# Further Evaluation of Promising Chemical Additives for Accelerating Hardening Of Soil-Lime-Fly Ash Mixtures

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The results of an investigation on the effect of several amounts of 12 chemicals on the strength of a mixture of Ottawa sand-lime-fly ash are presented. The effects of four selected chemical additives on the strength of soil-lime-fly ash mixes—including four soils, two limes and three fly ashes—are also presented. An evaluation of competitive mixes of soil-lime-fly ash was made, including freeze-and-thaw studies.

●SINCE 1954 the Engineering Experiment Station Soil Research Laboratory at Iowa State University has been engaged in investigations of lime and fly ash as admixtures for soil stabilization. (Fly ash is an artificial pozzolan, by-product of the power plants burning powdered coal.) Most fly ashes give relatively low early strengths, which has raised the problem of finding an economic means of accelerating the lime-fly ash pozzolanic reaction.

Handy (9, 10), in an investigation of chemical additives in soil-cement, found that immersion of cement-treated specimens in a solution of sodium hydroxide increased their strength about 15 percent. He also discovered that the strength of soil-cement could be increased by addition of sodium hydroxide in the mixing water. In another Iowa State investigation, Goecker et al. (8) observed that calcium chloride was beneficial to the strength of compacted soil-lime-fly ash mixtures. These findings led to an evaluation of 47 chemicals as additives to accelerate the lime-fly ash reaction and the discovery that small amounts of several of the chemicals greatly increased the early and/or long-term strength of Ottawa sand-lime-fly ash mixtures (6). The results of a further investigation of these promising chemical additives is the subject of this paper.

A preliminary survey was made using 12 chemicals in varying amounts in mixtures with Ottawa sand, a calcitic hydrated lime and a selected fly ash. On the basis of the results, four chemicals (sodium hydroxide, sodium carbonate, sodium metasilicate and sodium chloride) were chosen for studies with each of four natural soils (a dune sand, a friable loess, an alluvial clay and a heavily weathered glacial till) in mixtures with a calcitic (high-calcium) hydrated lime and a dolomitic monohydrate (Type N) lime, and three different fly ashes. An evaluation of the effects of chemical additives at low curing temperatures was also made. Finally a few mixtures were selected and submitted to a freezing and thawing test.

## MATERIALS USED

### Soils

Ottawa sand is a natural silica sand assumed to be unreactive with lime and water at the curing temperatures used. Its gradation met the requirements for graded standard sand (ASTM Designation: C 109-58):

| Sieve Size | Percent Passing |
|---|---|
| No. 16 (1,190-micron) | 100 |
| No. 30 (590-micron) | 98 ± 2 |
| No. 50 (297-micron) | 28 ± 5 |
| No. 100 (149-micron) | 2 ± 2 |

The four natural soils were selected as being representative of important Iowa soil types. A field description of each sample is given in Table 1, and physical and chemical properties are given in Table 2.

## Fly Ashes

Three fly ashes were selected to represent variations in the properties of this by-product material. Analysis of the samples are given in Table 3 and additional information on each follows:

Fly ash No. 1 was collected by multiple cyclone and electrical precipitators. The coal was from districts 3 and 8 in Ohio and from northern West Virginia, and was processed through pulverizing mills so that 70 percent passed a No. 200 mesh. The sample was sent from the St. Clair (Mich.) Power Plant of the Detroit Edison Company.

TABLE 1

DESCRIPTION OF NATURAL SOILS

| Soil | Dune Sand (S-6-2)[a] | Friable Loess (20-2) | Alluvial Clay (627-1) | Kansan Gumbotil (528-8) |
|---|---|---|---|---|
| Location | Benton County, Iowa | Harrison County, Iowa | Harrison County, Iowa | Keokuk County, Iowa |
| Geological description | Wisconsin-age eolian sand, fine-grained, oxidized, leached | Wisconsin-age loess, friable, oxidized, calcareous | Recent fill, alluvial plastic, slightly calcareous | Kansan-age gumbotil, highly weathered, plastic, noncalcareous |
| Soil series | Carrington | Hamburg | None | Mahaska[b] |
| Horizon | C | C | Undefined | Fossil B |
| Sampling depth, ft | 6-11 | 49-50 | 0-4 | 7.5-8.5 |

[a] Numbers in parentheses are those assigned by the Soil Research Laboratory of the Iowa Engineering Experiment Station.

