

Correlation Between Chemical and Mortar Bar Tests for Potential Alkali Reactivity of Concrete Aggregates

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Certain siliceous constituents of aggregates can react with cement alkalis to cause abnormal expansion and cracking in concrete. The ASTM mortar bar expansion test is generally considered to be the most reliable method available for determining the potential alkali reactivity of such aggregates. Because this test requires considerable time, a quick chemical test was also adopted by the ASTM in order to obtain a rapid evaluation of concrete aggregates. This investigation was made to determine the degree of correlation between the two methods of test.

Fifty-two concrete aggregates were evaluated by means of the rapid chemical test for potential alkali-aggregate reactivity and the results generally showed good correlation with the data obtained in the mortar bar tests. However, the chemical test does not always give reliable results for some aggregates because of the interference of certain carbonates. An empirical division of the chemical tests results is proposed which would serve to isolate those aggregates which may contain such interferences, and thereby indicate the need for further tests.

Some aggregates showed a high degree of reactivity in the chemical test but did not produce excessive mortar bar expansion. An additional empirical division of the chemical test results is suggested which would separate chemically reactive aggregates into two groups. Such a separation would eliminate the need of supplementary mortar bar tests on many reactive aggregates. Chemical test results which fall into one such group are indicative of very highly reactive but not necessarily expansion-producing aggregates. Special mortar bar tests are necessary for such materials.

The general chemical test criteria established by this study for separating reactive from nonreactive aggregates agree fairly well with those proposed by ASTM specifications and the Corps of Engineers. The present ASTM chemical test method permits two titration procedures for the determination of alkalinity reduction. Neither procedure showed any distinct advantage over the other as a means for evaluating the potential reactivity of aggregates.

● BEFORE 1940, most aggregates were usually considered to be chemically inert when used in concrete. However, it has since been clearly demonstrated that certain siliceous constituents, present in some aggregates, can react with the alkalis in cements to cause abnormal expansion and cracking in concrete.

The most reliable laboratory test now available for determining the potential alkali reactivity of concrete aggregates is considered to be the mortar bar expansion test (1). This test has been adopted as a tentative standard (Method C227) by the American Society for Testing Materials (2). Because of the time required to obtain reliable information by this method of test, extensive investigations have been made to develop a more rapid method of test. A rapid chemical test was developed by Mielenz and others (3) and was later adopted by ASTM as tentative standard Method C289 (2). Briefly

the chemical test measures the amount of reaction during 24 hr at 80C, between a 1 normal sodium hydroxide solution and aggregate that has been crushed and sieved to definite size. At the end of the reaction period, the mixture is filtered and the solution is analyzed to determine its final alkalinity and silica content, the latter arising as a result of the partial dissolution of the aggregate. These values are then used to determine the potential reactivity of the aggregate with alkalis in portland cement concrete.

The reliability of the chemical test was established by the original authors of the method, mainly on the basis of an empirical correlation with mortar bar expansion test results. Unfortunately, many investigators have subsequently reported discrepancies in evaluating concrete aggregates by both methods of test.

A search of the literature failed to reveal any additional published work in which a large number of aggregates were evaluated by both methods of test. Comparisons of a few aggregates have been reported by several investigators (4, 5, 6). Two other reports (7, 9) showed considerable comparative data, but most of the results shown were either reported earlier by Mielenz et al. (3), or were based upon modifications of the presently used chemical test.

Consequently, the Bureau of Public Roads initiated a study of a large number of aggregates in order to compare the results by both methods of test. A specific objective of the study was to determine the degree of correlation between the results of the quick chemical test and the mortar bar test. It was anticipated that the present criteria of the chemical test could be suitably altered or extended in order to make better use of the test results, thereby eliminating the need for further extensive testing of many aggregates.

PROCEDURE

Chemical Tests

Fifty-two concrete aggregate samples were prepared and tested in accordance with ASTM Method C289 (2), except that the sodium hydroxide solution was prepared by standardizing with standard hydrochloric acid. The acid was standardized against reagent grade sodium carbonate using methyl purple indicator.

The reaction containers used were fabricated from 18-8 stainless steel, fitted with unvulcanized neoprene gaskets. Ethylene glycol was used for the constant temperature liquid bath. Filtration vacuum was maintained at 15 in. of mercury by means of a Cartesian Manostat. Immediately following filtration, the diluted solutions were stored in polyethylene containers and sealed until analyzed.

The reduction in alkalinity was determined by means of both the single and double end points given in the ASTM method. The single end point titration involves a neutralization with standard acid using phenolphthalein as the indicator, and measures the alkalinity produced by all the hydroxide ions as well as part of the carbonate ions present. In the double end point procedure, the titration of the same sample is continued to the methyl orange end point which on calculation gives a measure of the hydroxide ions only.

Dissolved silica was determined colorimetrically with a Beckman DU spectrophotometer using 1-cm cells. The readings were made at exactly 5 min after the addition of the oxalic acid reagent.

Mortar Bar Tests

Mortar bar test data had been obtained for these same aggregates over a considerable number of years and, in a large number of cases, well before the development of the ASTM standard method. Consequently, the procedures used in the preparation and storage of the test bars varied somewhat. The details and conditions of test are shown in Table 1.

