of the laboratories.

TABLE 1

RESULTS OF A COOPERATIVE TEST ON ASTM METHOD C 289 SPONSORED BY THE CORPS OF ENGINEERS, UNITED STATES ARMY<sup>1</sup>

Laboratory	Data on $S_c$						Data on $R_c$					
	Phase I			Phase II			Phase I			Phase II		
	$S_c$	$SD^2$	$CV^3$	$S_c$	$SD^2$	$CV^3$	$R_c$	$SD^2$	$CV^3$	$R_c$	$SD^2$	$CV^3$
WES	163.6	2.6	1.6	163.6	2.6	1.6	75.5	3.0	4.0	75.5	3.0	4.0
BR	166.2	3.8	2.3	174.4	5.8	3.3	70.6	3.9	5.5	76.2	3.4	4.5
ORD	155.4	13.7	8.8	178.8	3.8	2.1	96.0	5.9	6.1	78.4	2.8	3.6
MRD	174.2	4.0	2.3	164.3	6.4	3.9	72.7	2.1	2.9	79.4	3.7	4.7
SWD	176.9	5.6	3.2	187.0	2.4	1.3	131.7	15.0	11.4	76.3	3.2	4.2
SPD	190.7	3.5	1.8	180.9	2.7	1.5	68.3	6.5	9.5	77.4	2.4	3.1
SAD	133.8	4.2	3.1	162.8	2.6	1.6	85.6	3.0	3.5	73.9	3.3	4.5
NPD	202.4	0.9	5.4	168.9	4.1	2.4	82.6	4.4	5.3	69.1	5.5	8.0
Grand avg	170.4	6.0	3.5	172.7	3.8	2.2	85.4	5.5	6.4	75.7	3.4	4.5
Over-all	---	7.1	4.2	---	4.1	2.4	---	6.7	7.8	---	3.5	4.6

<sup>1</sup> Test conducted in accordance with ASTM Method C 289-52T on one sample of chert gravel, Murfreesboro, Arkansas ( $\frac{3}{4}$ - to  $\frac{3}{8}$ -inch fraction). In Phase I material processed at Laboratory WES was tested by the indicated laboratories. In Phase II material processed at the indicated laboratory and tested at Laboratory WES. The table is taken from Table 40 of Reference 8.

<sup>2</sup> Standard deviation.

<sup>3</sup> Coefficient of variation.

TABLE 2

AGGREGATE MATERIALS USED IN INVESTIGATION OF THE QUICK CHEMICAL  
TEST FOR ALKALI REACTIVITY (ASTM METHOD C 289-54T)

Aggregate No.	Identification and Source	Maximum Expansion of Mortar at 1 Year Percent <sup>1</sup>
1	Arkose, Byllesby Dam, Virginia	<sup>2</sup> 0.147
2	Novaculite, Hot Springs, Arkansas	0.561
3	Sand, Sargent, Nebraska (Lab. No. M-915)	0.114
4	Sand, Scottsbluff, Nebraska (Lab. No. M-436)	0.088
5	Gravel, Phoenix, Arizona (Lab. No. M-659)	0.107
6	Gravel, Mullen Dam site, Nebraska (Lab. No. M-226-B)	0.096
7	Gravel, Scottsbluff, Nebraska (Lab. No. M-436)	---
8	Phyllite, Buck Dam, Virginia	<sup>2</sup> 0.310
9	Sand, Eklutna Dam site, Alaska (Lab. No. M-1060)	0.098
10	Gravel, Eklutna Dam site, Alaska (Lab. No. M-1060)	0.061
11	Sand, near Saco, Montana (Lab. No. M-365 to M-371)	---
12	Sand, Carryhurst, Utah (Lab. No. M-672)	0.090
13	Sand, Canyon Ferry Dam, Montana (Lab. No. M-310)	0.117
14	Sand, Canyon Ferry Dam, Montana (Lab. No. M-290)	0.089
15	Sand, Black Canyon Dam, Idaho	0.056
16	Sand, near Grand Coulee Dam, Washington (Lab. No. M-675)	<sup>3</sup> 0.075
17	Felsitic rhyolite, Mojave, California	0.045
18	Gravel, near Marsh, Montana (Lab. No. M-425)	0.093
19	Gravel, near Marsh, Montana (Lab. No. M-424)	0.126
20	Chalcedony, Serro do Mar, Brazil	0.264
21	Chalcedony, Lead Pipe Springs, California	0.940
22	Gravel, Hoover Dam, Arizona (Lab. No. M-610A)	0.159
23	Sand, White Narrows Dam site, Nevada (Lab. No. M-509)	0.122
24	Sand, Willow Creek, Colorado, (Lab. No. M-626)	0.095
25	Gravel, Putah Creek, Yolo County, California (Lab. No. M-1539)	0.049
26	Sand, near Marsh, Montana (Lab. No. M-425)	0.063
27	Basalt from Aggregate No. 16, above	0.028
28	Sand, Putah Creek, Yolo County, California (Lab. No. M-1540)	0.090
29	Sand, Platoro Dam site, San Luis Valley, Colorado (Lab. No. M-421)	0.119
30	Sand, Platoro Dam site, San Luis Valley, Colorado (Lab. No. M-422)	0.119
31	Sand, Putah Creek, Yolo County, California (Lab. No. M-1539)	0.108