[b] Underlies C horizon loess of Mahaska series.

Fly ash No. 2 was collected by mechanical equipment. The coal was from northern Illinois and was burned in a B and W boiler. This sample was sent from the Sixth Street Power Station in Cedar Rapids, Iowa, by the Iowa Electric Light and Power Company.

Fly ash No. 3 was collected by electrical precipitators from a dry bottom type of boiler using unwashed coal from western Kentucky. The sample was sent from the Paddy's Run Power Station at Louisville, Ky., by the Louisville Gas and Electric Company.

## Limes

Calcium hydroxide (calcitic hydrated) lime, reagent grade, from Fisher Scientific Company was used in the tests with Ottawa sand. Samples of commercial calcitic (high-calcium) hydrated lime, brand-name Kemikal, and commercial dolomitic monohydrate (Type N) lime, brand-name Kemidol, obtained from U.S. Gypsum Company were used in tests with the natural soils.

## Cement

The portland cement used was commercial Type I from the Penn-Dixie Cement Corporation, of Des Moines, Iowa.

## Chemicals

The following chemicals used were reagent grade, except magnesium oxide which was USP grade:

| Chemical | Formula |
|---|---|
| Sodium carbonate | $Na_2CO_3$ |
| Sodium hydroxide | $NaOH$ |
| Sodium metasilicate | $Na_2SiO_3 \cdot 9H_2O$ |
| Sodium chloride | $NaCl$ |
| Aluminum chloride | $AlCl_3 \cdot 6H_2O$ |
| Calcium chloride | $CaCl_2$ |
| Lithium carbonate | $Li_2CO_3$ |
| Magnesium oxide | $MgO$ |
| Manganese chloride | $MnCl_2 \cdot 4H_2O$ |
| Phosphoric acid | 85% $H_3PO_4$ |
| Potassium penmanganate | $KMnO_4$ |
| Sodium phosphate | $Na_3PO_4 \cdot 12H_2O$ |

TABLE 2

PROPERTIES OF SOILS

| Soil | Dune Sand | Friable Loess | Alluvial Clay | Kansan Gumbotil |
|---|---|---|---|---|
| Textural composition[a], % | | | | |
| Gravel (> 2 mm) | 0.0 | 0.0 | 0.0 | 0.0 |
| Sand (2-0.074 mm) | 95.5 | 0.7 | 2.4 | 19.4 |
| Silt (0.074-0.005 mm) | 1.5 | 82.3 | 25.6 | 14.6 |
| Clay (< 0.005 mm) | 3.0 | 17.0 | 72.0 | 66.0 |
| Colloids (< 0.002 mm) | 2.6 | 14.0 | 61.0 | 63.0 |
| Atterberg limits[b] | | | | |
| Liquid limit, % | - | 32 | 72 | 76 |
| Plastic limit, % | - | 25 | 26 | 26 |
| Plasticity index | Non-plastic | 7 | 46 | 50 |
| Classification | | | | |
| Textural[c] | Sand | Silty loam | Clay | Clay |
| Engineering (AASHO)[d] | A-3(0) | A-4(8) | A-7-6(20) | A-7-6(20) |
| Chemical | | | | |
| Cat. exch cap[e], me/100g | 1.0 | 14.5 | 44.4 | 39.2 |
| pH[f] | 6.6 | 8.4 | 7.7 | 7.4 |
| Carbonates[g], % | 0.4 | 10.4 | 3.6 | 2.0 |
| Organic matter[h], % | 0.1 | 0.1 | 1.6 | 0.1 |
| Predominant clay mineral[i] | Montmorillonite (trace) | Montmorillonite | Montmorillonite | Montmorillonite |

[a] ASTM Method D422-54T (3).
[b] ASTM Method D423-54T and D424-54T (3).
[c] Triangular chart developed by U.S. Bureau of Public Roads (11, p. 47).
[d] AASHO Method M145-49 (2).
[e] Ammonium acetate (pH = 7) method on soil fraction 0.42 mm (No. 40 sieve).
[f] Glass electrode method using suspension of 15 g soil in 30 cc distilled water.
[g] Versenate method for total calcium.
[h] Potassium bichromate method.
[i] X-ray diffraction analysis.