RESULTS

The results of the mortar bar and chemical tests are given in Table 1. Included

TABLE 1. RESULTS OF MORTAR BAR EXPANSION AND

Sample identification	Source of aggregate	Type of aggregate	Nature of aggregate	Mortar bar expansion	
				Brand and Lot No.	Brands and Lot No.
1	Burnt River, Oregon	Sand	R, Sc, G, Qs, Fe	A-1	0.11:0.97:0
1	Do.	Gravel	R, B, Sy, Sc, less than 1% Qs	C-1	0.27:0.70:0
2	Klamath Falls, Klamath Co., Oregon	Rock	B	B	0.20:0.47:0
3	Footello, Power Co., Idaho	Gravel	Qs, Felds, Qs, Calc. S, Q; some B & R	A-2	0.14:1.04:0
4	Idaho Falls, Bonneville Co., Idaho	Gravel	Qs, S, Felds, Qs, Calc. S, L, G	A-2	0.14:1.04:0
4	Do.	do.	do.	E	0.21:0.60:0
5	Footello, Bannock Co., Idaho	Sand	Qs, Felds, Qs, L; some Q & S	A-2	0.14:1.04:0
6	Campano, Bannock Co., Idaho	Sand	Q, Qs, L; some S & Ma	A-2	0.14:1.04:0
7	Huston, Fremont Co., Idaho	Sand	Q, G, Fe, Qs, O, Calc. fragments	A-2	0.14:1.04:0
7	Do.	Gravel	G, Qs, Felds, Qs; some Q, R, and L	A-2	0.14:1.04:0
8	Blackfoot, Bingham Co., Idaho	Sand	O, Q, Qs; some S and Ma	A-2	0.14:1.04:0
8	Do.	Gravel	Qs, Felds, Q, S	A-2	0.14:1.04:0
9	Manan, Jefferson Co., Idaho	Sand	Q, O, Fe; some S and Ma	A-2	0.14:1.04:0
9	Do.	Gravel	Felds, Qs, S, Fe, some Q, G, and Gr	A-2	0.14:1.04:0
10	Rupert, Blaine Co., Idaho	Sand	Qs, S, Fe, Q; some O, Pms, and Ma	A-2	0.14:1.04:0
10	Do.	Gravel	R, L; some S, Qs, and Q	A-2	0.14:1.04:0
11	Hamburg, Madison Co., Idaho	Sand	Q, O, Fe; some Qs	A-2	0.14:1.04:0
11	Do.	Gravel	R, G; some S, O, Felds, S, Q	A-2	0.14:1.04:0
12	Salt Lake City, Salt Lake Co., Utah	Gravel	Qs, Calc. S, L; some Q, Qs, Dol., and G	C-2	0.18:0.87:0
13	Hoover's Shding, Chesterfield Co., S.C.	Sand	Qs; some S	A-2	0.14:1.04:0
14	Mr. Sapinero, Gunnison Co., Colo.	Gravel	B, R, volcanics with some G, dark Aph.	C-2	0.18:0.87:0
15	Sta. 621, Loveland-Fremont Pass, Colo.	Sand	Q, G, and dark Aph.	C-2	0.18:0.87:0
16	Mr. Baud, Jackson Co., Colo.	Sand	Q, G, and M	C-2	0.18:0.87:0
17	Snake R., Mr. Hoback, Teton Co., Wyo.	Gravel	L, Qs, and S	C-2	0.18:0.87:0
18	Oral, Fall River Co., S. Dak.	Gravel	L, S, Calc. S and Qs	C-2	0.18:0.87:0
19	Hill City, Pennington Co., S. Dak.	Rock	Micaceous Qs	C-2	0.18:0.87:0
20	Snake River, Teton Co., Wyo.	Gravel	Qs, Calc. S, Fe, R and B	C-2	0.18:0.87:0
21	Dayton, Sheridan Co., Wyo.	Rock	Altered G	C-2	0.18:0.87:0
22	Do.	Gravel	Qs, L, G	C-2	0.18:0.87:0
23	Do.	Sand	Q, G and L	C-2	0.18:0.87:0
24	Nederland, Boulder Co., Colo.	Gravel	G and Qn	C-2	0.18:0.87:0
25	Do.	Sand	G; some Q and Qn	C-2	0.18:0.87:0
26	St. Vrain, Weld Co., Colo.	Gravel	G and Qn	C-2	0.18:0.87:0
27	St. Vrain, Delta Co., Colo.	Sand	Q, Fe, dark Aph; some F	C-2	0.18:0.87:0
28	Mr. Mesa, Mesa Co., Colo.	Rock	Olivine B	C-2	0.18:0.87:0
29	Mr. Reserve, Catron Co., N. Mex.	Gravel	L, S, An; some G	C-2	0.18:0.87:0
30	El Paso, El Paso Co., Texas	Sand	B, Q; some F	C-2	0.18:0.87:0
31	Dry Canyon, Mr. Lelan, Otero Co., N. Mex.	Rock	L	C-2	0.18:0.87:0
32	Ruidosa R., Mr. Mondo, Lincoln Co., N.H.	Gravel	L, S, Qs, and Fe	C-2	0.18:0.87:0
33	Do.	Sand	Dark Aph., G, L; some D1	C-2	0.18:0.87:0
34	Cheraw, Chesterfield Co., S. C.	Gravel		C-2	0.18:0.87:0
35	Columbia, Michland Co., S. C.	Rock	G	C-2	0.18:0.87:0
36	Beverly, Pickens Co., S. C.	Rock	Biotite G	C-2	0.18:0.87:0
37	Blair, Fairfield Co., S. C.	Rock	G	C-2	0.18:0.87:0
38	Chattahoochee, Gadsden Co., Fla.	Sand		D-1	0.32:0.95:0
39	Columbus, Lowndes Co., Miss.	Gravel	C	D-2	0.33:0.86:0
40	Dixie, Russell Co., Ala.	Sand		D-2	0.33:0.86:0
41	Montgomery, Montgomery Co., Ala.	Sand		D-2	0.33:0.86:0
42	Chattanooga, Hamilton Co., Tenn.	Sand		D-2	0.33:0.86:0
43	Camak, Warren Co., Ga.	Rock		D-2	0.33:0.86:0
44	Footello, Power Co., Idaho	Sand	Q, Qs; some S and Sc	A-2	0.14:1.04:0
44	Do.	Gravel	Qs, Felds, Qs; some S and Q	A-2	0.14:1.04:0
45	San Ramon Quarry, Nicaragua	Rock		D-1	0.32:0.95:0
46	Clinton Point, Dutchess Co., N. Y.	Rock	Dol	D-2	0.33:0.86:0
47	San Marcos R. (rt. side), Salvador	Sand		D-2	0.33:0.86:0
48	Do. (l. side), do.	Rock		D-2	0.33:0.86:0
49	Do. (rt. side), do.	Rock		D-2	0.33:0.86:0
50	Pioneer Pit, Crackerville Junct., Mont.	Gravel	Qs, Fine grained volcanics, G	D-3	0.20:0.80:0
51	Stearns Bros., Do.	Gravel	Qs, (Ser.), Fine gr. volcanics; some O, S, R	D-3	0.20:0.80:0
52	Ottawa, Ill.	Sand	Q	C-2	0.18:0.87:0

A/	An	- andesite	Fe	- feldite	Pm	- pumice	B/	Sand and coarse aggregate sieved and crushed
	Aph	- asphaltes	Felds	- feldspathic	Q	- quartz		respectively, to pass No. 4 sieve. 1-2
	B	- basalt	G	- granite	Qs	- quartzite		1x1x11-in. bars, moist air storage at 12
	C	- chert	Qn	- gneiss	R	- rhyolite		Exceptions to these conditions are noted
	Calc	- calcareous	Gr	- greenstone	S	- sandstone		table under Remarks.
	D	- diabase	L	- limestone	Sc	- schist		
	Dol	- diorite	M	- mica	Ser	- sericitic		
	Dol	- dolomite	Ma	- magnetite	Sy	- syenite		
	F	- feldspar	O	- obsidian				