TABLE 2 (Continued)

32	Sand, near Merrill, Oregon (Lab. No. M-440)	0.154
33	Rhyolite tuff, Castle Rock, Colorado	0.400
34	Andesites and rhyolites, Bill Williams Ranch, Arizona	0.723
35	Siliceous, magnesian limestone, Paso Robles, California	<sup>2</sup> 0.361
36	Dolomite, Tuckahoe, New York	0.026
37	Graywacke, near Monticello Dam, California	0.035
38	Serpentine, Warren County, New York	0.030
39	Quartzite, Sioux Quartzite, Jasper Stone Company, South Dakota	---
40	Rhyolite porphyry, Deadwood, South Dakota	0.041
41	Sand, near Marsh, Montana (Lab. No. M-424)	0.074
42	Sand, Blue River, Kansas	0.064
43	Sand, Republican River, Kansas	<sup>2</sup> 0.167
44	Sand, Friant Dam, California	0.072
45	Slate, source unknown	0.192
46	Opal, Quincy, Washington	1.610
47	Quartz, Buffalo Park, Colorado	0.033
48	Marble, near Marble, Colorado	0.022
49	Prochlorite, Chester, Vermont	<sup>3</sup> 0.042
50	Scolecite, Challis, Idaho	---
51	Pectolite, Patterson, New Jersey	---
52	Prehnite, West Patterson, New Jersey	---

<sup>1</sup> Except as otherwise indicated bars are 1 by 1 by 10 inches in size; mix parts 1: 2; water-cement ratio = 0.40 by weight; aggregate graded 20 percent by weight each No. 4-8, 8-16, 16-30, 30-50, and 50-100; cured 24 hours or 7 days in fog room at 70° - 73.4° F; then stored at 100° F in sealed cans in the presence of moisture; alkali content of the cement: Na<sub>2</sub>O = 1.16-1.30 percent; K<sub>2</sub>O = 0.04-0.12 percent.

<sup>2</sup> Bars are 2 by 2 by 10 inches in size; mix parts 1: 2; water-cement ratio = 0.40 by weight; aggregate graded 19 percent by weight each No. 4-8, 8-16, 16-30, 30-50, 50-100 and 5 percent passing No. 100; cured 7 days in fog room at 70° F, then stored in sealed cans in the presence of moisture; alkali content of cement: Na<sub>2</sub>O = 1.30 percent, K<sub>2</sub>O = 0.12 percent.

<sup>3</sup> Test performed on previous sample from same source.

## CHANGE OF PROCEDURE TO IMPROVE REPRODUCIBILITY AND RELIABILITY OF THE METHOD

### Continuous Titration

One cause of variation in the value of R<sub>C</sub> is observation of the colorimetric end point during titration. Also, it is possible that titration to pH values other than that of the phenol-phthalein end point or even the trajectory of the pH with titration might yield more significant and reproducible data.

The chemical test was performed on eight aggregates (Nos. 21, 27, 34-39, Table 2) of various lithologic types in accordance with the stipulated procedure, except that S<sub>C</sub> was not determined, and the titration was followed continuously by means of a pH meter. Distinctly different curves are obtained for the materials, the potentially deleterious materials producing filtrates of lower pH than are produced by innocuous siliceous aggregates (Figure 1). Dolomite also reduces the pH of the filtrate, but the shoulder at pH 9 to 8.5 resulting from titration of the carbonate in solution is characteristic and permits separation of this curve from those produced by potentially deleteriously reactive aggregates. Nevertheless, it is apparent that difficulties would be encountered if a potentially deleteriously reactive siliceous dolomite were tested.

## Rotation of Reaction Vessels; Determination of Change of Alkali Concentration

Probably the most fundamental cause for difficulty in obtaining satisfactory reproducibility in the test is the lack of attainment of equilibrium in the reaction vessels. This condition is unavoidable in any chemical procedure to evaluate alkali reactivity of aggregate, inasmuch as attainment of equilibrium manifestly would mask the inherent differences in rate and magnitude of reaction to which differing rocks and minerals are susceptible. Nonetheless, if the contents of the reaction vessel were maintained in a quasi-homogeneous condition, the reactions could proceed farther and approach more closely a condition of equilibrium. This can be accomplished by appropriate continuous agitation during the reaction period.

A mechanism designed for use in a previously developed chemical test for alkali reactivity of pozzolans (9) was used to cause continuous end-over-end rotation of the reaction period. The chemical test was performed as stipulated on 14 aggregates of various lithologic types, except that continuous agitation was supplied.  $S_C$  was determined, and the concentration of sodium and potassium in the filtrate was measured by flame photometry.

Agreement between duplicate determinations was remarkably good (Table 3). The titration curve shows features similar to those observed previously (Figure 2). However, three potentially deleterious aggregates (Nos. 2, 31, and 43) produced curves lying within the zone occupied by curves representing innocuous aggregates. Aggregates No. 42 and 43 produced almost identical curves, even though Aggregate No. 42 is innocuous and Aggregate No. 43 is potentially deleterious.

