Improvement of Soil-Cement with Chemical Additives

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The search for chemical additives to improve the properties of soil-cement has been carried out intensively at the Massachusetts Institute of Technology Soil Stabilization Laboratory during the past few years. Previous papers have described the effectiveness of a group of alkali metal compounds in improving the properties of a spectrum of cement-stabilized soils of widely different origins, degrees of fineness, and mineralogical and chemical compositions. A general pattern of behavior was established whereby the most effective additive type and concentration for a particular soil type could be designated.

This paper summarizes the most recent results obtained from further detailed study on the use of alkali additives in soil-cement. Salient results presented include the following:

1. Study of the long-term effects of immersion in sulfate solution on four cement-stabilized soils indicates that sodium additives materially improve the resistance of soil-cement to possible sulfate attack. The four soils studied included a clean sand, a clay, a sand containing organic matter, and a silty clay with high soluble salt content.
2. Calcium and magnesium sulfates, in addition to sodium sulfate, are found to be very effective in increasing the strength of organic sand-cement.
3. Attempts to find a general formulation of sodium additives for all soil types by combining sodium hydroxide and sodium sulfate at various molar ratios have not been successful.
4. Pretreatment of heavy clays with small quantities of polyvalent metal salts and salts of organic cations improves their response to cement-additive stabilization by reducing the expansion of the montmorillonitic soils in water immersion.
5. Study of the effects of soda-to-silica ratio in sodium silicate when used as an additive to cement-stabilized silt indicates that the silicates of high soda content are very effective in strength improvement.

● RESEARCH on improving the properties of soil-cement by the use of chemical additives has been carried out intensively at the Massachusetts Institute of Technology Soil Stabilization Laboratory during the past few years. Two of the primary objectives of the investigation are (1) to increase the effectiveness of portland cement as a soil stabilizer so as to reduce the quantity of cement required to treat responsive soils and (2) to find trace chemicals that will enhance the effectiveness of cement as a stabilizer for "problem" soils; i.e., those that cannot be stabilized economically with cement alone. Previous papers by the authors (1, 2) have described the unique effectiveness of a group of metal alkali compounds in improving the properties of a spectrum of cement-stabilized soils of widely different geological and geographical origins and widely different physical, mineralogical, and chemical compositions. A general pattern of behavior was established whereby the most effective additives for a particular soil-type of known composition could be designated with an element of assurance. Based on the soils studied, at that time were the following general findings:

1. Sodium hydroxide is effective in improving strength of all soils with low to moderate amounts of organic matter.
2. Sodium salts of weak acids are not effective in heavy clays.
3. Sodium sulfate is uniquely effective on sandy soil containing organic matter.
4. The effectiveness of sodium compounds decreases with increasing plasticity and/or organic matter content of the soil.

This paper describes the most recent results obtained from further laboratory studies on the use of alkali additives in soil-cement.

The research summarized herein covers the following topics:

1. Examination of the long-term effects of sulfate on the stability of cement-stabilized soils with and without additives.
2. Evaluation of other sulfate compounds (calcium and magnesium) as additives to organic sand-cement.
3. Investigation of the possibility of a general formulation of additives for all soil-types.
4. Examination of the use of secondary additives to improve the effectiveness of sodium hydroxide in cement-clays.
5. Examination of the effect of soda-to-silica ratio in sodium silicate as an additive to soil-cement.

MATERIALS AND PROCEDURES

Materials

Soils. The seven soils employed in the five studies reported in this paper were selected from the large number of soils investigated previously. Their response to the treatment of alkali sodium additives and portland cement has been established (2, 3).

Four soils were chosen for the examination of sulfate attack on soil-cement: a sand - Wisconsin Sand 2 (1057), a clay - Iraq Clay 2 (1067), a silty clay with high soluble salt content - Iraq Silty Clay (1068), and a sand containing organic matter - Wisconsin Sand 1 (1056).

The response to cement stabilization of the organic sand (Wisconsin Sand 1) was further examined by incorporating one of several sulfate compounds other than sodium sulfate as an additive. Study of the effect of soda-to-silica ratio in sodium silicate when used as an additive was carried out with New Hampshire Silt, the soil least complex in composition and most responsive to treatment.

Two heavy clays, Texas Clay 2 (1059) and Vicksburg Buckshot Clay (VBC), were selected for evaluation of secondary additives to improve their response to cement-sodium additive treatment.

The three soils selected for investigation of the possibility of a general formulation of sodium additives (i.e., mixtures of sodium hydroxide and sodium sulfate) for all soil types were New Hampshire Silt, Wisconsin Sand 1, and Texas Clay 2.

The properties of all seven soils tested are summarized in Table 1.

Cement and Additives. Type 1 portland cement was used: Table 2 summarizes its properties. For most of the tests, 5 percent (on dry soil weight) was used.

Table 3 lists the additives employed in the investigation. Selection was based on observations from earlier studies. In addition to the primary additives, several polyvalent metal salts and salts of organic cations were investigated as a means for reducing the lattice expansion of heavy clays on immersion. These compounds are listed as secondary additives.

TABLE 1

PROPERTIES OF SOILS INVESTIGATED

	New Hamp. Silt	Vicksburg Buckshot Clay	Texas Clay 2	Iraq Clay 2	Iraq Silty Clay	Wis. Sand 1	Wis. Sand 2
	NHS NHS	VBD VBC	TCI 1059	Ircl 1067	IrSC 1068	WS 1 1056	WS 2 1057
Textural composition[a] (% by wt)							
Sand, 0.06 to 2mm	3	4	3	17	13	82	85
Silt, 0 002 to 0.06mm	90	61	28	46	62	18	15
Clay, < 0.002mm	7	35	69	37	25	0	0
Physical property							
Liquid limit (%)	28	60	71	39	31	---	---
Plastic limit (%)	20	28	42	20	20	---	---
Plasticity index (%)	8	32	29	19	11	N P.	N. P.
Specific gravity, 20°c/20°c	2.72	2.67	2.71	2.72	2 80	2.64	2.64
Max. dry density[b] (pcf)	99 5	103.0	94.0	106.3	110 5	102.0	103.0
Optimum water content (%)	19 9	22.0	25.8	19 5	16.6	14.2	12.5
Classification							
Unified	ML	CH	OH	CL	CL-ML	SM	SM
Bur. Pub Roads	Silty Loam	Clay	Clay	Clay	Silty Clay	Sand	Sand
Hwy Res. Board	A-4(8)	A-7-5(19)	A-7-5(20)	A-6(12)	A-6(9)	A-2-4	A-2-4
Chemical Property[c]							
Organic matter (% by wt)	0 4	1.1	2.9	0 9	1.3	1.9	0.2
pH	5.4	4.6	7.3	7.5	7.2	6.7	6.2
Carbonates (% by wt)	---	---	---	27	50	---	---
Total soluble salts m eg NaCL/100gm	---	0.3	1.6	1.7	73.0	0.1	0.1
Cation ex. capacity m eg/100 gm	3	30	27	20	16	16	10
Glycol retention (mg/gm)	6	65	93	45	88	32	24
Mineralogical composition[c]							
Clay composition (% by wt)	10	50	65	45	30	0	0
Illite montmorillonoid clay chlorite	1 0 0	1·1 0	3 2.5 1	1 1 1	1·2 1	---	---
Chlorite, nonclay (%)	---	---	---	15	15	---	---
Calcite (%)	---	---	---	30	50	---	---
Free iron oxide (%)	1.0	1 9	2.0	1.0	1.3	---	---

[a]Massachusetts Institute of Technology Soil Classification.

[b]Harvard Miniature Compaction, 40-lb tamper, 3 layers, 25 blows per layer.

[c]For minus 74 micron fraction.

TABLE 2

COMPOSITION[1] OF CEMENT USED

Composition	% by Weight
Silica, SiO_2	19.78
Aluminum oxide, Al_2O_3	5.54
Ferric oxide, Fe_2O_3	3.45
Calcium oxide, CaO	62.59
Magnesium oxide, MgO	3.90
Sulfuric anhydride, SO_3	2.25
Sodium oxide, Na_2O	0.25
Potassium oxide, K_2O	0.71
Manganese oxide, Mn_2O_3	0.07
Insoluble residue	1.30
Loss on ignition	0.08
Specific surface (Blaine)	3270 sq cm/gm

[1]Analyzed by Analytical Laboratories, Portland Cement Association.

TABLE 3

CHEMICAL ADDITIVES TESTED

Additive	Formula	Source
Primary additive:		
Sodium hydroxide	NaOH	Reagent grade
Sodium sulfate	Na_2SO_4	Reagent grade
Sodium orthosilicate	Na_4SiO_4	Diamond alkali Co
Sodium silicate, grade 50	Na	
(43.5% solid)	$NA_2Si_2O_5xH_2O$	Diamond alkali Co.
Sodium silicate, grade 40 (37.5% solid)	$NA_2Si_{3.22}\ O_{7.44}\ x\ H_2O$	Diamond Alkali Co.
Sodium metasilicate	$Na_2SiO_3\ 9H_2O$	Reagent grade
Magnesium sulfate	$Mg\ SO_4$	Reagent grade
Calcium sulfate anhydrite	$CaSO_4$	Reagent grade
Gypsum	$CaSO_4\ 2H_2O$	Reagent grade
Secondary additives:		
Barium chloride	$BaCl_2$	Reagent grade
Ferric chloride	$FeCl_3$	Reagent grade
n - Octylamine	$CH_3\ (CH_2)_6\ CH_2NH_2$	Sharples Chemical Co.
Arquad 2 HT	Di-hydrogenated tallow dimethyl ammonium chloride	Armour & Co.
Arquad 12	Lauryl trimethyl ammonium chloride	Armour & Co.