# METHODS

## Mixture Proportions

The proportions, by weight, of the Ottawa sand or soil, lime and fly ash components of mixtures were 75, 5 and 20 percent in the preliminary survey and 76.5, 6 and 17.5 percent in the tests with natural soils. The chemical additive, which was computed on a dry basis excluding the crystal water, is expressed as a percentage of the dry weight of the total Ottawa sand or soil-lime-fly ash mixture. Chemicals were added either in powder form or as a component of the mix water.

## Mixing and Molding

Mixing of batches for preparing test specimens was done in a Hobart kitchen mixer, model C-100, at low speed in the following sequence of operation: The dry ingredients were mixed for 30 sec, the mix water was added and machine mixed for 1 min, the mixture was hand mixed for about 30 sec to clean the sides and bottom of the mixing bowl, and the mixture was machine mixed for 1 min. The final moisture content, based on maximum strengths after 7, 28 and 90 days curing, was on the dry side of the optimum moisture content for Standard Proctor (ASTM-AASHO) density for both sands used, and on the wet side for both clays. The optimum moisture content for maximum strength and density in the friable loess soil was the same.

TABLE 3

ANALYSIS OF FLY ASHES

| Determination | Fly Ash No. 1 | Fly Ash No. 2 | Fly Ash No. 3 |
|---|---|---|---|
| Source | Detroit Edison Co., St. Clair Station | Cedar Rapids, Iowa, Sixth St. Station | Louisville, Ky., Paddy's Run Sta. |
| Loss on ignition, % | 3.9 | 7.20 | 2.6 |
| Specific surface, Blaine (sq cm/g) | 2,820 | 2,663 | 3,226 |
| Specific gravity | 2.58 | 2.39 | 2.60 |
| Fineness (percent passing No. 325 sieve) | 91.8 | 49.8 | 86.1 |
| Silicon dioxide ($SiO_2$), % | 43.54 | 36.68 | 42.5 |
| Magnesium oxide (MgO), % | 0.17 | 0.98 | 0.8 |
| Calcium oxide (CaO), % | 2.86 | 3.45 | 5.7 |
| Aluminum oxide ($Al_2O_3$), % | 23.25 | 21.29 | 23.4 |
| Iron oxide ($Fe_2O_3$), % | 24.80 | 24.33 | 20.0 |
| Sulphur trioxide ($SO_3$), % | 0.80 | 2.02 | 2.3 |

Molding of specimens was started immediately after a batch was mixed. A double plunger drop-hammer apparatus was used to mold 2-in. diameter by 2-in. high specimens. With this apparatus the equivalent of Standard Proctor compactive energy was obtained (8).

## Curing

Specimens of each batch were moist cured at 70 ± 4 F and more than 90 percent relative humidity for 7 days, 28 days, and 3 or 4 months. To preserve moisture better and to reduce absorption of carbon dioxide from the air, all specimens were wrapped in wax paper and were sealed with cellophane tape before being placed in the humid room.

## Strength Testing

After each curing period, specimens were unwrapped and immersed in distilled water for one day. Then they were tested for unconfined compressive strength using a load travel rate of 0.1 in. per minute. Tests were run in triplicate, and the average strengths are reported in psi.