CHEMICAL REACTIVITY TESTS ON CONCRETE AGGREGATES

Specimen No.	Year	Reactivity	Chemical test data d/		Dissolved silica (Sc)	Remarks
			Alkalinity (Ac)	Reduction (Rc)		
		Single end point:	Double end point:			
		Millimoles per liter (mM/L)				
08	Q	(134)	(151)	(122)	170°F. storage	
04	NR				170°F. storage	
12	R	137	159	160	Medium alkali cement used in mortar bars	
11	R	45.3	63.7	106		
12	R	(49.2)	(70.8)	(108)	Sand fraction was reactive with same cement	
04	NR				do.	
05a/	Q	86.3	111	136	Bars reactive with 1% NaOH, admixture	
04	NR	126	152	279	do.	
07	NR	(116)	(129)	(466)	do. , and at 2 years without NaOH	
06	NR				do. , do do.	
35	R	(108)	(126)	(354)		
12	R					
15	R	(67.1)	(82.8)	(217)		
34	R					
08	Q	(148)	(156)	(302)	Bars reactive with 1% NaOH, admixture	
17	R					
09	Q	(130)	(151)	(476)	Bars reactive with 1% NaOH, admixture	
07	NR					
11	R	66.8	110	26.7	Dolomite present. Bars also reactive with med. alk. cement	
05	NR	9.2	17.6	20.7	Bars reactive in 2 years	
22	R	215	236	472		
04	NR	40.4	54.9	20.7		
03	NR	62.4	77.9	27.0		
06	NR	45.2	57.2	66.0	Sand fraction showed questionable reactivity in 2 years	
03	NR	163	233	74.0	Limestone present	
04	NR	36.6	55.2	29.8		
02	NR	178	199	537	Bars reactive with 1% NaOH, Sand fraction reactive in 2 years	
03	NR	71.1	84.4	16.8		
03	NR	135	209	86.0	Limestone present	
04	NR	73.1	111	18.8	do.	
03	NR	35.7	42.9	39.4		
05	NR	43.7	60.9	22.4		
04	NR	20.4	31.9	22.0		
04	NR	135	182	38.6		
07	NR	89.5	110	128	Questionable reactivity in 2 years	
10	R	176	199	236	Limestone present	
62	R	79.8	91.0	234		
08	Q	46.5	68.0	11.5	Limestone present, Dolomite and magnesite absent	
02	NR	106	179	13.6	Limestone present	
02	NR	127	172	16.4	do	
10	R	8.3	11.5	24.3	Bars nonreactive at 70°F. storage or with 1% NaOH admixture	
08	Q	7.0	14.0	15.6	do.	
06	NR	10.6	23.5	14.8		
06	NR	9.3	17.6	13.1		
04	NR	16.1	25.1	19.1	100°F. storage	
03	NR	154	198	454	do. , concrete bars - 2x2x11", uncrushed aggregate	
04	NR	13.7	20.4	20.1	do.	
05	NR	17.2	24.0	27.9	do.	
08	Q	39.3	56.1	62.0	do.	
03	NR	9.6	18.6	17.2	do.	
12	R	(66.3)	(85.8)	(169)		
14	R					
22	R	78.7	106	124	100°F. storage	
05	NR	98.5	173	10.6	do. , Dolomite	
03	NR	140	166	131	do.	
14	R	130	149	212	do.	
09	Q	137	151	340	do.	
02f/	NR	124	140	226	do. , uncrushed gravel, 2x2x11", bars, mix 1-2.3	
02f/	NR	198	216	373	do. , do. do	
04	NR	0.7	4.1	14.9	Stack Ottawa Sand, 30-100 mesh size in bars	

a/ Criteria based on mortar bar expansion data at 1 year "C" (questionable) represents results in doubt or 1 year expansions of 0.08 to 0.09%. "R" (reactive) represents expansions of 0.10% or more, and "NR" (nonreactive) represents expansions of 0.07% or less.

d/ A.S.T.M. Method C 289-54 T. Values in parenthesis were obtained on combined aggregates as shown

g/ Expansion data at 6 months. Specimens broke after this value was determined

f/ Data at two years.

in the table are the sources and petrographic analysis for most of the aggregates. An evaluation of the potential reactivity of the aggregates based upon the amount of expansion exhibited by mortar bars at an age of one year is also shown. Expansions of 0.10 percent or more were considered indicative of reactive aggregates as suggested by ASTM Specification C33-55T, Section 4c (2). Expansions of less than 0.08 percent were considered to be indicative of nonreactive materials, while aggregates having expansions of 0.08 or 0.09 percent were classified as questionable. The latter criteria conform to established practice at the Bureau of Public Roads.

Some of the aggregates studied consisted of sand and gravel fractions which were evaluated separately in the mortar bar test. However, because of limited amounts of material available after the mortar bar tests, several such companion fractions were combined and prepared as a single sample for the chemical test. In such cases, no special problem arose where the mortar bar data for companion fractions indicated the same degree of reactivity or nonreactivity. In a few cases, however, companion fractions were classified into different categories of mortar bar reactivity. In these few cases, namely Sample Nos. 1, 4, 10 and 11, the result representing the greatest degree of mortar bar reactivity was arbitrarily selected for comparison with the chemical test result.

Table 2 shows the results of the chemical test only, on several additional materials. These were special materials which included carbonate minerals and well-known reactive materials.

The results of the chemical test for each material are graphically represented in Figures 1 and 2. The units used in both figures and the manner of presentation are in accordance with ASTM Method C289 (2) and as suggested by the original authors of the chemical test (3). Figure 1 represents the results obtained by using the single end point in the alkalinity reduction titration, and Figure 2 shows the results obtained by means of the double end point titration.

Each chemical test result is represented by a symbol to denote both the cement used and the degree of reactivity as found by the mortar bar test. These symbols are described in the legends to both figures.

DISCUSSION OF TEST RESULTS

In both Figures 1 and 2, a solid line was drawn to best separate the bulk of the reactive from the nonreactive aggregates. The classification for degree of reactivity was based upon the mortar bar test results as previously described. This manner of separation was proposed by Mielenz et al. (3) and is included in a recent revision of ASTM Method C289. Once a line of demarcation is established, it serves as a criterion for future chemical test results in evaluating additional aggregates. Chemical test results to the right of the line should be indicative of potentially reactive aggregates, while results to the left of the line should represent nonreactive aggregates.

TABLE 2
RESULTS OF CHEMICAL REACTIVITY TEST ON SPECIAL MATERIALS

Sample Identification	Nature of Aggregate	Chemical Test Data ^a		
		Alkalinity Reduction, mM/1 (Rc)		Dissolved Silica, mM/1 (Sc)
		Single End Point	Double End Point	
A	Limestone (97.2% CaCO ₃)	14.2	26.5	5.3
B	Dolomite (55.1% CaCO ₃ ; 44.3% MgCO ₃)	363	689	0.8
C	Magnesite (Wards)	405	792	1.5
D	Magnesite (Pennsylvania)	440	855	0.5
E	Opal (Virgin Valley, Nev.)	325	369	778
F	Opal (Virgin Valley, Nev.) ^b	246	296	949
G	Sil. Magnesian Limestone (Calif.)	218	278	557
H	Pyrex glass cullet	120	175	747

^a ASTM Method C 289-54T.

^b Mix of 50% Opal; 50% Ottawa Sand.