Procedure

Strength Tests. All air-dried soils were pulverized and screened through a No. 10 sieve. Each batch of soil was first hand-mixed with half of the molding water and with the secondary additive (when used), and the equilibrated for 24 hours. (This step of equilibration was omitted for the two sandy soils.) A solution or slurry of chemical and cement was mixed into the soil. After equilibration, mixing was completed in a finger-blade mechanical mixer. (Mixing time was 7 minutes for the two Iraq soils and 5 minutes for all others.)

Specimens were molded by two-end static compaction in a Harvard miniature-size mold to constant density. The molding water content and density corresponded approximately to the optimum moisture content and maximum density of the untreated soil-cement or soil.

All specimens were cured under approximately 100 percent relative humidity and room temperature for various periods of time. Specimens were then immersed in distilled water for one day prior to testing to failure by unconfined compression. Weights and dimensions of the specimens were measured both after curing and after immersion.

Sulfate Attack Study. Specimens were prepared as if for the usual strength test and cured for 7 days. Half the samples were then immersed in distilled water and the other half in saturated calcium sulfate solution with excess solid calcium sulfate for various lengths of time and then tested in unconfined compression.

RESULTS AND DISCUSSION

Effect of Sodium Additives on the Resistance of Soil-Cement to Sulfate Attack

This study was aimed at evaluating the effects of sodium additives on the resistance of soil-cement to sulfate attack, inasmuch as several investigators (4, 5) had reported that sulfates are generally as detrimental to soil-cement as to concrete.

Two sets of samples from each of the four soils selected for study were prepared. One set was immersed in saturated calcium sulfate solution and the other in distilled water to study the long-term effects from up to one year of immersion. Figures 1 through 4 compare the strength, density, and water-content changes for each type of soil-cement sample, with or without additives, immersed in water or in sulfate solution.

Sand - Soil WS 2 (1057). The left half of Figure 1 shows that the soil cement samples (with ten percent cement, no additive) immersed in sulfate solution absorbed considerably more water and suffered more swelling (as shown by dry density decrease) than those immersed in pure water. The continuous increase in strength and the relatively small volume change of samples immersed in water indicate that prolonged immersion does not have any detrimental effect on soil-cement. The large and continuous decrease in the sulfate-immersion strength after 28 days, however, along with large volume expansion, clearly indicates the detrimental effects of the sulfate.

On the other hand, the right half of Figure 1 shows that the sulfate-immersion strength of the sodium metasilicate-treated samples (with 7 percent cement) continued to increase up to 90 days of immersion, with very little swelling and water pickup. The drop in strength after 90 days indicates that the sodium metasilicate in this sand-cement greatly delays or reduces the deteriorating effects of the sulfate; in other words, the additive prolongs the life of soil-cement. After 1 year of immersion in the sulfate solution, the strength was still higher than the early strength of the untreated soil-cement.

Clay - Soil IrC 2 (1067). The differences in the behavior of the clay-cement with and without the additive, when immersed in either water or sulfate solution, were not as pronounced as in that of the sand-cement. Figure 2 shows that sulfate has no adverse effect on the strength development of either soil-cement or soil-cement-sodium hydroxide systems. However, the soil-cement (no additive) swelled slightly more when immersed in sulfate solution than in water, while the reverse was true for soil-cement-sodium hydroxide samples. Furthermore, strengths of additive-treated soil-cement were higher than untreated at all immersion ages and in both solutions.

Soils with High Soluble Salt Content - Soil IrSC (1068). Results of Iraq Silty Clay with 10 percent cement, with and without 1.0 Normal sodium hydroxide, are shown in Figure 3. This soil, due to its high salt content, showed considerable water absorption during curing and loss of dry weight during immersion, as was described previously (2).

The general behavior of this soil after prolonged immersion in either water or sulfate solution was similar to that described for the Iraq Clay 2. Sulfate did not a detrimental effect on the soil-cement with or without additive up to 1 year of immersion.

Sand Containing Organic Matter - Soil WS 1 (1056). The results obtained with Wisconsin Sand 1, shown in Figure 4, are extremely interesting. The sulfate, rather than being detrimental to the soil-cement, appears to be beneficial. The strengths of soil-cement (no additive) samples immersed in sulfate solution were much higher than those immersed in water. The strengths after 28 days immersion in sulfate solution were the same for soil-cement with or without additive (10 percent cement plus 1.0 Normal sodium sulfate with additive and 16 percent cement without additive), while the strength after 1-day immersion was very low in the case of untreated soil-cement compared to the sulfate-treated samples.

Effect of Magnesium and Calcium Sulfate on the Strength of Organic Sand WS 1 (1056)-Cement

Earlier test results (2) had shown clearly that the poor response of the Wisconsin Sand 1 to cement and alkali additive treatment (except sodium sulfate) was due solely to the presence of the organic matter in the sand. The addition of sulfate ions appeared to depress the reactivity of the organic components. Also, as noted in the preceding section (on Figure 4), cement WS 1 immersed in saturated calcium sulfate solution was found to develop much higher strengths than that immersed in water. Hence, it was logical to examine other sulfate compounds in addition to sodium sulfate as additives to organic sand-cement. Sulfate compounds included in this investigation were anhydrous calcium

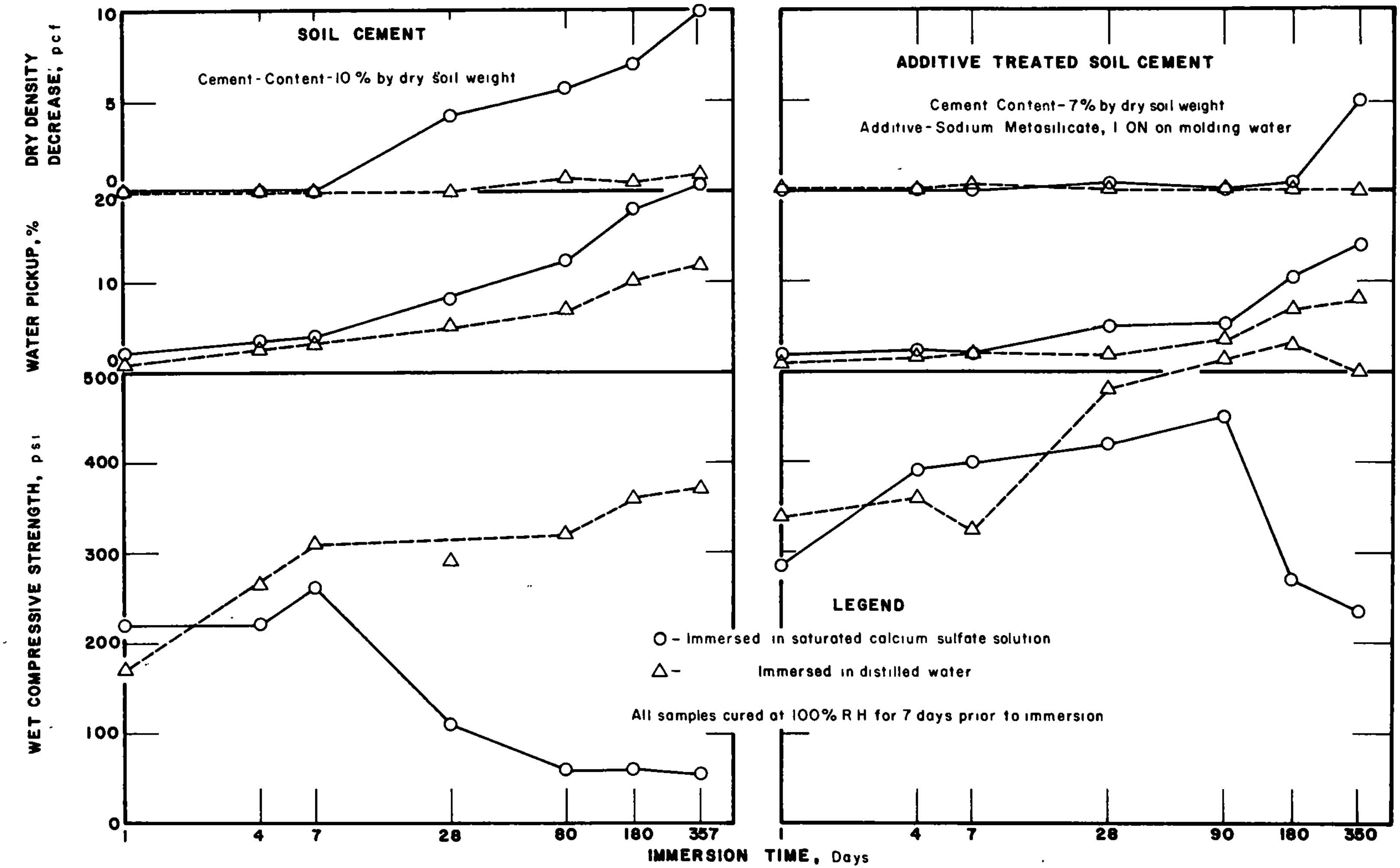

Figure 1. Strength, density, and water-content changes of cement-stabilized Wisconsin sand 2 (1057) immersed in water and in sulfate solution.