The reduction in alkali concentration is calculated as the difference between the sodium concentration of the original NaOH solution and the sum of the sodium and potassium in the filtrate. The potassium concentration usually is negligible, but several aggregates released substantial amounts of potassium into solution. The results of the test are plotted in Figure 3, indicating the reduction in alkalinity alternately as  $R_C$  and the equivalent reduction in alkali concentration. Results of the standard test on these aggregates are shown also. Introduction of agitation produces substantial shifts in the position of the data points.  $S_C$ , determined after agitation, is equal to or greater than

$S_C$  determined in the standard test.  $R_C$  usually is reduced by introduction of agitation, although for two aggregates, the reverse is true. The reduction of alkali concentration usually is close to  $R_C$ . This procedure justifies further investigation. Its adoption would require shifting of the boundary line considerably to the right.

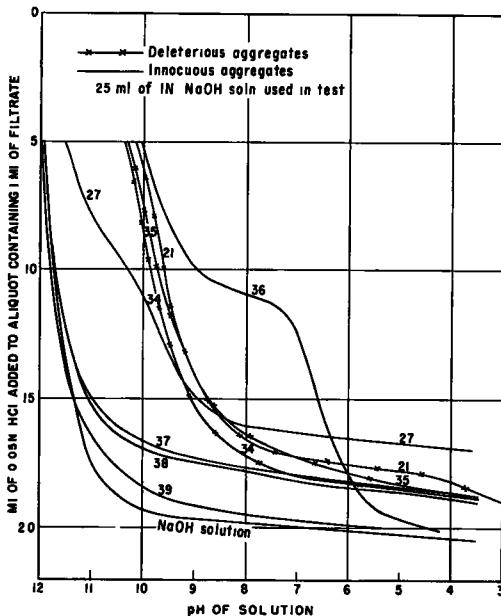


Figure 1. Titration curves obtained on the filtrate from the quick chemical test (ASIM Method C 289-54T).

## Modification of the Reaction Vessel; Reduction in Amount of NaOH Solution

One of the important reasons for the variation observed in duplicate or triplicate determinations in the current procedure of the chemical test is the existence during the reaction period of a large amount of solution above the solids. In the presence of reactive materials, this portion of the solution differs in composition from the solution in the interstices of the sample because diffusion does not keep pace with the chemical reaction. In the interstitial solution, the concentration of alkalis becomes low and the concentration of silica becomes high with respect to the supernatant solution, the degree of variation

**TABLE 3**  
**DUPLICATE VALUES OF  $S_C$  AND  $R_C$  IN TEST INCLUDING CONTINUOUS**  
**AGITATION OF REACTION VESSELS<sup>1</sup>**

Aggregate No. <sup>2</sup>	$S_C$ , mM/1		$R_C$ , <sup>3</sup> mM/1	
	1	2	1	2
2	336	338	20	25
15	76	77	85	90
16	229	227	117	122
17	67	66	72	72
20	864	868	102	82
21	1,032	1,036	72	82
25	199	197	144	146
27	397	399	202	192
31	228	222	205	207
33	956	936	302	292
40	58	60	82	72
42	60	62	35	38
43	76	77	28	30
44	65	63	60	62

<sup>1</sup> ASTM Method C 289-54T except for continuous end-over-end rotation of reaction vessels at about 30 rpm during the reaction period.  $R_C$  was determined by analysis for alkalis, rather than by titration (see footnote 2 below).

<sup>2</sup> See Table 2 for identification of the aggregates.

<sup>3</sup> Reduction in alkalis (Na+ and K+); NA + and K+ determined by flame photometry at conclusion of test; reduction calculated by subtracting the sum of the concentrations of Na+ and K+ from the original concentration of Na+.

depending upon the kind and degree of reaction taking place. The concentration of alkalis and silica in the filtrate depends upon details of the techniques used during filtration, especially the degree of agitation used before drainage of the solution and the completeness with which the solution is extracted from the solids. Particularly for highly reactive aggregate, the composition of the filtrate depends largely on the magnitude of the vacuum attained, the time allowed for filtering, and whether the supernatant liquid is decanted through the filter first or stirred with the aggregate.

In order to reduce these variables, a number of the reaction vessels were modified to include a bottom drain (Figure 4). A series of tests was carried out with 25 grams of sample prepared as stipulated in the procedure, but only 10 milliliters of 1-N NaOH solution were added. The aggregates were selected so as to study more closely those producing mortar expansion in the range 0.040 to 0.160 percent at 1 year. Ten milliliters of solution is sufficient to saturate the sample, but very little excess supernatant liquid is present. After the specified reaction period, the cover to each vessel was loosened to vent air, the cap was removed from the drain, and vacuum was applied to the bottom. The filtrate recovered usually exceeded 6 milliliters. The analytical procedure was carried out as stipulated, except that 5 milliliters of the filtrate were diluted to 100 milliliters rather than 10 milliliters to 200 milliliters.