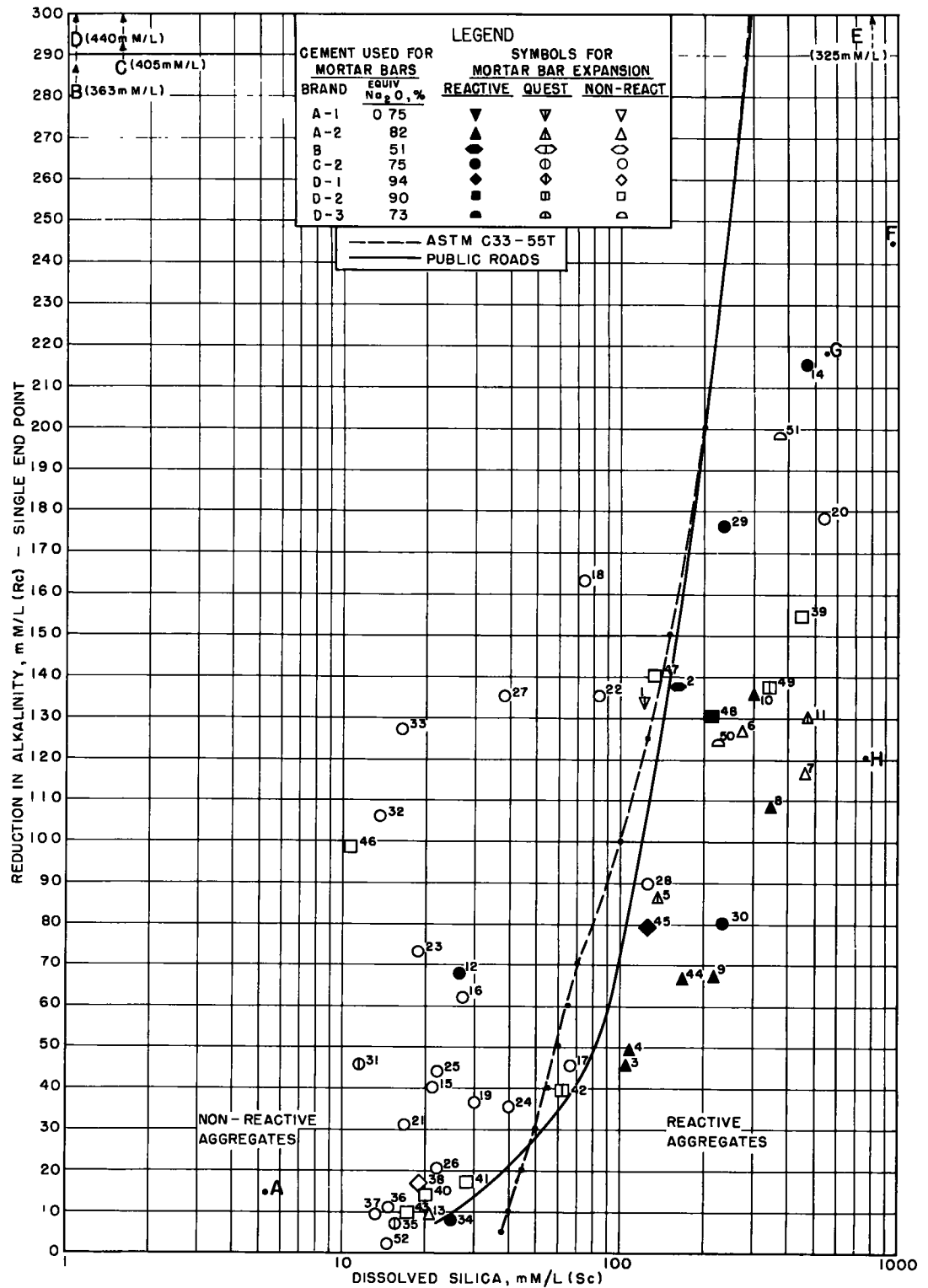


Figure 1. Results of chemical test for reactivity of aggregate (single end point).

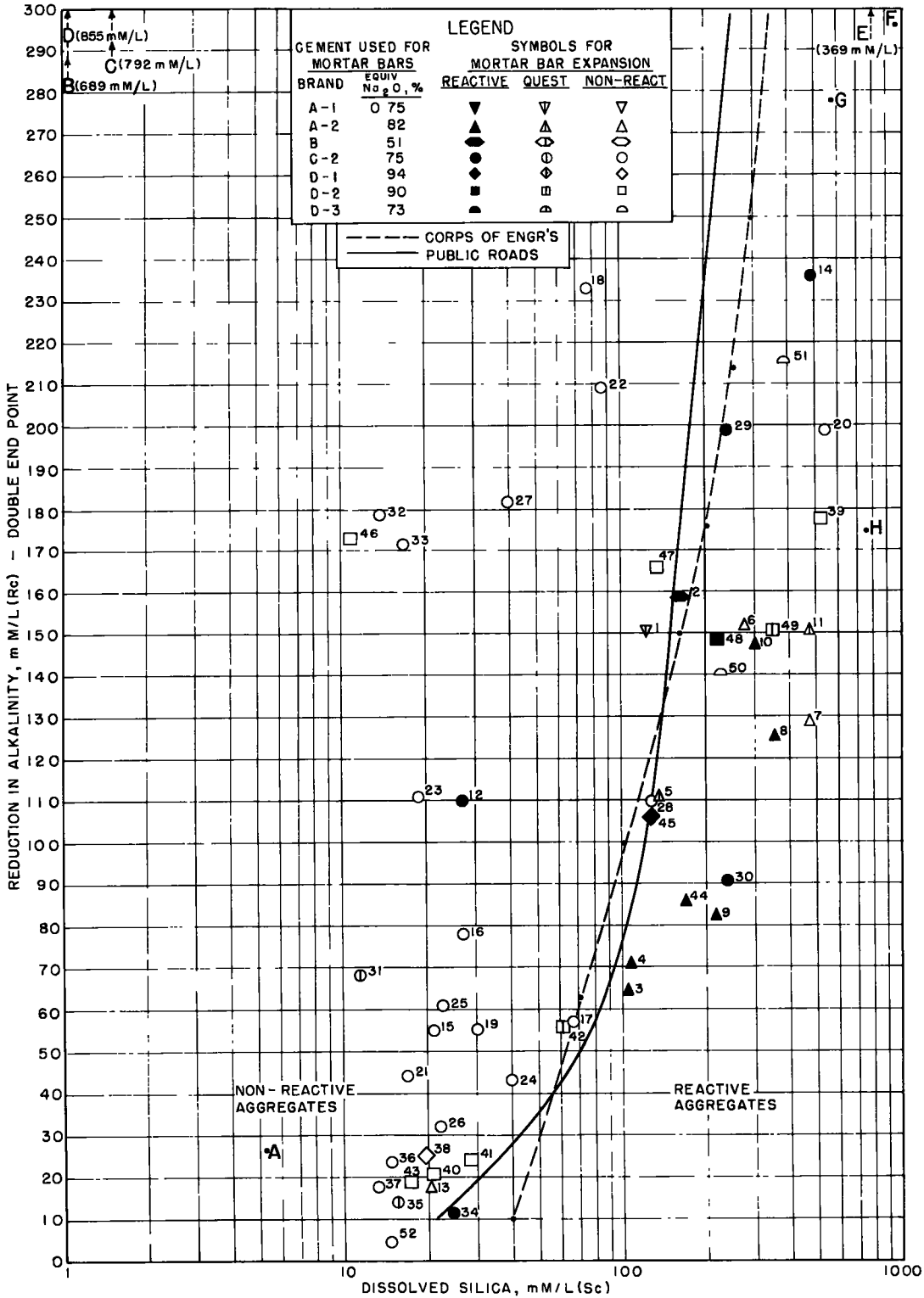


Figure 2. Results of chemical test for reactivity of aggregate (double end point).