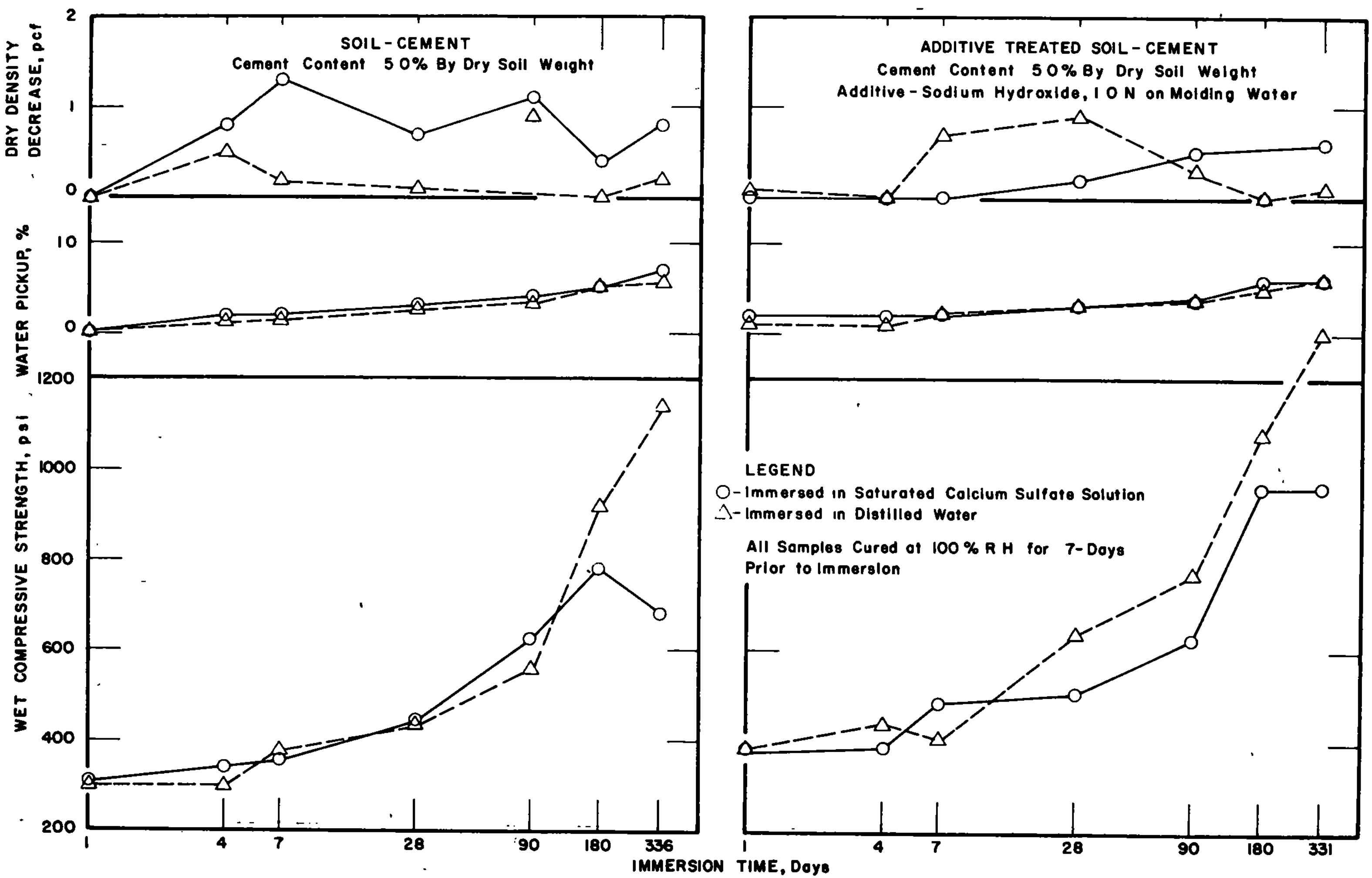

Figure 2. Strength, density, and water-content changes of cement-stabilized Iraq clay 2 (1067) immersed in water and in sulfate solution.

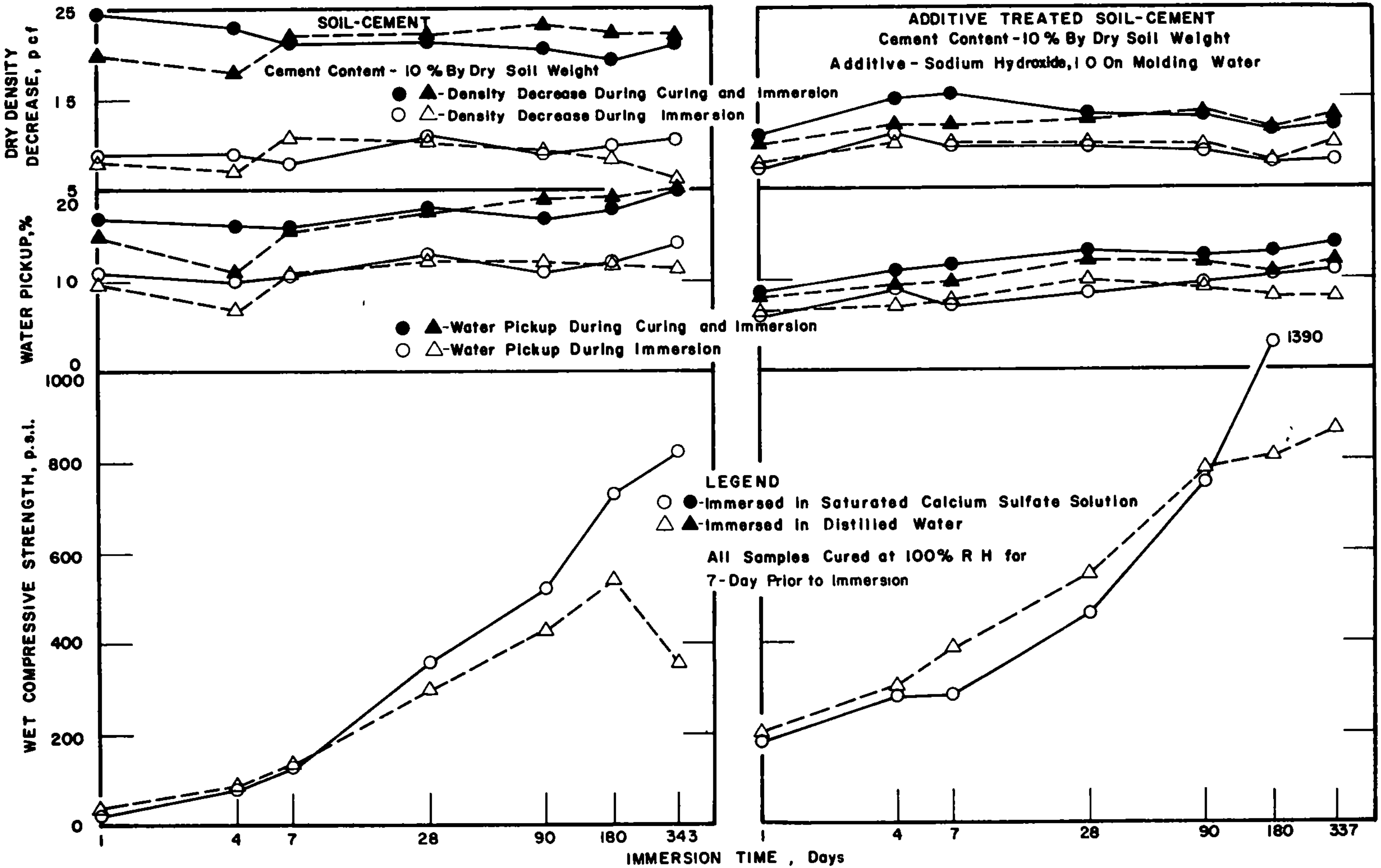

Figure 3. Strength, density, and water-content changes of cement-stabilized Iraq silty clay (1068) immersed in water and in sulfate solution.