An attempt was made to classify the resulting data points into three groups on the basis of mortar bar expansion; namely: (1) innocuous (less than 0.080 percent expansion in 1 year); (2) marginal activity (0.080 to 0.150 percent expansion in 1 year); and (3) deleteriously reactive (more than 0.150 percent expansion in 1 year (Figure 5). In the figure, a line has been drawn between the area occupied by the innocuous aggregates and the others. Data points representing two of the aggregates (Nos. 10 and 24) lie on the wrong side of the line. Nevertheless, the relationships are sufficiently good to de-

<sup>1</sup> See footnotes 1 and 2 to Table 2.

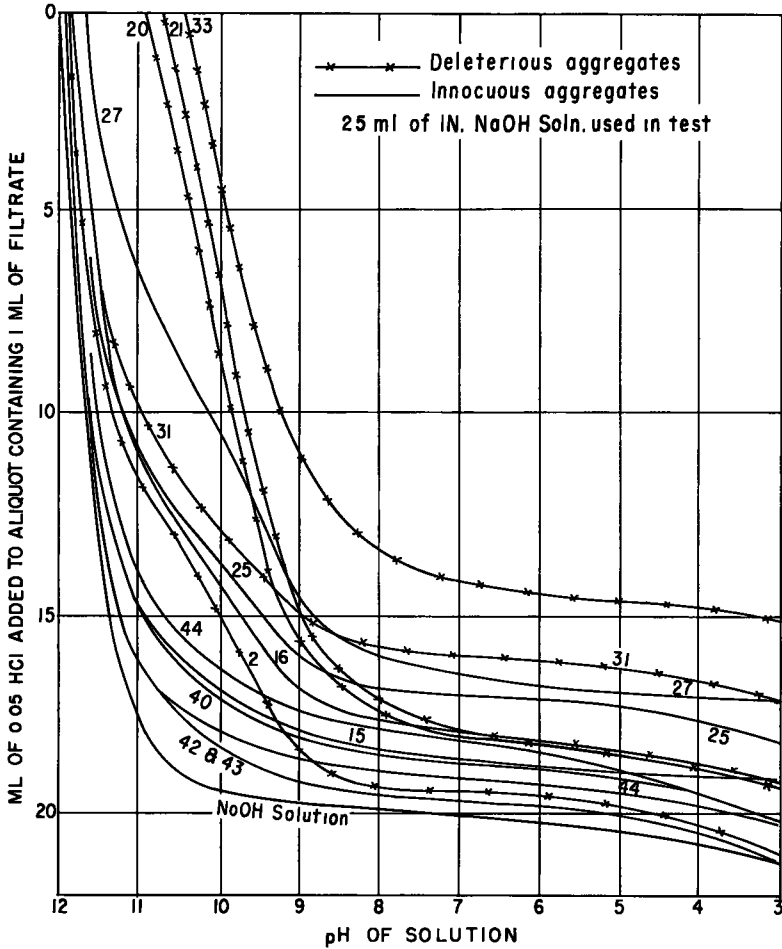


Figure 2. Titration curves obtained on the filtrate from the quick chemical test after continuous agitation during the reaction period.

monstrate conclusively that the factors determined by this modification of the chemical test relate rather closely to the processes resulting in expansion of mortar bars containing alkali-reactive aggregate and high-alkali cement.

An attempt to divide the aggregates on the basis of an expansion of 0.100 percent at 1 year likewise leaves anomalies. Points 9, 10, 18, and 28 would fall to the left of such a boundary, and the boundary must lie to the left of Points 29 and 8. In this situation, Points 3, 4, 12, and 14 are located erroneously to the right of the boundary.

Note that this is a severe test of the criteria to be applied to the results of the test. Of the 34 aggregates included in this phase of the program, 25 produced mortar expansion in the range 0.040 to 0.160 percent at 1 year. Some of these aggregates may be potentially more deleterious than indicated because the optimum ratio of alkalis to reactive siliceous material may not have been achieved in the mortar bars.

In any event, this procedure was not followed further because of these anomalous or erroneous indications.

It is appropriate here to comment briefly upon a moist-stored mortar test, such as ASTM Method C 227, as a basis for evaluating other tests designed to determine the potential alkali reactivity of concrete aggregate. In our opinion, moist-stored mortar tests, such as ASTM Method C 227 and the analogous procedure used by the Bureau of Reclamation, are the most widely available and generally applicable techniques by which deleterious alkali reactivity of aggregates or cement-aggregate combinations can be re-



cognized. Nevertheless, these tests are not completely dependable either for predicting reactivity of particular cement-aggregate combinations or for determining the deleterious degree of reactivity to be expected in use of a given aggregate with high-alkali cements in general. For example, a certain aggregate known to produce a deleterious degree of alkali-aggregate reaction in structures fails to produce significant expansion in moist-stored, high-alkali mortars in the laboratory (10). Reproducibility of the mortar test is usually not satisfactory either within the laboratory or from laboratory to laboratory, not only because of lack of uniform procedures but also because the inherent reactivity of given cements varies with storage in the laboratory and from shipment to shipment from the mill. Hence, in evaluating an alternative procedure, such as ASTM Method C 289-54T, we should not assume that there are available other methods which are free from significant difficulties.

#### Variation of Concentration of the NaOH Solution

Two groups of tests were designed to investigate the significance of the concentration of NaOH solution, using a procedure identical with that described in the previous section, except that concentrations of 0.5 N and 1.5 N were used.