Line of Separation

Two lines of separation are shown. The solid line in each case was drawn as a result of the data obtained in this study, while the dashed line represents other published criteria.

In Figure 1, the dashed line is based upon the calculations suggested in ASTM Specification C33-55T (2). Both the dashed and solid lines coincide fairly well, thus the criteria established by this study are in substantial agreement with those suggested by the ASTM specification. A slight spread exists between the two lines in the lower part of the figure. The position of the solid line (Public Roads) in this area was dictated by the plotted results of Sample Nos. 17, 42 and 34. No. 34 showed a mortar bar expansion of 0.10 percent in one year, the minimum value necessary for classifying an aggregate as reactive. In addition, mortar bars of this material were stored at 70F and failed to show significant expansion at 1 year (11). Since No. 34 is a borderline aggregate, the location of the solid line in the extreme lower portion of Figure 1 may not be rigorous, as it is based upon the results of this aggregate alone.

In Figure 2, the dashed line represents the criteria used by the Corps of Engineers (10), and again there is good agreement between the position of both lines, except for the same type of spread in the lower part of the figure.

Single Versus Double End Point Titrations

An inspection was made of both figures in order to determine if either the single or double end point titration procedure offered any distinct advantage. The Corps of Engineers apparently prefers the double end point titration (10), while the Bureau of Reclamation and many other laboratories rely mainly on the single end point titration. Table 3 lists the aggregates that failed to give good correlation between the chemical and mortar bar tests and shows that there is no difference between Figures 1 and 2 in either the identification, or total number of such discrepancies. Therefore, these results show no substantial advantage of one type of titration over the other.

COMPARISON OF TEST RESULTS

In some instances, the empirical classification of the aggregates into reactive and nonreactive materials, based upon the chemical test results, differs from the classification obtained by means of the mortar bar test. Specific consideration of those samples showing such differences is of interest.

A total of 29 numbered symbols appear to the left of the solid line (Fig. 1). Of these, 24 are clear symbols denoting nonreactive aggregates and consequently are properly located in the figure. Three other aggregates in this area (Nos. 1, 35 and 42) were found to be of questionable reactivity, with mortar expansions of 0.08 percent

TABLE 3
IDENTIFICATION OF AGGREGATES SHOWING POOR CORRELATION
BETWEEN CHEMICAL AND MORTAR BAR TESTS

Position of Plotted Chemical Test Results	From Figure 1		From Figure 2	
	Identification of Aggregates	Total No. of Samples	Identification of Aggregates	Total No. of Samples
To the left of solid line:				
Reactive aggregates ^a	No. 12 ^b	1	No. 12 ^b	1
Questionable aggregates ^a	Nos. 1, 31, 35, 42	4	Nos. 1, 31, 35, 42	4
All aggregates		29		29
To the right of solid line:				
Nonreactive aggregates ^a	Nos. 6, 7, 20, 28 and (39, 50, 51) ^c	7	Nos. 6, 7, 20, 28 and (39, 50, 51) ^c	7
All aggregates		23		23

^aBased on mortar bar test results and criteria shown in text and Table 1.

^bSample contains 16 percent dolomite as determined by DTA.

^cThe three samples in parentheses were not tested in mortar bars but rather as concrete specimens prepared from gravel size aggregate.

at 1 year. However, the chemical test results of all three samples are located close to the dividing line where it might be expected to find questionable aggregates.

Only two aggregates (Nos. 12 and 31), classified as either reactive or questionable, are located well to the left of the dividing line. There is no question as to the potential reactivity of No. 12, since this aggregate was found to cause significant mortar expansion even when combined with a medium alkali cement (11). However, both of these aggregates contain limestone or dolomitic constituents which, as will be discussed later, may invalidate the chemical test results.

A total of 23 numbered symbols appears to the right of the solid line (Fig. 1). It would be expected that all aggregates located in this area should be reactive. However, 7 were shown to be nonreactive by the mortar bar test. The identification of all 7 aggregates is given in Table 3. Three of these (Nos. 39, 50 and 51) may be eliminated from this discussion since they were not tested in mortar bars, but rather as concrete specimens prepared from gravel size aggregate and were included only for information purposes.

Therefore, only 4 samples (Nos. 6, 7, 20 and 28) are considered as limiting the degree of correlation between the chemical and mortar tests in this area. However, it was noted that all four materials in question, exhibited some degree of mortar bar reactivity in supplementary tests. Nos. 6, 7 and 20 caused considerable mortar expansion when the mortar contained an admixture of sodium hydroxide, while No. 28 began to show a questionable degree of reactivity in the mortar bar test at an age of 2 years (11). These latter findings lend support to the chemical test data obtained for these aggregates. Although some aggregates may be potentially reactive and are so characterized by the chemical test, these same aggregates may not be capable of producing dangerous expansion in the standard mortar bar test.

FACTORS AFFECTING CORRELATION BETWEEN CHEMICAL AND MORTAR TESTS

Carbonate Interference

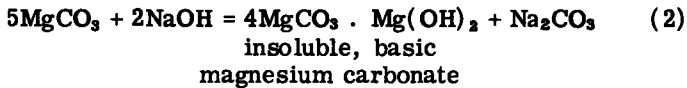
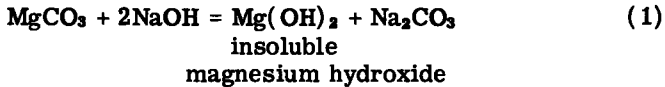
The two aggregates (Nos. 12 and 31), which appeared as distinct discrepancies in the area to the left of the solid line, (Fig. 1) were classified petrographically as containing certain carbonate constituents. Differential thermal analysis showed that No. 12 contained both calcite and dolomite, while No. 31 contained essentially calcite with dolomite and magnesite absent. Mielenz and Benton (9), as well as Swenson (6), have indicated that dolomites and perhaps even limestones may at times cause significant interference in the chemical test. It was demonstrated that although certain opal-dolomite mixtures were found to be deleterious by mortar bar tests, the chemical test results gave false information concerning the reactivity of the mixture (9). Such misleading information was attributed to the interference of dolomite and other minerals such as magnesite, siderite and serpentine. When present along with reactive constituents, these minerals produce greater reductions in alkalinity (Rc) and lower dissolved silica values (Sc) in the chemical test than would otherwise be obtained. The net effect of such interference is to shift the chemical test data both to the left and upwards in Figure 1 and thereby at times yield misleading information concerning a truly reactive aggregate.

A separate study of several carbonate materials was made in order to understand more fully their possible effects on the chemical test. Table 2 shows the chemical test results obtained on four carbonate minerals. Relatively pure limestone, dolomite and two magnesites were tested and the results were plotted in Figures 1 and 2 as points A, B, C, and D.