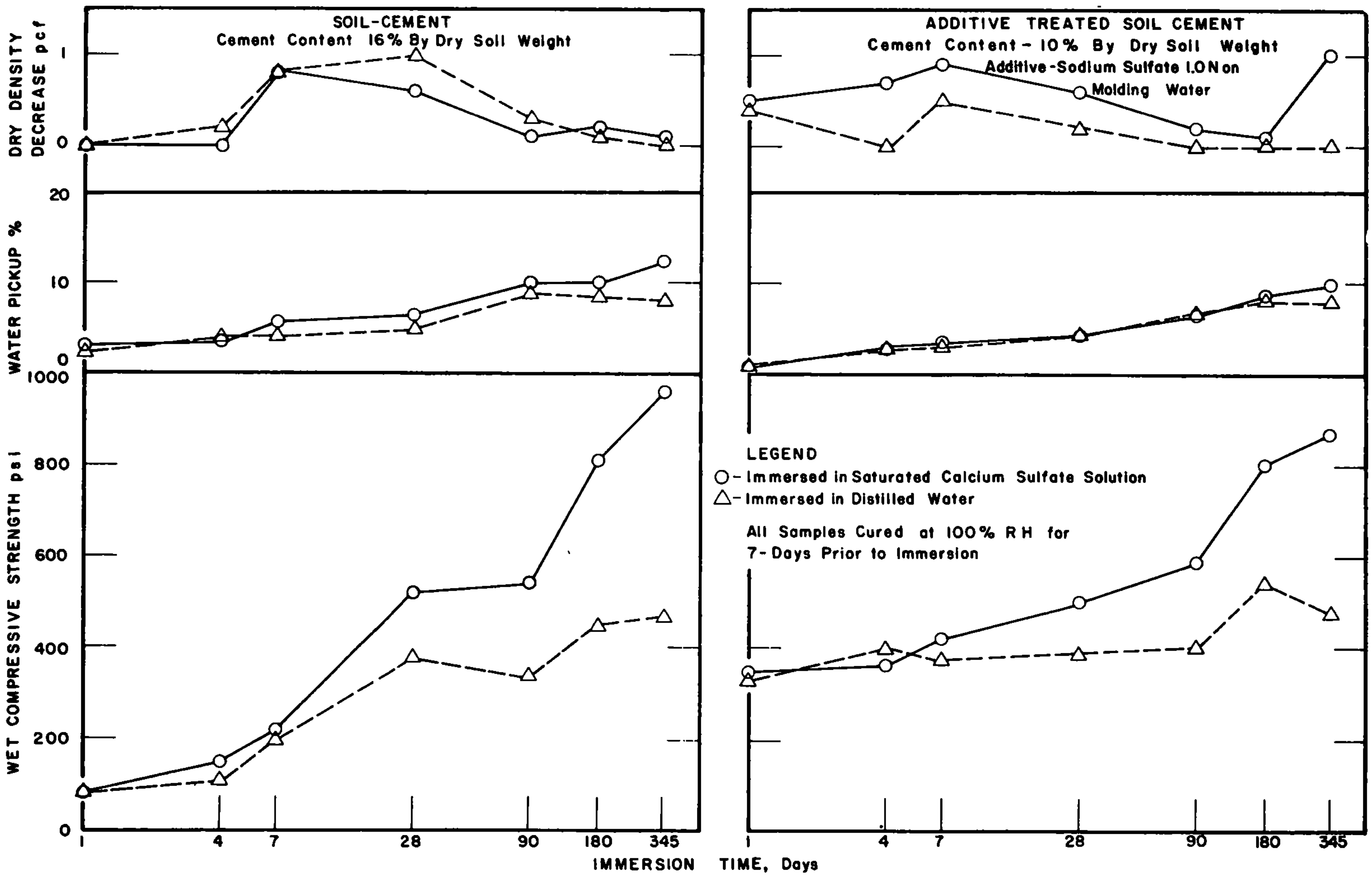

Figure 4. Strength, density, and water-content changes of cement-stabilized Wisconsin sand 1 (1056) immersed in water and in sulfate solution.

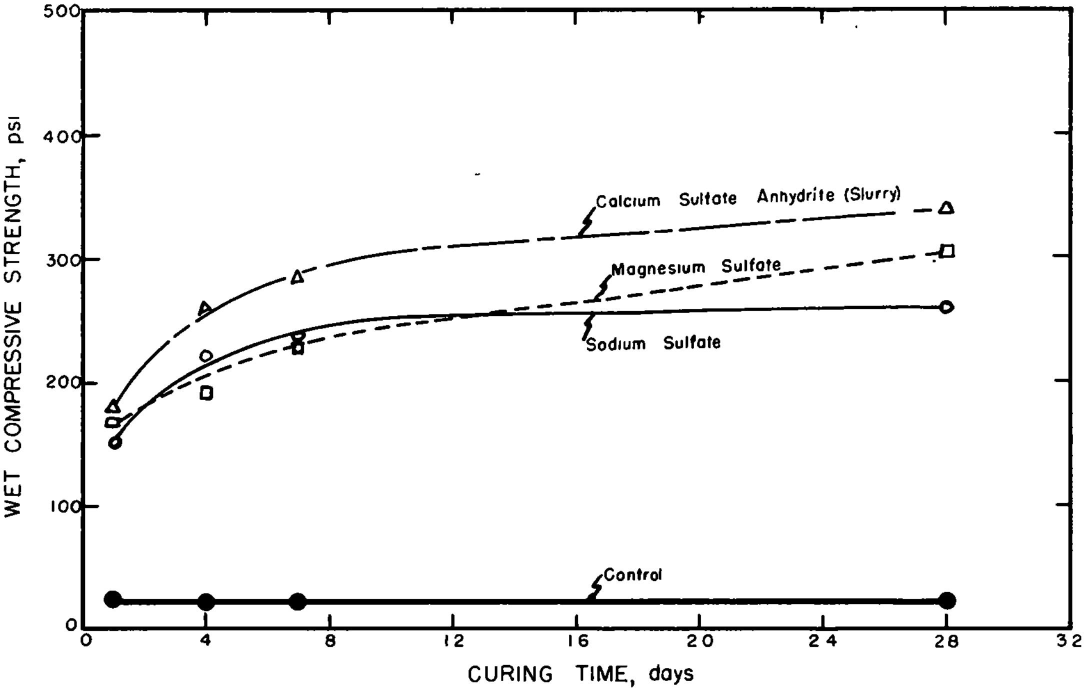

Figure 5. Effect of three sulfate compounds at 0.5 N concentration on the strength of Wisconsin sand 1 (1056) with 10 percent cement.

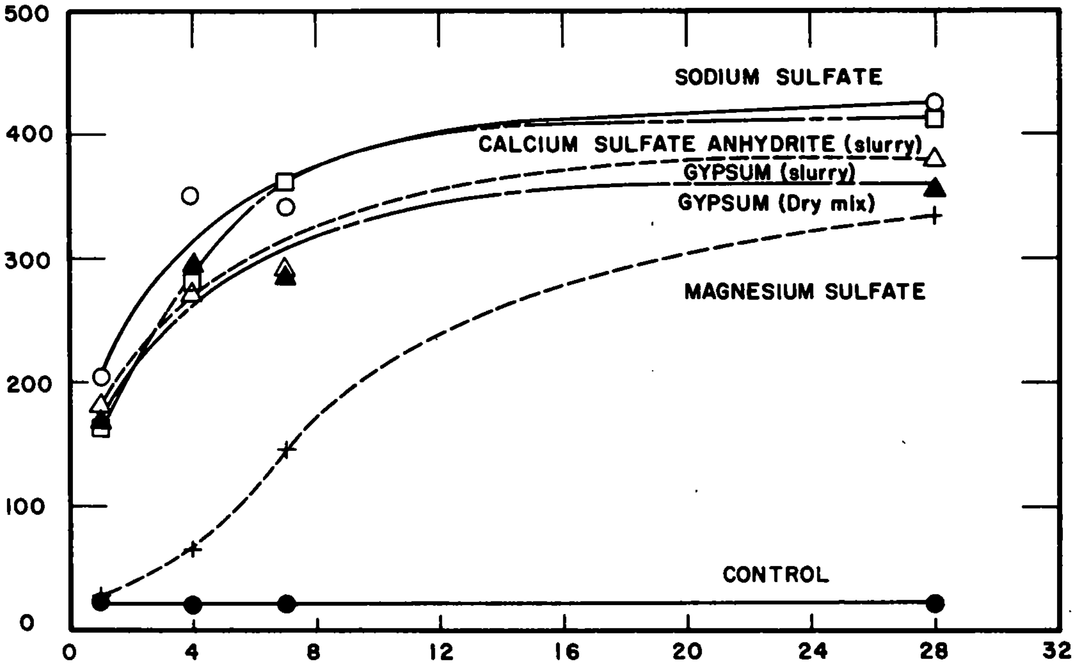

Figure 6. Effect of four sulfate compounds (1.0 N) on the strength of Wisconsin sand 1 (1056) with 10 percent cement