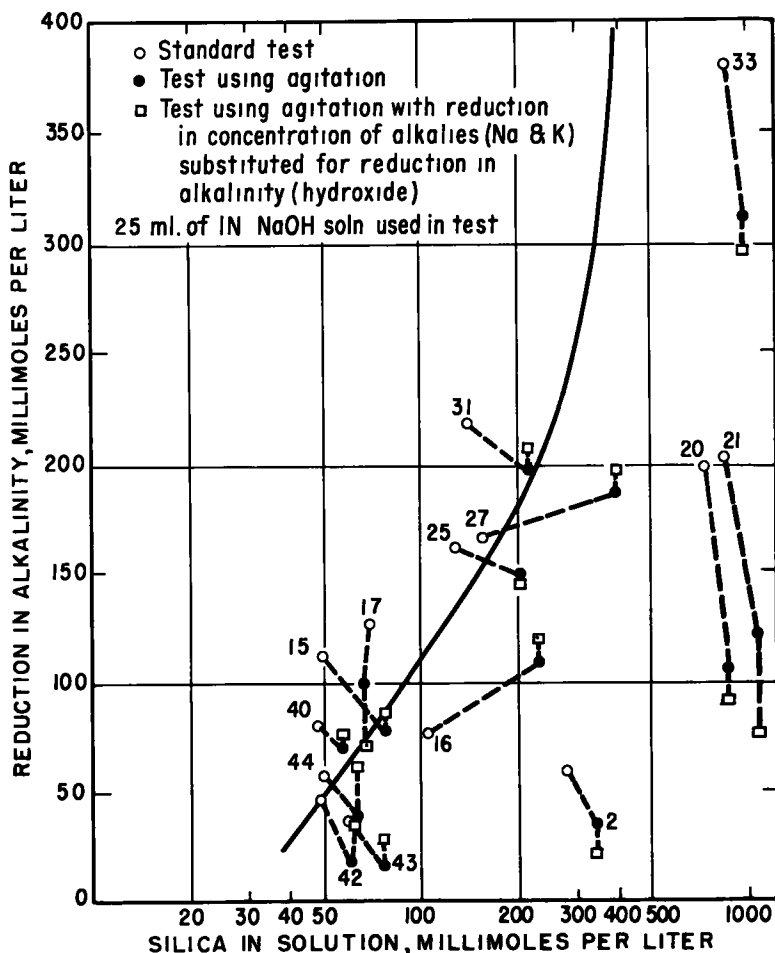


Figure 3. Correlation of results of the quick chemical test (ASTM Method C 289) with results obtained after continuous agitation during the reaction period. Reduction in alkalinity ( $R_c$ ) is compared with the reduction in concentration of alkalis.

The results are shown in Table 4. No improvement in reliability of the method is indicated.

### EXTRANEOUS EFFECT OF CERTAIN MINERALS

#### Effect of Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and Antigorite ( $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ )

As was indicated in the original work on the chemical test, dolomite and probably magnesium and ferrous carbonates produce a reduction in alkalinity unrelated to alkali-silica reaction. This reduction is caused by precipitation of hydroxyl as hydroxides of magnesium or ferrous iron. Similarly, it was suspected that certain magnesium silicates might also produce spurious changes in  $R_c$ .

In order to investigate these effects more completely, the chemical test was applied to a series of mixtures of opal (Aggregate No. 46) with dolomite (Aggregate No. 36), serpentine (Aggregate No. 38), and quartz (Aggregate No. 47, respectively, the opal content of the mixtures ranging from 0.1 to 2.5 percent, by weight of the test sample. The opal was added in the form of granular material in the No. 50-100 size range.

Because some investigators had suggested informally that the activity of the dolomite and other minerals might indeed play a role in alkali-aggregate reactions, a series of mortar bars was prepared and tested in accordance with the procedure similar to ASTM Method C 227 (3). The aggregates were mixtures of the same constituents in the same proportions employed in the sample for the chemical test.

The results of the chemical test indicate that all of the mixtures of serpentine employed (including up to 2.5 percent of opal) and the dolomite-opal mixtures containing up to 1.50 percent of opal are innocuous (Figure 6). The data point representing the serpentine-opal mixture containing 2.5 percent of opal is close to the boundary separating innocuous from deleterious aggregates. On the other hand, all of the quartz-opal mixtures are indicated to be potentially deleteriously alkali reactive.

In the mortar bars, all of the aggregates containing more than 0.25 percent of opal produced expansion greater than 0.1 percent in 1 year, regardless of the composition of the remainder of the mixture. Hence, the result of the chemical test is in error for the serpentine-opal mixtures containing 0.25 to 2.5 percent of opal and for the dolomite-opal mixtures containing 0.25 to 1.50 percent of opal. The result of the quartz-opal mixture containing 0.10 percent of opal is in error also since a deleterious indication is obtained in spite of the lack of significant expansion in the mortar bar test.