## Durability Tests

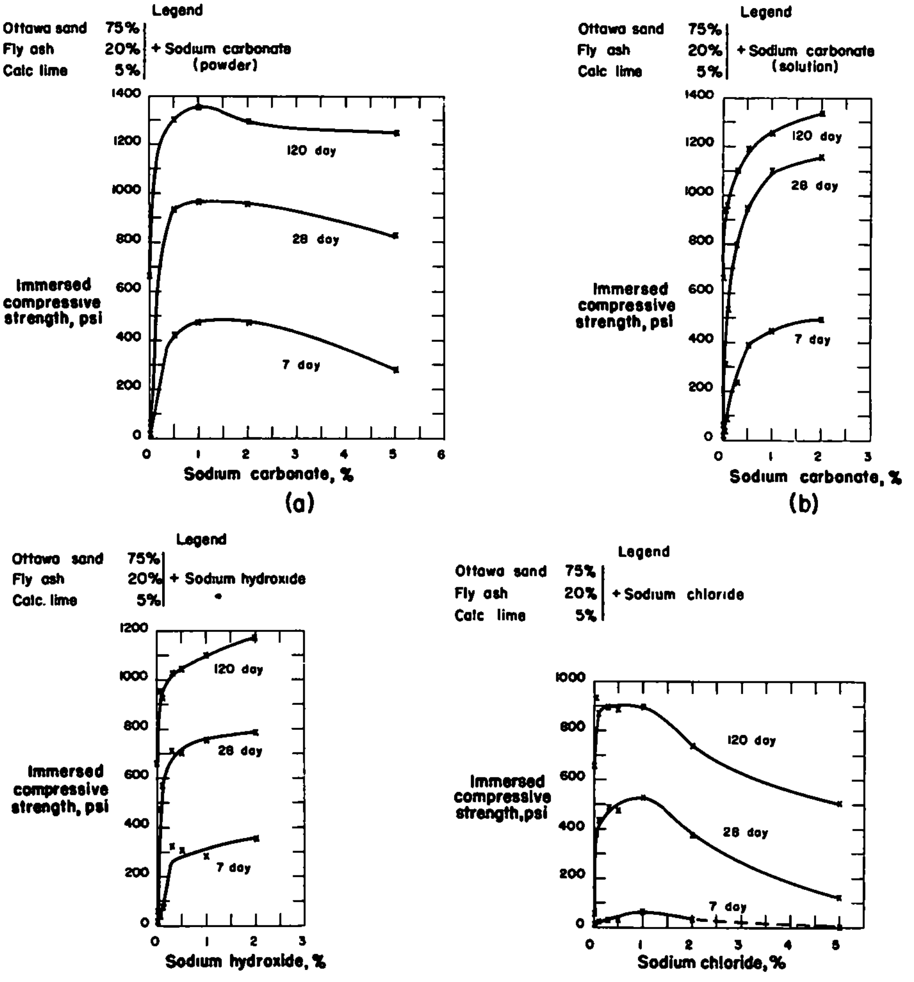
The Iowa freeze-thaw test (7) was used to evaluate the durability of selected mixtures. Four 2-in. by 2-in. specimens from each mixture were cured 28 days in the moisture room. Two specimens, designated the control specimens, were then immersed for 10 days; and the other two specimens, designated the freeze-and-thaw specimens, were exposed alternately to temperatures of 20 ± 2 F (16 hr) and 77 ± 4 F

(8 hr) for ten cycles, each cycle lasting 24 hr. A vacuum flask specimen container (4) was used to cause freezing to occur from the top down and to supply unfrozen water, kept at 35 ± 2 F by a light bulb, to the bottom of the specimen throughout the test. After these treatments, the unconfined compressive strength of the freeze-thaw specimens ($p_f$) and of the control specimens ($p_c$) were determined. These values were used to evaluate the durability of the stabilized soils. The index of resistance to the effect of freezing ($R_f$) was calculated from the formula:

$$R_f = \frac{100\,p_f}{p_c}\ (\%)$$

## PRELIMINARY SURVEY OF CHEMICALS

The preliminary survey was made using 12 chemicals in varying amounts to determine the minimum amount of each required for substantial improvement of the lime-fly ash reaction and to serve as the basis for selecting a smaller number of chemicals for more detailed studies. Ottawa sand was used as the soil component because its gradation and monomineralic composition, silica, may make it behave as an inert ma-