As seen in Table 2 and in Figure 1, the limestone (A) did not cause any significant alkalinity reduction, while the dolomite and both magnesites (B, C and D) produced unusually large alkalinity reduction values (Rc). It would appear from these results, that pure limestone (calcium carbonate) does not react significantly with the sodium hydroxide solution used in the test, while dolomite and magnesite do. Furthermore, the ratio of, and absolute difference between, the double and single end point values

of Rc, for both dolomite and magnesite, suggest the formation of considerable quantities of weakly basic material in solution during the test.

The sodium hydroxide solution was analyzed in each case after the test was completed. No significant amounts of calcium or magnesium were detected nor was there any apparent decrease in the concentration of sodium below the level of the initial test solution. It was concluded that, in the case of dolomite and magnesite, the test solution had lost some hydroxide ions in exchange for an equivalent amount of carbonate ions. The latter material accounts for the presence of a weak base after test. From these considerations, two possible equations can be written for the reaction between magnesite and the sodium hydroxide solution.



Such reactions appear reasonable from a consideration of the solubility products of magnesium carbonate (2.6×10^{-5} at 12 C) and magnesium hydroxide (1.2×10^{-11} at 18 C) (12). The latter material, a possible end product in the reaction, is much more insoluble in water than is magnesium carbonate, the reactant. The reaction between dolomite and the test solution no doubt is similar to that involving magnesite.

No special study was made to explain the depressed values of dissolved silica (Sc) caused by the presence of dolomite or similar materials (9). The following thoughts are offered as possible explanations of this effect: (a) The large reduction in alkalinity caused by such minerals may so reduce the alkalinity of the solution as to minimize its attack upon reactive forms of silica, (b) the formation of insoluble magnesium hydroxide or the basic carbonate may act as a protective film in limiting the attack of the solution upon reactive forms of silica, or (c) dolomite or its decomposition products may react with dissolved silica to form insoluble silicates and thereby remove silica from solution.

Elimination of Carbonate Interference

Efforts by Mielenz and Benton completely to eliminate carbonate interference in the chemical test by prior treatment of the aggregate with hydrochloric acid have not given satisfactory results (9). They have suggested that an analysis of the change in concentration of sodium and potassium rather than the reduction in alkalinity (Rc) would probably remove a large part of the spurious effects induced by such carbonates. Although such a procedure would eliminate the falsely high Rc values (alkalinity reduction), it would not eliminate the low Sc values (dissolved silica) produced by this interference.

Continued study of the "carbonate effect" on the chemical test is necessary in order to eliminate its interference. Because of such interference, a recent revision of the present ASTM chemical test recommends petrographic examination as a supplement to the chemical test data. This recommendation would involve a time-consuming petrographic examination of many aggregates whose chemical test data would place them to the left of the dividing line in Figure 1.

However, a more expedient alternative is suggested here. It has been shown that the "dolomite interference" is characterized by rather high Rc values in the chemical test. A level of Rc might be established so that all results below this level and to the left of the main dividing line may safely be considered to be nonreactive aggregates and consequently no further testing will be necessary. Results above this Rc level would require additional study by chemical, petrographic, X-ray, or DTA methods in order to detect the presence of either interfering or reactive minerals. The presence of small amounts of dolomite, magnesite or calcite may be detected by spot tests or differential thermal analysis (DTA), while serpentine is conveniently identified by X-ray analysis. If the presence of such interfering minerals should be so detected,

mortar bar tests would then be necessary in order to evaluate more fully the potential reactivity of the aggregate.

Highly Reactive Materials

In addition to the results of this study, other investigators have found that many chemical test results to the right of the main dividing line fail to correlate with mortar bar test results (4, 7, 8). Both Sprague (8) and others (7) have attributed such discrepancies to the fact that certain aggregates contain such a large proportion of reactive constituents to available cement alkalies that they fail to produce mortar bar expansion. This is a consequence of the "pessimum proportion" (defined by T. E. Stanton as that proportion of reactive constituent in an aggregate at which maximum mortar bar expansion occurs) of the aggregate being materially exceeded.

It is well known that certain opals and siliceous magnesium limestones are highly reactive and are so characterized by the chemical test. Yet when these materials are present in large proportions, they actually cause little or no expansion in the mortar bar test (11, 13, 14). It was shown by Woolf that, although 1 or 2 percent of opal combined with an inert material will produce dangerous mortar bar expansion, much larger amounts of opal will cause insignificant expansion for a given cement alkali content (16).

Table 2 shows the chemical test results on several well-known reactive materials; namely opal, siliceous magnesium limestone, and pyrex glass. These results are plotted in Figures 1 and 2 as points E, F, G and H. In Figure 1, points F and G are particularly interesting since they approach the area where discrepancies (clear symbols) are shown. Point F represents a blend containing 50 percent each of opal and Ottawa sand. McConnell and others have shown that a similar mixture failed to produce mortar bar expansion (15). Point G represents 100 percent siliceous magnesium limestone which Stanton has shown to cause negligible mortar bar expansion when tested in its entirety (13).

Division of Reactive Area into Two Parts

As a partial solution to the problem of such recurring discrepancies, Mielenz and Witte (7) have suggested an arbitrary division of the area containing the aggregates classified as reactive by the chemical test. They suggested that such a division would be useful in interpreting the chemical test results. Their proposed division would separate the reactive area into an upper and lower portion. Chemically reactive aggregates which always caused mortar expansion were found to give chemical test results lying in the lower area, while chemically reactive aggregates which did not cause mortar expansion, when tested in their entirety, gave chemical test results in the upper area.

On the basis of the results obtained in this study, the proposed dividing line appears to have considerable merit. However, in order better to separate the apparent discrepancies found in this study, such a dividing line should be located at a lower R_c level than that proposed by Mielenz and Witte. This study showed that all four of the aggregates showing major discrepancies and located in the reactive area of Figure 1 had R_c values of 90 or more. The data points for these aggregates should be located in the upper area of any arbitrary division.

PROPOSED MAIN BOUNDARY LINE AND NEW AREAS FOR CHEMICAL TEST

To establish acceptable area boundaries, all discrepancies between chemical test and mortar test data were evaluated. Figure 3 shows the location of all such data points both from this study and the available literature. In addition, data related to the proper location of a main boundary line was similarly plotted.

Location of Main Boundary Line

The data chosen for presentation with respect to the main boundary line are shown in the lower third of the figure and generally fall within the area between the two dividing lines.