Difficulty of this type might be avoided by analysis for sodium and potassium rather than by determination of reduction of alkalinity as a function of the reduction of titratable hydroxyl ion. Sodium is not removed from solution by the precipitation of the secondary hydroxides, whereas the reduction in alkalinity effected by the alkali-silica reaction does correlate with a reduction in the concentration of total of sodium and potassium in solution. The close relationship of reduction of titratable hydroxyl ion to reduction of total sodium and potassium has been demonstrated in extensive tests of pozzolans by somewhat similar procedures (9). This point is discussed further below.

#### Effect of Calcite ( $\text{CaCO}_3$ )

The possible effect of calcite on results of the chemical test originally was ignored because tests applied to marble or limestones containing minimal proportions of silica or silicate minerals produced virtually no re-

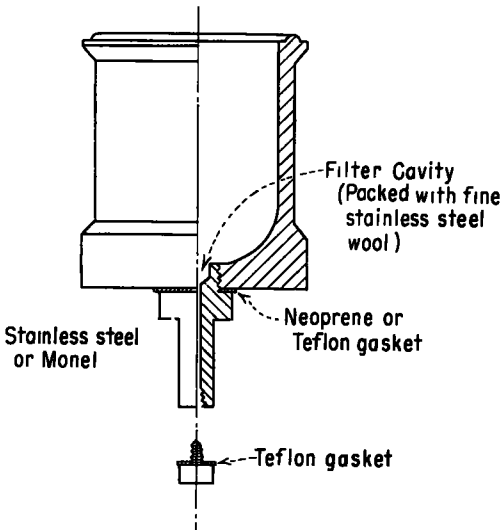


Figure 4. Modified reaction vessel used in filtration by drainage at the bottom.

duction in alkalinity or release of silica into solution. Conversely, several opaline or chalcedonic limestones known to be deleteriously alkali reactive were indicated as being deleterious by the chemical test. Nevertheless, calcium carbonate is slightly soluble in alkaline solutions, and the thought finally arose that calcium released into solution by calcium carbonate might cause spurious reductions of  $S_c$  by the precipitation of one or more calcium silicates.

Two series of mixtures of opal (No. 46), calcite (No. 48), and quartz (No. 47) were prepared and subjected to the test in order to study possible effects of this type. The test was conducted in accordance with standard procedure, except that only 10 milliliters of sodium hydroxide was added to each container, and the bottom-drain procedure was employed. All of the mixtures in both series included 2 percent by weight of opal in the No. 50-100 size range. Calcite constituted 4, 16, 40, and 98 percent of the mixture, the residual being quartz in the No. 50-100 size range. In one series, the calcite was introduced as granular material in the No. 50-100 size range, whereas in the other the calcite was introduced in the No. 100-200 size range. (The mixture con-

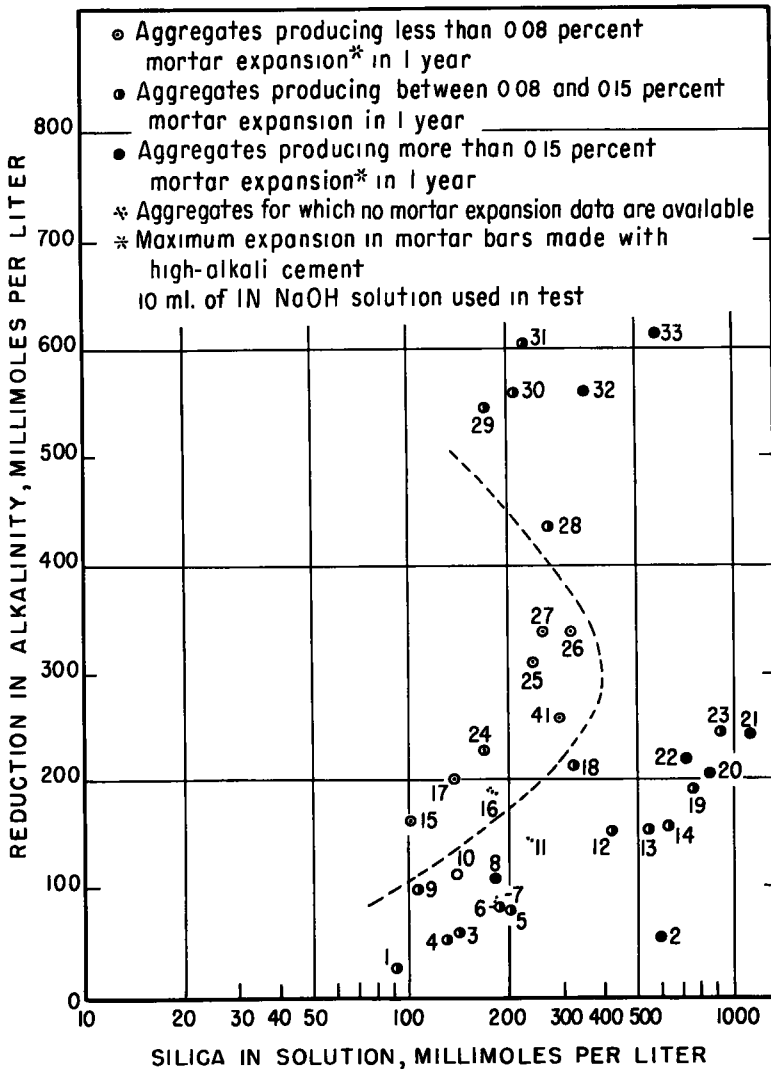


Figure 5. Results of the quick chemical test including bottom-drain reaction vessels and use of only 10 ml 1 N Na OH solution.