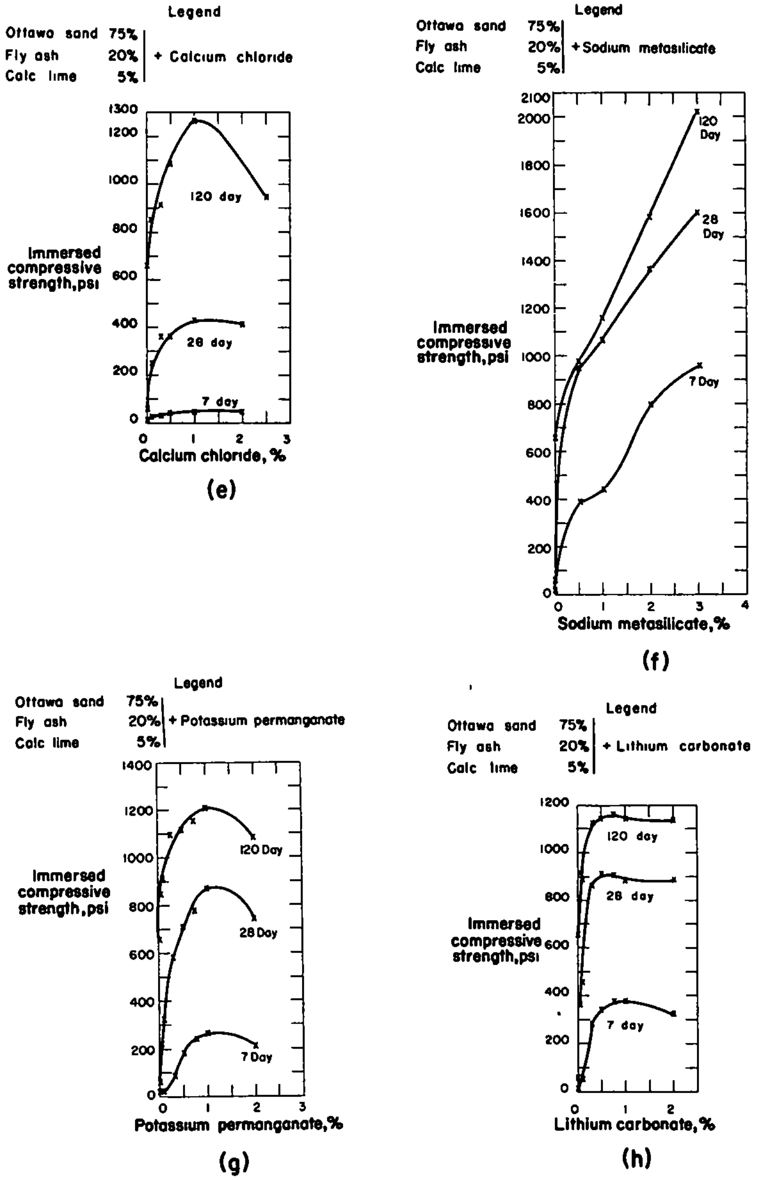


(a) (b) (c) (d)

Figure 1 (a, b, c, d). Effect of amount of chemical additive on strength of 75:5:20 Ottawa sand—calcitic hydrated lime—fly ash No. 1 mixture.

terial at the curing temperatures used, thus minimizing the effect of the soil component on the lime-fly ash reaction. A calcitic hydrated lime was chosen because, although of reagent grade, it was representative of a great amount of commercial limes produced in the U.S. A medium quality fly ash from the midwest (St. Clair Power Plant) was used as the pozzolan component. The Ottawa sand-lime-fly ash mix proportions were 75, 5, 20 percent, respectively, near optimum for these materials. Specimens were molded at optimum moisture for strength.

The test results are shown in Figure 1 (a through m). Any or certain amounts of all chemicals increased the strength of the Ottawa sand-lime-fly ash mixture. Following is an analysis of each chemical evaluated.



(e) (f) (g) (h)

Figure 1 (e, f, g, h). Effect of amount of chemical additive on strength of 75:5:20 Ottawa sand—calcitic hydrated lime—fly ash No. 1 mixture.

## Sodium Carbonate

Even the smallest amount of sodium carbonate tried, 0.05 percent, increased the strength substantially. Seven- and 28-day strengths were increased over 30 times for amounts of chemical greater than 0.5 percent. There are some differences in strength between the use of sodium carbonate in powder form or in liquid solution, but the increase in strength is great and warrants the use of the chemical in either form. The optimum amount is about 1.0 percent when used in powder form. The commercial price of this product, $35 to $65 a ton, makes it a promising additive for lime-fly ash stabilization.