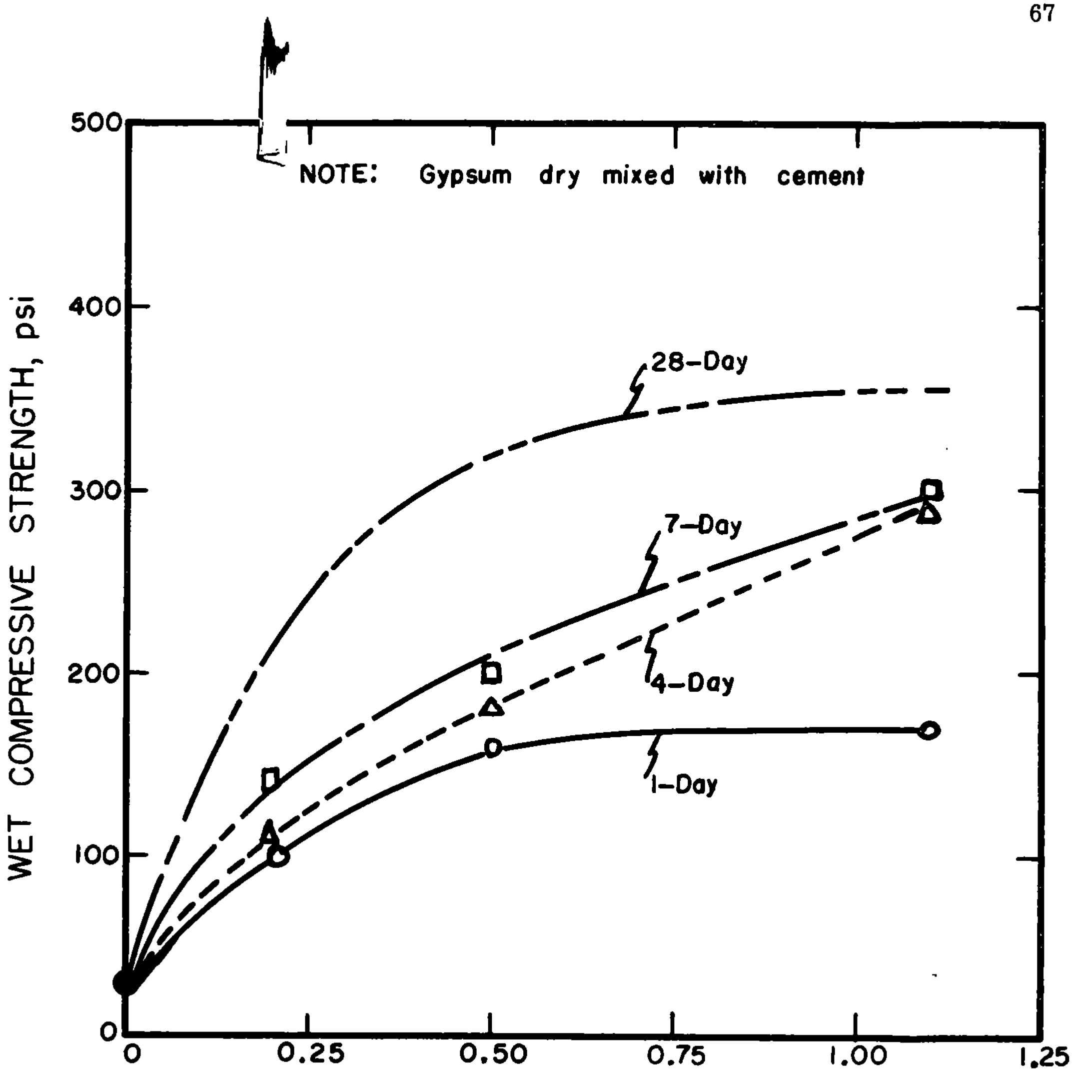

Figure 7. Effect of concentration of gypsum on strength of Wisconsin sand 1 (1056) with 10 percent cement.

sulfate, calcium sulfate hydrate (gypsum), and magnesium sulfate. As the two calcium sulfates are insoluble in water, incorporation as a water slurry and as a dry powder mixed with the cement were both investigated.

At 0.5 Normal concentration, as shown in Figure 5, both magnesium sulfate and a hydrous calcium sulfate (slurry) produced higher strength than sodium sulfate, particularly after 28 days of cure. Furthermore, calcium sulfate was more effective than magnesium sulfate. At higher additive concentration, i.e., 1.0 Normal (Figure 6), the anhydrous calcium sulfate gave about the same results as sodium sulfate, and gypsum slurry gave a somewhat lower 28-day strength. The magnesium sulfate was not only the least effective (28-day strength, about 25 percent lower than sodium sulfate) but it also retarded strength development considerably.

With both anhydrous calcium sulfate and gypsum, the dry-mix process produced slightly lower strength than the slurry, but both processes were very effective. From the economic standpoint, it is rather significant that gypsum dry-mixed with cement is an effective additive to organic sand-cement, inasmuch as several cement manufacturers

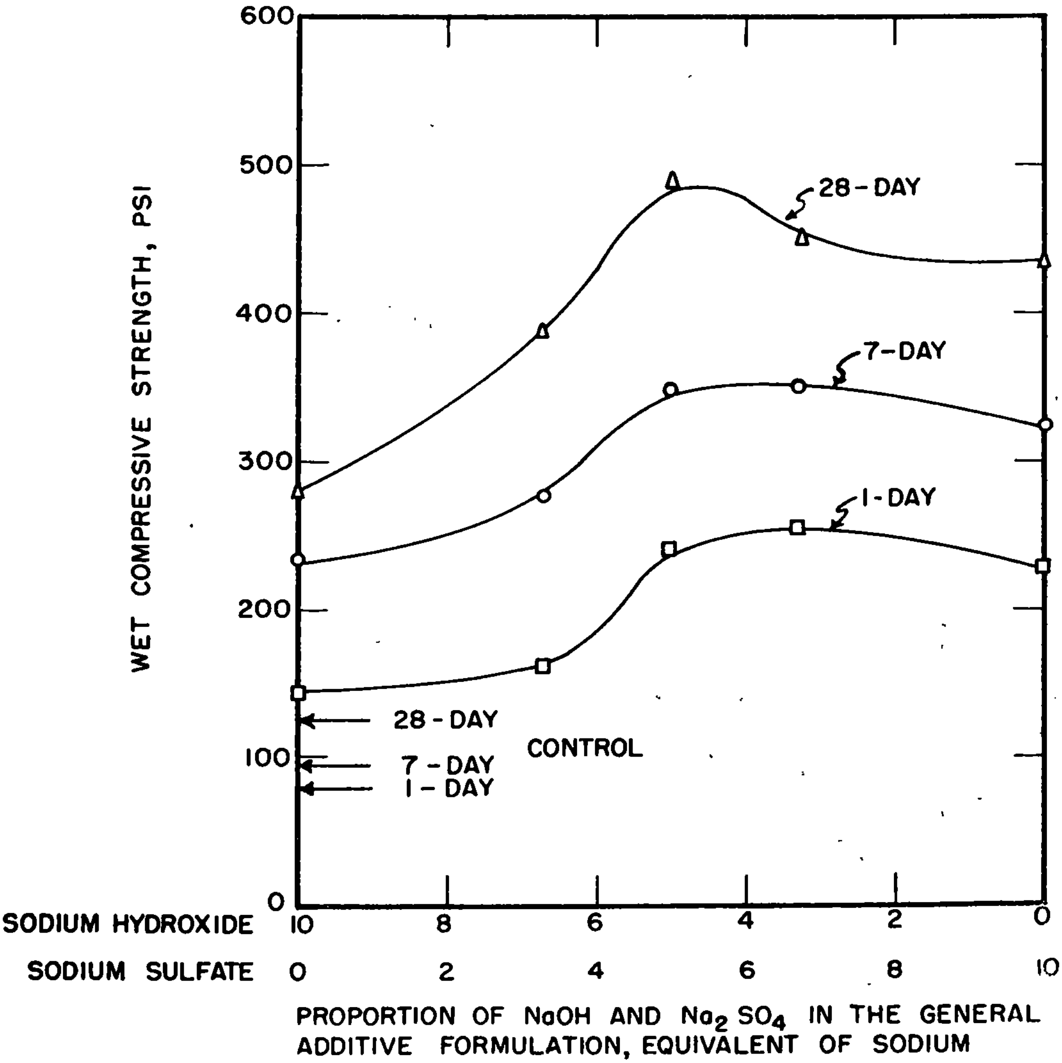

Figure 8. Effect of general additive formulation on strength of cement—New Hampshire silt (NHS); cement content = 5.0% on dry soil weight, additive concentration = 1.0 N sodium in molding water.

produce high-gypsum cement. Gypsum was further investigated by using various percentages of gypsum dry-mixed with the cement. Figure 7 shows that the strength of gypsum-cement WS 1 increased with gypsum content (at the same cement level) up to 1 percent.

Effectiveness of Mixtures of Sodium Hydroxide and Sodium Sulfate as a Possible General Additive Formulation for All Soil Types

Previous results (3) have shown that the effectiveness of a particular additive to soil-cement is largely dependent on the soil in question. In a summary by Lambe, Michaels, and Moh (2), sodium hydroxide was reported as the only beneficial additive to clay-cement; on the other hand, sodium sulfate was reported uniquely effective on sandy soil containing organic matter. Therefore, it appeared desirable to investigate the possibility of a general additive formulation for all soil types.