**TABLE 4**  
**EFFECT OF CONCENTRATION OF NaOH SOLUTION ON RESULTS OF THE QUICK CHEMICAL TEST<sup>1</sup>**

Aggregate No. <sup>2</sup>	Concentration of NaOH SOLN Used--Determined Values for R <sub>C</sub> and S <sub>C</sub>					
	0.5 N NaOH		1.0 N NaOH		1.5 N NaOH	
	S <sub>C</sub> , mM/1	R <sub>C</sub> , mM/1	S <sub>C</sub> , mM/1	R <sub>C</sub> , mM/1	S <sub>C</sub> , mM/1	R <sub>C</sub> , mM/1
1	56	42	92	26	123	45
5	78	58	203	79	306	91
6	106	70	190	84	264	103
8	60	71	184	108	328	155
12	167	120	420	152	712	203
18	78	159	316	212	508	275
22	228	141	726	220	1,816	321
26	76	252	316	337	748	432
28	84	340	269	434	440	493
29	—	—	172	547	1,104	655

<sup>1</sup> ASTM Method C 289-54T except as follows: (1) 10 ml NaOH solution in indicated concentration; (2) solution extracted at conclusion of reaction period by bottom drain; (3) R<sub>C</sub> not corrected by use of a blank.

<sup>2</sup> See Table 2 for identification of the aggregates.

taining 98 percent of calcite was not included in the latter series.)

The results demonstrate that calcium carbonate causes a change in the values of S<sub>C</sub> and R<sub>C</sub>. R<sub>C</sub> is increased progressively with addition of calcium carbonate, the reduction being greater with addition of the finer calcite (Figure 7). S<sub>C</sub> is decreased in the tests of this series as the proportion of calcium carbonate is increased.

In another determination following the same test procedure, mixtures of a deleteriously reactive slate (No. 45) and quartz (No. 47), or calcite (No. 48) were tested to determine the effect of the calcite on the values of R<sub>C</sub> and S<sub>C</sub>. All constituents of the mixture were prepared as stipulated in the procedure to the No. 50-100 size range. The quartz and calcite constituted 20 percent by weight of the respective mixtures.

As was found with the quartz-opal-calcite mixture, the value of R<sub>C</sub> is higher for the slate-calcite mixture than for the slate-quartz mixture. Surprisingly, the value of S<sub>C</sub> is higher also.

Apparently, calcium released by calcite (calcium carbonate) into an alkaline solution containing dissolved silica causes precipitation of calcium silicate carrying adsorbed or combined alkalis, in this instance primarily sodium. This action reduces the concentration of alkalis in solution, with consequent reduction of titratable hydroxyl ion. If sufficient silica is precipitated, S<sub>C</sub> may decrease because of depletion of soluble silica. Also, if the alkalinity of the solution is decreased sufficiently, the concentration of silica at saturation may be reduced. At intermediate or low values of S<sub>C</sub>, the data indicate that the concentration of silica may increase as a result of reaction of calcium released from calcium carbonate.

In none of these determinations did the added calcite cause a data point to shift across the boundary separating innocuous and deleterious aggregates. It is probable that aggregates otherwise falling close to but to the right of the boundary will be shifted across it as a result of such action. However, the shift to the right (higher S<sub>C</sub>) evident for Aggregate No. 45 produces a trajectory tending to parallel the boundary and so reduces this possibility.

#### EFFECT OF PRELIMINARY ACID TREATMENT OF THE SAMPLES

As a means to eliminate the extraneous effect of carbonates on the results of the chemical test, preliminary acid treatment of the prepared samples was investigated.

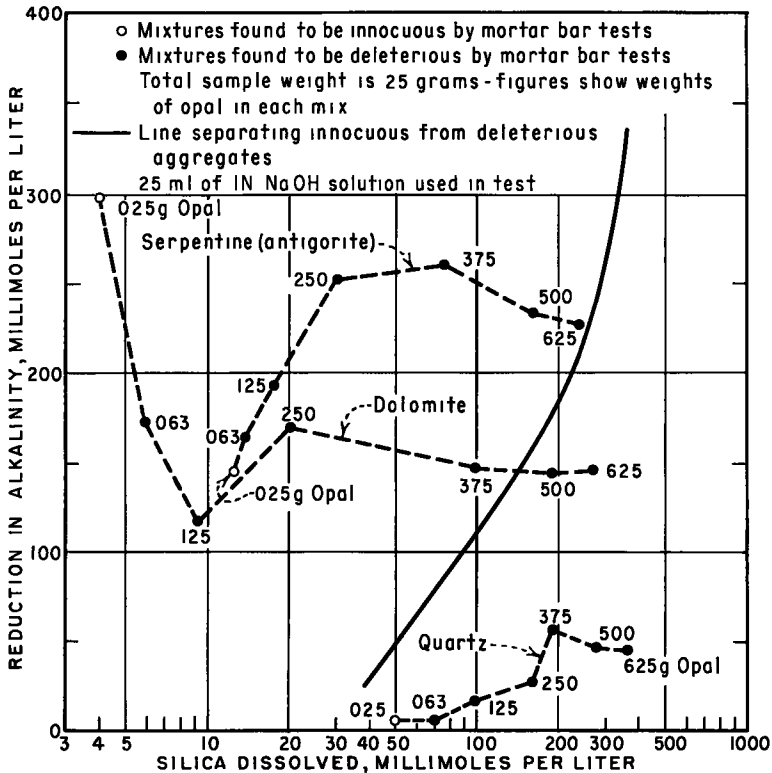


Figure 6. Results of the quick chemical test (ASTM Method C 289-54T) on mixtures of dolomite, serpentine, and quartz with opal.