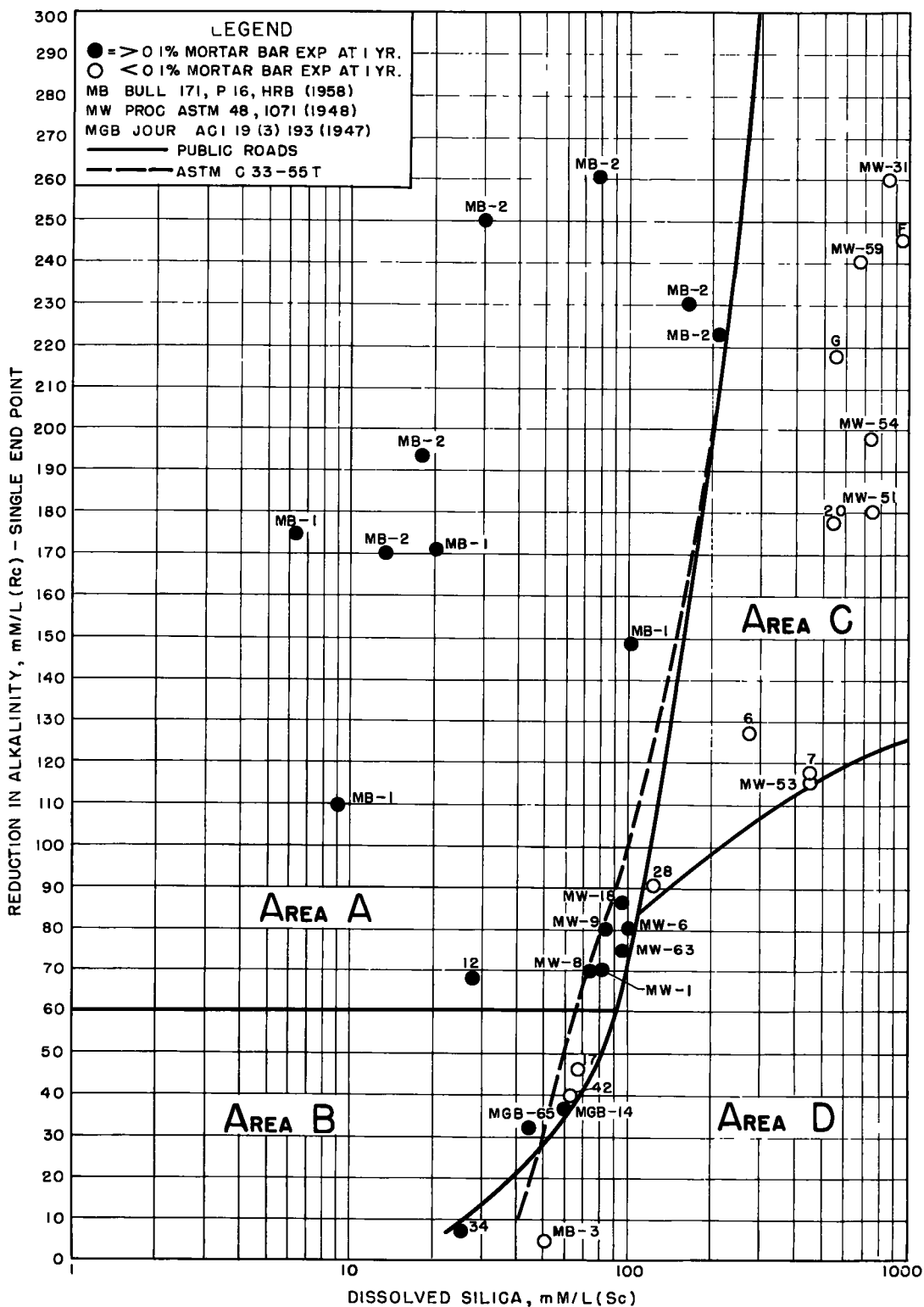


Figure 3. Location of chemical test results that fail to correlate with mortar bar tests or different criteria.

The different positions of the two lines may be partially explained on the basis of the cements used in the mortar bar tests. The high-alkali cements in this study had an equivalent alkali content of less than 1.0 percent. The data given by Mielenz and others (3, 7), which provided the major basis for the ASTM line, was obtained with a cement of 1.38 percent equivalent alkali. Such differences in cement alkalies could cause a borderline aggregate to produce expansions less than 0.1 percent in one case and greater than 0.1 percent in the other. This, of course, would affect the position of any boundary line which is empirically drawn to best separate reactive from non-reactive aggregates.

To establish a suitable boundary line for general use, the following considerations were taken into account:

1. The present ASTM line occupies a more conservative position with respect to the Public Roads line in that there would be less danger of the nonreactive area containing chemical results of unsafe aggregates.
2. Samples MW-1, 8, 9, 18, 63 and MGB-14 were reported as causing deterioration in field concrete (3). Consequently such aggregates should properly appear to the right of any dividing line.
3. Sample No. 42 in this study showed 0.08 percent expansion at 1 year and could conceivably have given 0.1 percent expansion with a higher alkali cement.

In view of these considerations, the present ASTM line is preferable, except that the lower portion should be adjusted to indicate clearly the deleterious nature of aggregates 34 and MGB-65. This can be accomplished by changing the slope of the ASTM line below an Rc value of 40. When Rc has a value of 10 to 40, the formula for the adjusted line is as follows: $\log Sc = 1.2553 + .01213 Rc$.

Figure 4 shows the proposed change in the ASTM line between Rc = 40 and Rc = 10. All available published data were reviewed with respect to this change and only one conflict was observed. This is the aggregate shown as MB-3 in Figure 3. This material was a synthetic opal-quartz mixture with 0.1 percent opal which failed to show excessive mortar expansion (9). Its position is anomalous, even with respect to the original unchanged ASTM line, and no explanation of its position is attempted here.

Areas A and B

The left portion of Figure 3 was evaluated, disregarding the above-mentioned aggregates which had to do with the location of the main boundary line. It can be seen that all the discrepancies (aggregates which produced mortar expansion) are in the upper portion of this area. No discrepancies appear below an Rc level of 60, therefore this value can be used to divide this part of the figure into two areas, A and B. In each case, the anomalous result shown in area A represents an aggregate which contains constituents which are known to interfere in the chemical test. Sample 12 contained dolomite, MB-1 contained various dilutions of opal in dolomite, and MB-2 various dilutions of opal in serpentine.

On the basis of the available data, area B should be clearly indicative of safe aggregates. Chemical results appearing in this area should be reliable and no further tests are required. Aggregates that appear in area A will also generally be safe, however the presence of interfering minerals such as dolomite and serpentine may at times result in an unsafe aggregate appearing in area A. Consequently, all aggregates that fall in area A should be evaluated further for the presence of either reactive constituents or interfering minerals. In cases of doubt, mortar bar tests should be made on such aggregates.

Areas C and D

The right portion of Figure 3 was similarly evaluated. All discrepancies appear in the upper portion of this area. Consequently, this portion of the figure may be divided into two areas, C and D. No discrepancies appear in area D, therefore chemical results that would appear in this area should be indicative of unsafe aggregates which are capable of producing excessive mortar expansion. No further tests on such aggregates would be necessary.

Area C contains numerous aggregates that did not produce mortar expansion (clear symbols). Of course, this area also contains unsafe aggregates (Fig. 1). Therefore, the purpose of area C is to focus attention upon those aggregates requiring special investigation as a result of the chemical test data.

All the aggregates in the upper portion of area C (Fig. 3) do in fact produce excessive mortar expansion when diluted to very small concentrations with inert material. F is a 50-50 opal-Ottawa sand mixture; G and MW-59 are undiluted siliceous magnesium limestones from California; and MW-31 is an undiluted rhyolite tuff from Colorado.

On the other hand, several of the aggregates in the lower portion of area C, namely MW-51, 53, and 54, will cause excessive and maximum mortar bar expansion when present in about 20 percent concentrations with inert material (7). It may be that aggregates 6, 7, and 20 (from this study) are of a similar nature and might have shown unsafe expansion upon dilution.