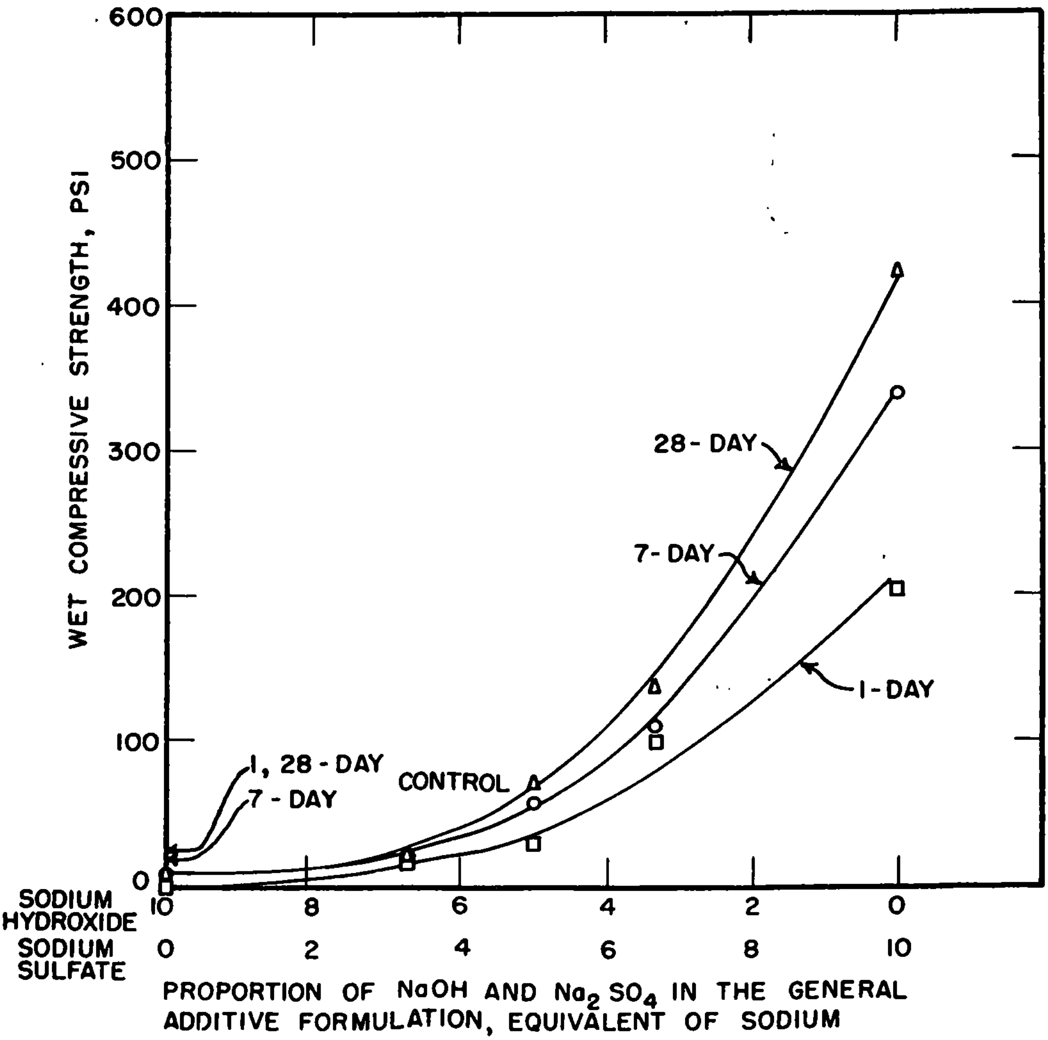

Figure 9. Effect of general additive formulation on strength of cement—Wisconsin sand 1 (1056); cement content = 10.0 percent on dry soil weight, additive concentration = 1.0 N sodium in molding water.

Because sodium hydroxide and sodium sulfate appeared to have contradictory effects on the properties of clay-cement and organic sand-cement, combinations of these two compounds in various proportions were chosen as a possible general additive formulation. The three soils selected, TC 2 (1059), WS 1 (1056), and NHS, represent three types of soils with distinctly different mineralogical compositions, chemical properties, and established responses to additive treatment. The results of this investigation are shown in Figures 8, 9, and 10 for NHS, WS 1, and TC 2, respectively.

The first general observation from these data is that this attempt to find a general additive formulation for all soil types was unsuccessful. The effectiveness of the additive mixture was no greater than that of the active component of the mixture. In other words, the effectiveness of this combination in WS 1 cement increased as the ratio of NaOH to Na_2SO_4 decreased, while the reverse was true for TC 2 cement.

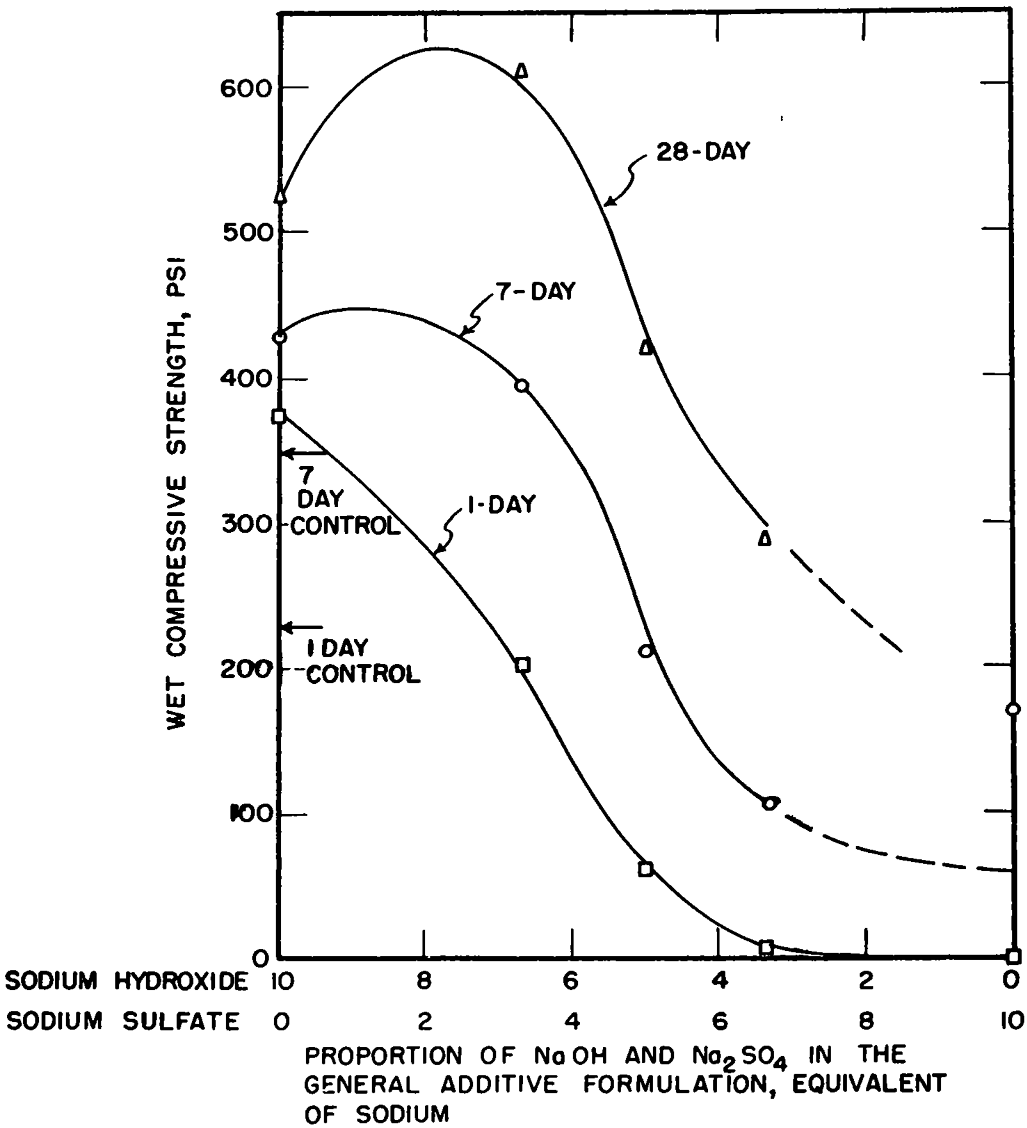

Figure 10. Effect of general additive formulation on strength of cement—Texas clay 2; cement content = 10.0 percent on dry soil weight, additive concentration = 1.0 N sodium in molding water.

Silt - Soil NHS (5 Percent Cement). At the same additive contentration (1.0 Normal of sodium in molding water), the strength of additive-treated specimens increased with a decreasing ratio of hydroxide to sulfate in the additive and achieved optimum effect at a ratio of about one, as shown in Figure 8.

As discussed elsewhere by the authors (2), by adding sodium sulfate to soil-cement the rate of formation of soluble silicate is slower and the calcium solubility in the pore fluid is less suppressed than when sodium hydroxide is added. The processes of formation of soluble silicate and precipitation of calcium silicate gel are gradual and more or less simultaneous. On the other hand, when hydroxide is the additive, there is rapid formation of soluble silicate but delayed gelation by calcium due to the high pH of the

TABLE 4

EFFECT OF SEQUENCE OF ADDITION OF GENERAL ADDITIVE FORMULATION (MIXTURE OF SODIUM HYDROXIDE AND SODIUM SULFATE) ON THE STRENGTH OF CEMENT - WISCONSIN SAND 1

Cement Content = 10.0% on dry soil wt

Total Additive Concentration (N)[a]	Ratio[b] of Na OH to Na_2SO_4 in Additive	Curing Days	Wet Compressive Strength (psi)	Method of Adding Additive
Control	---	1	25±5	
		4	20±0	
		7	19±1	
		28	23±2	
1.0	1 : 1	1	28±1	Together[c]
		4	45±5	
		7	57±6	
		28	71±2	
		1	29±5	Sulfate pretreatment[d]
		4	88±8	
		7	88±10	
		28	95±5	
1.5	1 : 2	1	12±1	Together[c]
		4	14±0	
		7	16±1	
		28	16±1	
1.5	1 : 2	1	176±6	Sulfate pretreatment[d]
		4	267±3	
		7	310±2	
		28	310±50	

[a]Normality of sodium in molding water. [b]Equivalent basis.
[c]NaOH and Na_2SO_4 added mixed solution.
[d]Soil treated with sodium sulfate solution for 24 hours, cement and sodium hydroxide solution.

system. The fact that there is an optimum ratio of hydroxide to sulfate in this silt-cement clearly indicates that there must be a proper balance between the rate of attack of silica by the caustic and the rate of silicate precipitation by calcium in order to obtain both rapid cure and high ultimate strength.