Because certain silicate minerals decompose in hydrochloric acid and might therefore cause erroneous results, several zeolites and prochlorite were included also in the series of tests.

Twenty-five grams of the No. 50-100 size prepared material were treated in beakers with 500 milliliters of 1:10 HCl and heated to near-boiling. After 1 hour of heating, the supernatant liquid was decanted and another 500 milliliters of the acid added and the heating repeated. After decantation of the acid solution, the residuum was washed five times with 500 milliliters of distilled water and then dried in an oven at 105° C. Each residue was then subjected to a stipulated procedure.

The results demonstrate that the zeolites tested; namely, scolecite, pectolite, and prehnite (Nos. 50, 51, and 52, respectively), were partially or completely decomposed by the acid treatment, and high values of  $S_C$  are obtained (Table 5).  $R_C$  is high for the scolecite and pectolite. The prochlorite apparently is not decomposed by the acid treatment.

Surprising relationships are developed in the tests of the aggregate materials. These are largely inexplicable at this time. However, the results indicate clearly that such a procedure cannot be applied routinely as a part of this test.

### CONCLUSIONS

1. ASTM Method C 289-54T is a useful means to evaluate potential deleterious reactivity of aggregates with cement alkalis. It is especially valuable because it yields results within 2 work days.

2. Reproducibility of the method is acceptable in view of the difficulties inherent in evaluating the alkali-aggregate reaction and the limited reproducibility of alternative procedures, provided the stipulated procedures are followed in all details and the specified equipment and apparatus are used.

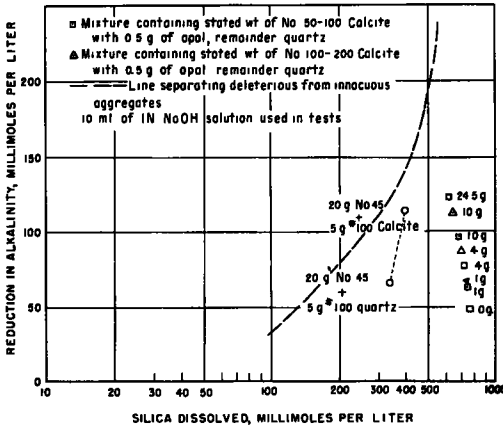


Figure 7. Results of the quick chemical test (ASTM Method C 289) on mixtures containing calcite (calcium carbonate).

of the several minerals, it is recommended that petrographic examination be applied in conjunction with performance and interpretation of the chemical tests.

5. No changes are recommended in the procedure (ASTM Method C 289-54T) at this time. Additional work on the procedure is justified, especially in use of agitation of the vessels during the reaction period, reduction of the volume of NaOH solution used, use of a bottom drain on the vessels, and evaluation of reduction of alkalinity by determination of the change of concentration of sodium and potassium rather than of reduction of the titratable hydroxyl ion. Determination of  $R_c$  by analysis for sodium and potassium probably will remove a large part of the spurious effects induced by magnesium, ferrous carbonates, and hydrous silicates.

3. Reliable results are not obtained with the method if certain minerals or rocks are present. Magnesium and ferrous carbonates (dolomite, magnesite, and siderite) and the hydrous magnesium silicate antigorite (serpentine) have been identified as minerals producing spurious increase in the reduction of alkalinity and concentration of silica. Calcite (calcium carbonate, the essential constituent of limestone and marble) causes an increase in the reduction of alkalinity and changes of the silica concentration if alkali-reactive siliceous phases are present in the aggregate. The effects of calcite are not expected to produce an erroneous indication of potential alkali reactivity of an aggregate unless the potential reactivity is marginal.

4. Because of the extraneous influence

TABLE 5

EFFECT OF PRELIMINARY ACID TREATMENT OF AGGREGATE ON RESULTS OF THE QUICK CHEMICAL TEST<sup>1</sup>

Aggregate No. <sup>2</sup>	With Prior Acid Treatment		Standard Procedure	
	$S_c$ , mM/1	$R_c$ , mM/1	$S_c$ , mM/1	$R_c$ , mM/1
8	184	82	91	76
16	152	77	104	77
28	656	139	149	214
31	544	202	142	218
34	360	171	720	184
35	352	65	650	240
38	340	531	7.5	236
49	32	2		
50	188	311		
51	552	109		
52	172	45		

<sup>1</sup> See accompanying text for the procedure used in the acid treatment.

<sup>2</sup> See Table 2 for identification of the aggregates.

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