## Sodium Hydroxide

This chemical is also very effective. A noticeable improvement of strength started with amounts of sodium hydroxide as low as 0.03 percent. A recommended amount is about 1.0 percent. This chemical, priced at about $100 a ton, may also be an economical activator of the pozzolanic reaction.

## Sodium Chloride and Calcium Chloride

The effects of these two additives are somewhat parallel. They gave little improvement to 7-day strength, but gave a substantial increase to 28-day and 4-month strengths with even small concentrations of chemical. The price difference, $20 a ton for sodium chloride and $60 for calcium chloride, and the small amounts of sodium chloride required for a maximum increase in strength, makes sodium chloride the choice when improvement of long-term strengths is the main interest. Three-tenths of a percent of sodium chloride increased the 28-day strength by about ten times, and the optimum amount was about 1.0 percent.

## Sodium Metasilicate

This chemical increased the strength greatly, even in small amounts. The strength increase was more or less proportional to amount used; the optimum was above 3.0 percent. The strength of 1,000 psi was found after 7 days curing with the largest amount of sodium metasilicate tested, 3.0 percent. The commercial price of this chemical is about

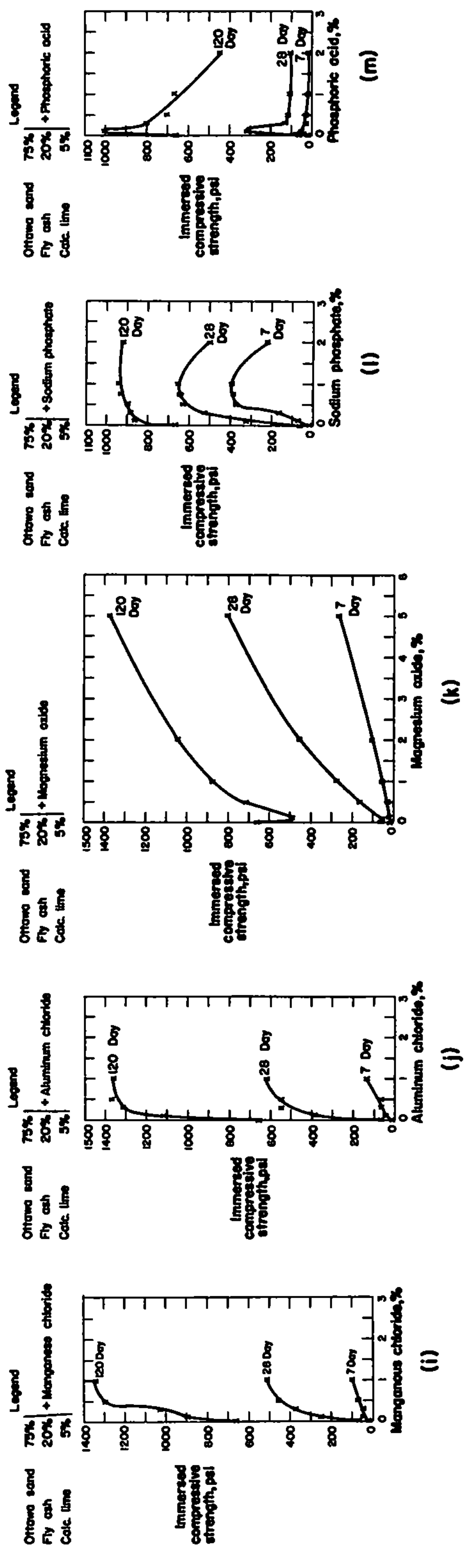


Figure 1 (i, j, k, l, m). Effect of amount of chemical additive on strength of 75:5:20 Ottawa sand—calcitic hydrated lime—fly ash No. 1 mixture.

$120 a ton on a dry basis, which makes it a promising chemical additive when used in small amounts.

### Lithium Carbonate, Potassium Permanganate, Manganese Chloride, Aluminum Chloride and Sodium Phosphate

These chemicals increase strengths, but the rate of increase, amounts required, and economical considerations make them less desirable than the chemicals previously discussed.