Sand Containing Organic Matter - Soil WS 1 (10 Percent Cement). Figure 9 shows that the effectiveness of the additive increased with a decreasing hydroxide-to-sulfate ratio. It is rather interesting to note that the sequence of addition of reagents has an important effect on the effectiveness of the combined additive; Table 4 illustrates this importance. The first method was to add the combined additive solution as in all other cases; the second method was to pretreat the soil with sulfate solution, then add the cement and hydroxide. The final hydroxide-to-sulfate ratio was kept the same as in the first series. The beneficial effect of pretreating the soil with sulfate was particularly obvious when the additive concentration was increased from 1.0 to 1.5 Normal. These results further indicate that the unique effectiveness of sodium sulfate is due to depressing the reactivity of the organic components in the soil.

Clay - Soil TC 2 (10 Percent Cement). Figure 10 shows that there appears to be an optimum hydroxide-to-sulfate ratio, (about 4 to 1) that gives the greatest increase in strength to the clay-cement. The need of a small portion of sodium sulfate in the additive probably can be attributed to the presence of 3 percent organic matter in this soil.

Use of Secondary Additives to Sodium Hydroxide-Treated Cement-Clays

It has been observed (3) that significant volume changes occur during the curing and subsequent immersion for samples of cement-clays treated with sodium additives. The amount of volume change depends on the curing time and cement content: the shorter the curing time, the more the expansion; and the higher the cement content, the less the volume change. It is believed that the observed expansion on immersion and the attendant deterioration of samples with consequent low strength and ineffectiveness of sodium additives result primarily from partial conversion of the montmorillonoid components of the clays into the highly swelling sodium form. If the montmorillonoids could be converted to a less hydratable form, i. e., rendered less water-sensitive, or be waterproofed while still retaining the beneficial action of sodium hydroxide, higher strengths could be expected. Three types of chemicals were selected as secondary additives in addition to sodium hydroxide. They were polyvalent metal salts, octalamine, and cationic organic compounds, as listed in Table 3. The two clays, TC 2 and VBC, were pretreated with the secondary additive and equilibrated for 24 hours prior to the addition of cement and sodium hydroxide.

Table 5 summarizes the effect of those beneficial secondary additives in improving the properties of the two caustic-treated cement-clays. Figure 11 shows the effect of secondary additives on the strength development of soil TC 2-cement-caustic-mixtures.

For soil TC 2 stabilized with 5 percent cement, pretreatment with 0. 5 percent Arquad 12, 0. 1 percent Arquad 2HT, or 0. 1 percent ferric chloride nearly doubled the effectiveness of sodium hydroxide on this clay-cement, producing strength higher than that with 10 percent cement; while 0. 5 percent of 1. 0 percent n-octylamine, and 1. 0 percent Arquad 12 increased the strength of the clay-cement with 1. 0 Normal caustic about 50 percent. However, none of the secondary additives tested was effective in TC 2 stabilized with 10 percent cement and 1. 0 Normal caustic.

TABLE 5
EFFECT OF BENEFICIAL SECONDARY ADDITIVES[a] ON STRENGTH OF SODIUM HYDROXIDE-TREATED CEMENT-CLAYS

Soil	Cement Content (%)[b]	Sodium Hydroxide Content (N)[c]	Secondary Additive	Secondary Additive Concentration (%)[b]	1-Day Cure: Immersed Compressive Strength (psi)	1-Day Cure: Strength Ratio Treated to Untreated	28-Day Cure: Immersed Compressive Strength (psi)	28-Day Cure: Strength Ratio Treated to Untreated
Texas	5	---	---	---	172	---	184	---
Clay 2	5	1 0	---	---	81	0 47	220	1 20
	5	1 0	Ferric chloride	0 10	235	1 37	390	2 12
	5	1 0	Ferric chloride	1 00	81	0 47	228	1 24
	5	1 0	n-Octylamine	0 50	186	1 08	362	1 97
	5	1 0	n-Octylamine	1.00	255	1.48	335	1 82
	5	1.0	Arquad 2 HT	0 10	100	0 58	390	2 12
	5	1 0	Arquad 12	0.50	208	1 21	423	2 30
	5	1 0	Arquad 12	1 00	293	1 70	364	1 98
	10	---	---	---	229	---	315	---
	10	1 0	---	---	376	1 64	525	1 67
	10	1 0	n-Octylamine	1 00	257	1 13	558	1.77
Vicksburg	5	---	---	---	45	---	107	---
Buckshot	5	1 0	---	---	148	3 29	208	1 94
Clay	5	1 0	Arquad 12	1.00	147	3 27	260	2 43

[a]Soil pretreated with secondary additive prior to addition of cement and sodium hydroxide.
[b]Percent on dry weight of soil
[c]Normality of sodium in molding water.

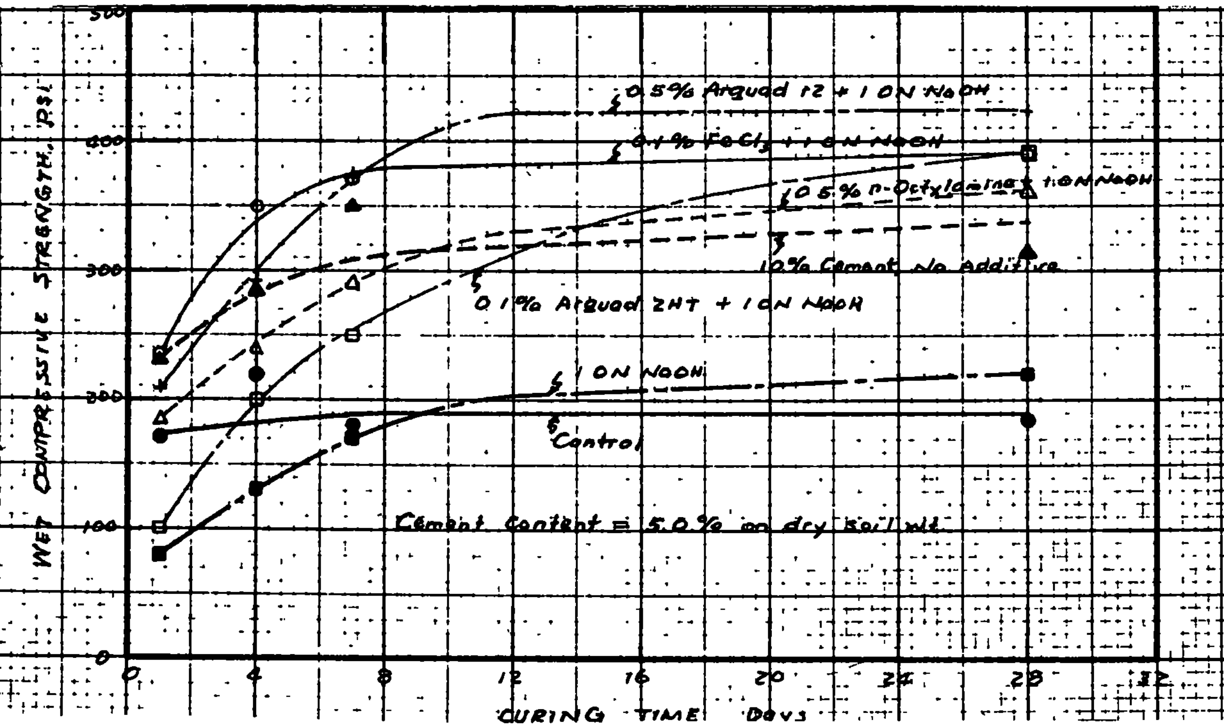

Figure 11. Effect of secondary additives on strength development of Texas clay-cement NaOH—treated.

Except with 1.0 percent Arquad 12, all of the secondary additives have an adverse effect on the strength of caustic-treated VBC-cement; although the measured strengths were higher than the control, they were lower than those obtained with caustic treatment alone. Nevertheless, it was observed that all these secondary additives reduced water pickup and swelling of the samples during immersion, as compared to the control and the caustic-treated samples.

It is noteworthy that the two heavy clays responded to cement and additive treatment to quite different degrees, although in the same direction. A comparison of these two clays shows Soil TC 2 has higher clay content, more organic matter, much higher pH, more soluble salts, and higher glycol retention, but slightly lower plasticity and exchange capacity than VBC. All these differences in properties indicate that Soil TC 2 should be less responsive to cement-additive stabilization. Two possible explanations for the inferior response of VBC are (1) the soil is too acidic or (2) the organic matter though less in quantity, is of a more reactive form than that in Soil TC 2. Furthermore, a more detailed mineralogical analysis was conducted, and the results indicate that in VBC the montmorillonoids are mostly montmorillonites, but in TC 2 they are mostly non-montmorillonites. This difference may be the main factor responsible for the different behavior of the two clays.