Consequently, chemical results which appear in area C suggest a highly reactive material, but do not necessarily preclude that all such materials will produce excessive mortar expansion. The ability to produce unsafe expansion will depend largely on the proportion of reactive constituent present. Therefore, all aggregates which yield chemical data in area C should be carefully examined by mortar bar tests. They should be tested in dilutions of 5, 10, 20, etc., percent with inert materials, as well as in their entirety. This procedure is especially important where local shortages or special conditions require that aggregates from different sources be blended to make concrete.

SUMMARY OF NEW AREAS AND BOUNDARY LINE

Figure 4 summarizes the significance of each of the proposed areas in evaluating chemical test results. It also shows the main ASTM boundary line, which has been modified at the lower end as discussed earlier.

The location of all boundary lines is, of course, empirical in nature, and dependent exclusively upon available mortar bar and chemical test data. The location of such boundary lines may require minor adjustments as new data becomes available in the future. In addition, the limited reproducibility of the mortar bar and chemical tests, as reported by the Corps of Engineers (10, 17) always raises some doubt as to the precise location of any dividing line. Consequently, marginal chemical test results, especially near the main boundary line, should be interpreted with some reservation.

Nevertheless, the present criteria (Fig. 4) should broaden the usefulness of the quick chemical test and in many cases eliminate the need for supplementing the chemical test with a long-term mortar bar test program or tedious petrographic analysis.

In one respect, the chemical test offers a unique advantage over the exclusive use of the mortar bar test. This is for aggregates that appear in area C (Fig. 4). The concrete engineer may obtain a false sense of security from a satisfactory (safe) mortar bar test result on such aggregates. However, it is possible for certain of these materials actually to cause deterioration in concrete if blended with other relatively inert aggregates. The chemical test result would indicate the need for more careful evaluation of such materials.

CONCLUSIONS

1. The chemical test for the potential reactivity of aggregates (ASTM C289-57T) generally shows good correlation with the results obtained by mortar bar tests.
2. The dividing line established by this study, for separating reactive from non-reactive aggregates by means of the chemical test, agrees fairly well with those proposed by ASTM Specification C33 and the Corps of Engineers.
3. Neither the single nor double end point titration, permitted by the ASTM chemical test method, offers any distinct advantage over the other in evaluating the potential reactivity of aggregates.

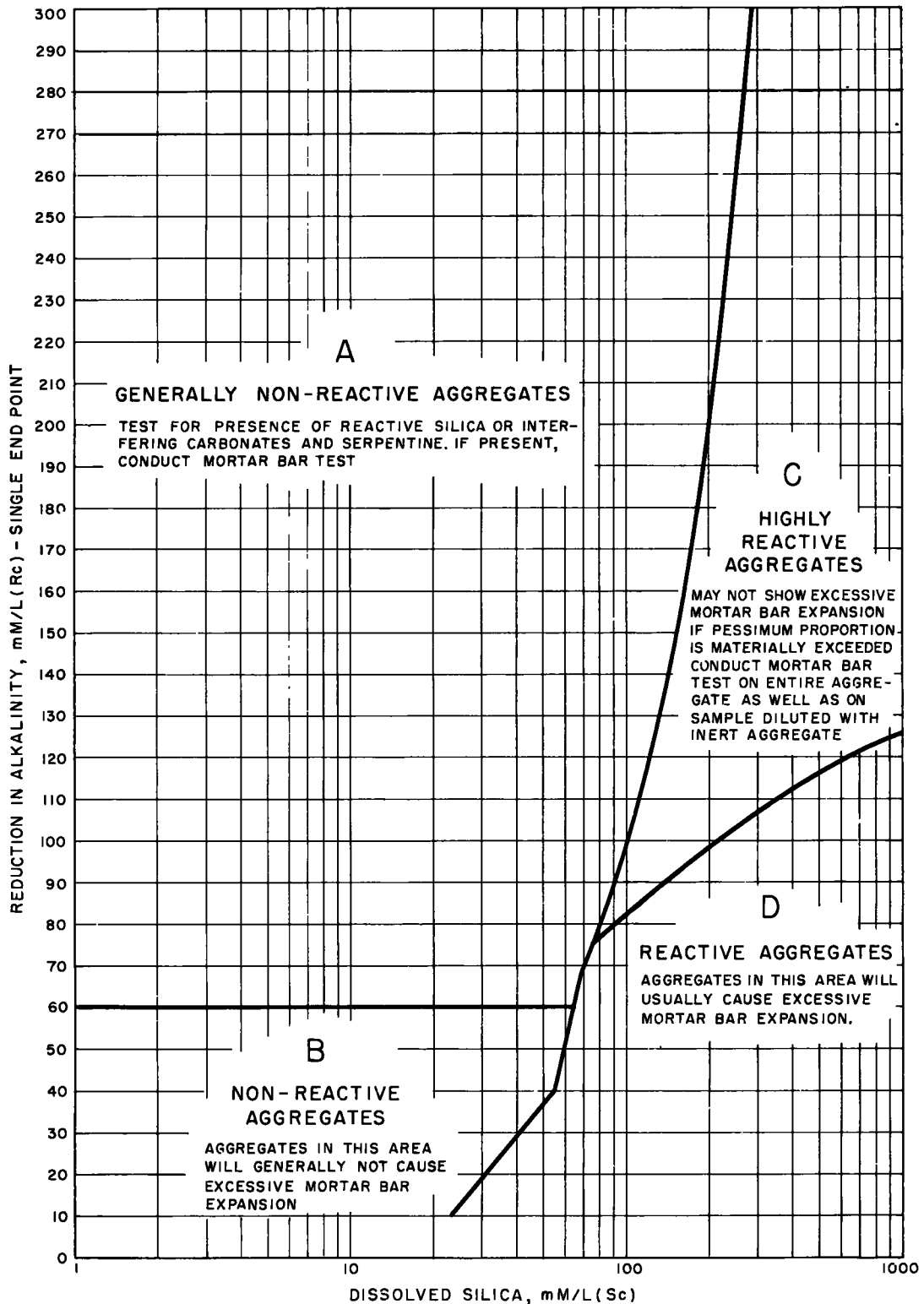


Figure 4. Evaluation of results of chemical test for potential reactivity of aggregates.

4. Reliable results are not always obtained in the chemical test when certain carbonates or serpentine minerals are present. An empirical division of the chemical test results is proposed which would serve to isolate such interferences and thereby indicate which aggregates require further study. This procedure would eliminate the need for additional time-consuming tests on many satisfactory aggregates.

5. Highly reactive aggregates may be classified as reactive in the chemical test and and yet fail to produce mortar expansion. An additional empirical division of the chemical test results is suggested which would serve to identify such aggregates. It is believed that many such aggregates may actually become dangerous in concrete if diluted with inert aggregates. The proposed division would focus attention upon those aggregates requiring special investigation.

6. A modification of the ASTM main boundary line is proposed as part of the general criteria for chemical test results. The adjusted line conforms more realistically to available data.

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