### Phosphoric Acid

Although very small amounts of phosphoric acid improved soil strength, concentrations larger than 0.03 percent caused a decrease in strength. Its use is therefore not recommended.

### Magnesium Oxide

One of the components of dolomitic monohydrate (Type N) lime is magnesium oxide; consequently the effects on strength caused by addition of this chemical should give an indication on the effects of using dolomitic monohydrate lime instead of calcitic hydrated in lime-fly ash stabilization.

Small amounts, up to 0.5 percent, resulted in a slight decrease of strength, but increased amounts up to the largest amount tried, 5.0 percent, increased the strength (Fig. 1, k). The results indicate that dolomitic monohydrate limes are more effective with the fly ash used here, but they are not as effective as calcitic hydrated lime plus treatment with some of the other chemical additives. The results also warranted an investigation on the effects of chemical additives to dolomitic lime-fly ash mixtures.

## EXTENDED EVALUATION

To complement the tests made with Ottawa sand, the study was extended to include four natural soils: a dune sand, a friable loess, an alluvial clay and a gumbotil (Tables 1 and 2).

The evaluation of magnesium oxide indicated that dolomitic monohydrate lime might be more effective than calcitic hydrated lime, and that the use of dolomitic lime might make unnecessary the addition of chemicals; therefore the use of both limes, calcitic hydrated and dolomitic monohydrate, was evaluated. Commercial type limes were used.

Three fly ashes were selected to include such desired variations in their properties as coarseness, carbon content, specific surface, etc.

From the preliminary studies, four chemicals warranted further evaluation based on strength improvement and economics: sodium carbonate, sodium hydroxide, sodium metasilicate and sodium chloride.

The proportions of soil, lime, and fly ash used were 76.5, 6 and 17.5 percent. The amount of chemical used was 1.0 percent in mixtures prepared with all soils, limes and fly ashes, except that 0.5 percent was also used with dune sand and fly ash No. 1. The evaluation was not intended to be an economic comparison of lime-fly ash-chemical stabilization of soils with other methods of soil stabilization, but rather to be a check on the possible beneficial effects of the selected chemicals on soil-lime-fly ash mixtures. Therefore, the mixture proportions are within the range commonly recommended for lime-fly ash stabilization, and the amount of chemical added is probably near the optimum amount, except for sodium metasilicate.

The molding moisture content for mixtures was deducted from the moisture-density and moisture-strength curves of soil-lime-fly ash mixtures without chemical additives. With friable loess, maximum density and maximum strength occurred at the same moisture content, and this was considered the optimum. The moisture requirements for maximum density and maximum strength of mixtures with sand were not the same, and as the moisture content for maximum density gave very low strengths, the moisture content for maximum strength was used as the optimum. The molding moisture of mixtures with alluvial clay and gumbotil was about two percentages above the optimum for maximum density, in order to get maximum strengths.

## Dune Sand

The data of tests made with this soil and combinations of calcitic hydrated or dolomitic monohydrate lime and fly ashes Nos. 1, 2 and 3 are plotted as bar graphs in Figures 2 through 5.

Sodium carbonate, sodium metasilicate and sodium hydroxide in amounts of 1.0 percent increased 7-, 28- and 90-day strengths of all dune sand-lime-fly ash mixtures considerably. Sodium chloride increased 28- and 90-day strengths of dune sand-calcitic lime-fly ash mixtures to a great extent and also increased substantially the 90-