Effect of Soda-to-Silica Ratio in Sodium Silicate as Additive on the Strength of Cement-Stabilized New Hampshire Silt

Because the rate of strength development of additive-treated soil-cement depends on the ratio of the alkali silicates to dissolved calcium and because the ultimate strength is a function of the total amount of cementitious material formed, it was reasoned that sodium silicate should be effective in accelerating the cure rate as well as improving the final strength. Sodium metasilicate has been shown to be one of the most effective additives for New Hampshire silt stabilized with 5 percent cement. Besides providing reactive silicates, sodium silicate also raises the pH of the soil-cement mixture and attacks the soil constituents. Therefore, it could be reasoned that the ratio of soda to silica in sodium silicates should have an important effect on the strength development of soil-cement.

Three sodium silicates with soda-to-silica ratios (Na_2SiO_2) varying from 2:1 to 1:3.22 were examined; the results are shown in Table 6 and Figure 12.

TABLE 6

EFFECT OF SODA-TO-SILICA RATIO IN SODIUM SILICATE AS ADDITIVE TO NEW HAMPSHIRE-CEMENT

(Cement Content = 5.0 Percent on dry soil wt)

Additive	Ratio of Na^2O to SiO_2	Additive Concentration (N)[a]	Additive Concentration (%)[b]	Curing Days	Wet Compressive Strength (psi)
Control				1	80±0
				7	95±0
				28	125±5
Sodium orthosilicate	1:0.5 (2:1)	0.50	0.54	1	175±0
				7	200±0
				28	352±8
		1.00	1.03	1	217±15
				7	286±14
				28	491±51
Sodium metasilicate	1:1	0.50	0.60	1	130±5
				7	202±6
				28	305±35
		1.00	1.33	1	135±15
				7	218±7
				28	344±45
Grade 50 silicate	1:2	0.51	1.00	1	123±28
				7	420±10
				28	553±3
		1.00	1.98	1	0[c]
				7	462±0
				28	626±24
Grade 40 silicate	1:3.22	0.40	1.00	1	290±2
				7	386±14
				28	530±35
		1.00	2.80	1	0
				7	40±20[d]
				28	607±23

[a]Normality of sodium in molding water.

[b]Percent of solid on dry soil weight.

[c]Specimens disintegrated upon immersion.

[d]Specimens partially disintegrated in water.

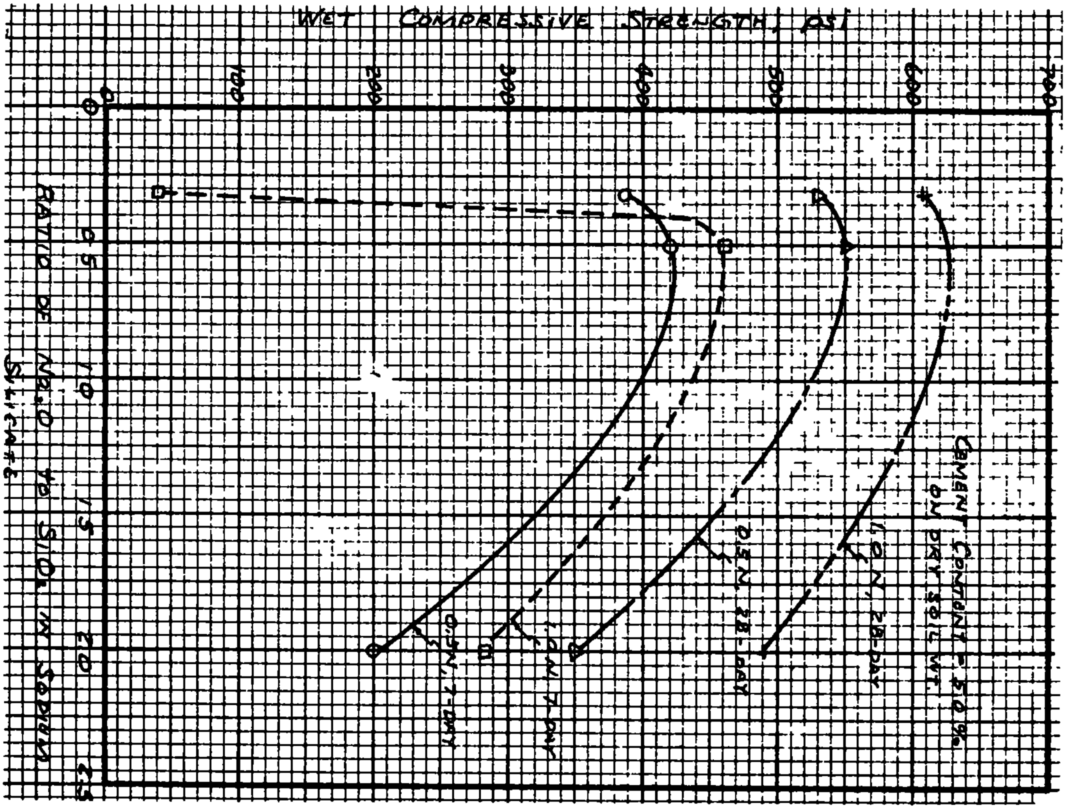

Figure 12. Effect of soda-to-silica ratio in sodium silicate as additive to New Hampshire silt-cement.

Careful examination of the results obtained with the three silicates suggests that, if either the 7-day or 28-day strength is used as a quantitative evaluation of additive effectiveness, there is an optimum soda-to-silica ratio for the most effective sodium silicate additive. This ratio appears to be 1:2 at both 0.5 and 1.0 Normal concentrations. At a given sodium concentration, the higher soda-to-silica-ratio silicate gave higher early strength but lower ultimate strength. The relatively smaller amount of silica added in orthosilicate could probably be readily precipitated by the available calcium. With increasing silica, the rate of diffusion of calcium is not sufficiently fast to precipitate all the alkali silicate in a short period of time. In other words, around the soil particles there are free soluble alkali silicates that have no cementing power. Therefore, a delay of strength development might be expected. On the other hand, the ultimate strength depends on the total quantity of cementitious material, which in turn is a function of the total amount of silicates and calcium available. Higher strength would thus be produced by the lower soda-to-silica silicate (Grade 40). However, the ultimate strength is also limited by the total calcium available, which depends on the cement content; if the amount of silicate added is too high, there is not enough calcium either to precipitate it or to form a low-calcium silicate hydrate, and consequently lower strength would occur. The results with specimens treated with 1.0 Normal Grade 40 illustrate this trend. Therefore, it can be reasonably predicted that the optimum soda-to-silica ratio would move toward a lower value if the cement content were increased.

The results with metasilicate do not fit into the pattern of these three silicates. This may be due to the difference in structure between metasilicate and the other silicates.

CONCLUSIONS

The laboratory test results presented in this paper further indicate the beneficial effects of chemical additives for improving the engineering properties of soil-cement. Detailed conclusions are as follows:

1. Sand-cement (no additive) deteriorates when in contact with sulfate solution; cement stabilized clays are susceptible to sulfate attack only after long periods of contact with concentrated sulfate solution.
2. Sodium additives considerably increase the resistance of all types of soil-cement to sulfate attack.
3. Sulfate compounds are uniquely effective in improving the strength of cement-stabilized sandy soils containing organic matter. At 0.5 Normal concentration, magnesium sulfate and calcium sulfate anhydrite are more effective than sodium sulfate; while at 1.0 Normal concentration, the order of effectiveness of the sulfate compounds is sodium, calcium anhydrite, gypsum, and magnesium.
4. Attempts to find a general formulation of sodium additive for all soil types have not been successful. Results obtained with the general formulations, e.g., combination of sodium hydroxide and sodium sulfate in various proportions, are in the same trend as each chemical used individually.
5. A molar ratio of 1:1 of sodium hydroxide to sodium sulfate appears to be the optimum for increasing strength of NHS with 5 percent cement, and a ratio of 4:1 gives highest strength improvement to TC 2 with 10 percent cement. The strength of WS-1 cement decreases with increased molar ratio of the general additive formulation.
6. The effectiveness of sodium hydroxide in clay-cement can be materially improved by pretreating the heavy clays with secondary additives.
7. Pretreatment with 0.5 or 1.0 percent Arquad 12, 0.1 percent Arquad 2HT, 0.1 percent ferric chloride, or 0.5 or 1.0 percent n-octylamine increases the effectiveness of sodium hydroxide on soil TC 2 stabilized with 5 percent cement, producing strengths higher than that 10 percent cement.
8. The strengths of VBC stabilized with 5 percent cement and 1.0 Normal caustic was not materially improved by use of the secondary additives tested.
9. A soda-to-silica ratio (Na_2O/SiO_2) of 1:2 in sodium silicate (at both 1.0 and 0.5 Normal) appears to be optimum for improving strength of New Hampshire silt with 5 percent cement. Higher soda-to-silica-ratio silicate tends to give higher early strength but lower ultimate strength, while lower ratio silicate retards the cementing process.

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