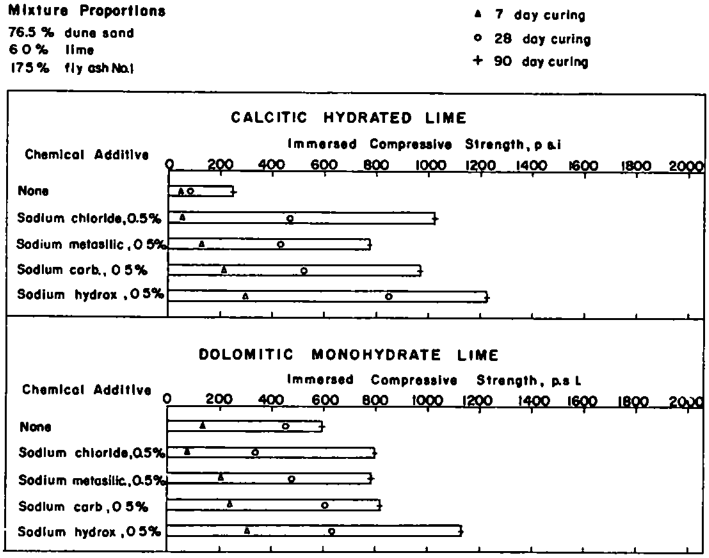


Figure 2. Effect of 0.5 percent chemical additive on strength of a 76.5:6:17.5 mixture of dune sand-lime-fly ash No. 1.

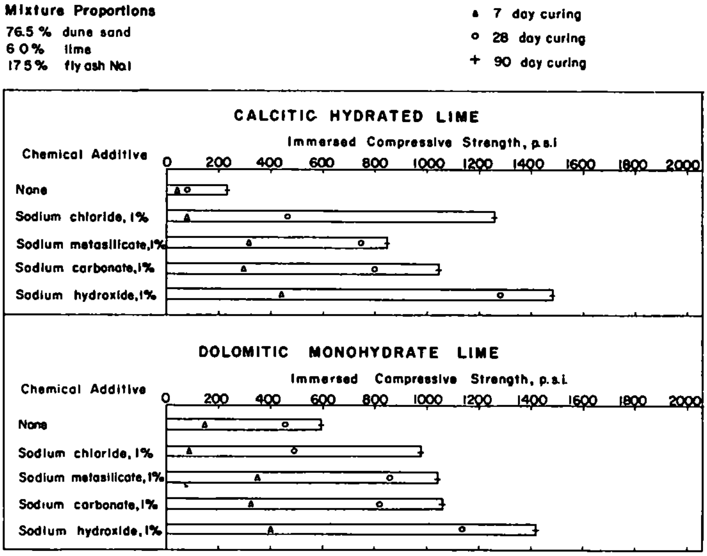


Figure 3. Effect of 1.0 percent chemical additive on strength of a 76.5:6:17.5 mixture of dune sand-lime-fly ash No. 1.

day strength of dune sand-dolomitic lime-fly ash mixtures except those made with fly ash No. 2, for which the strength increase was minor.

The strengths obtained using 0.5 percent chemical in mixtures with fly ash No. 1 are smaller than those obtained with 1.0 percent chemical additive, but the strength increases follow the same trend for both amounts.

## Friable Loess

All four chemicals increased the strength of loess-calcitic lime-fly ash mixtures

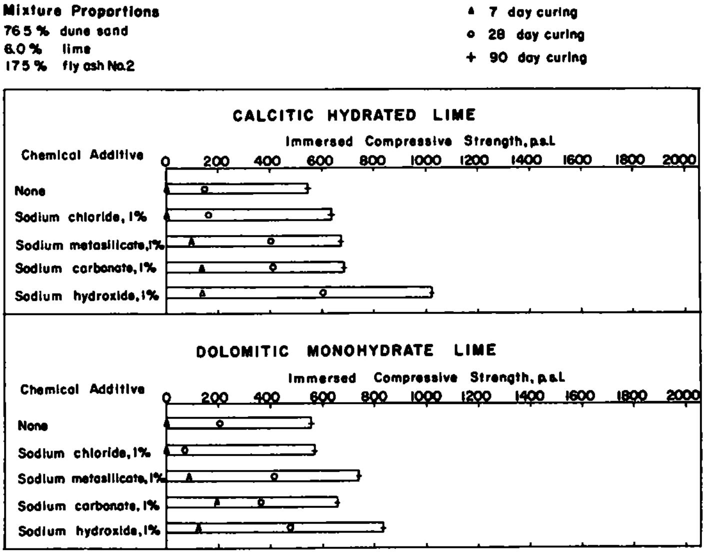


Figure 4. Effect of 1.0 percent chemical additive on strength of a 76.5:6:17.5 mixture of dune sand-lime-fly ash No. 2.

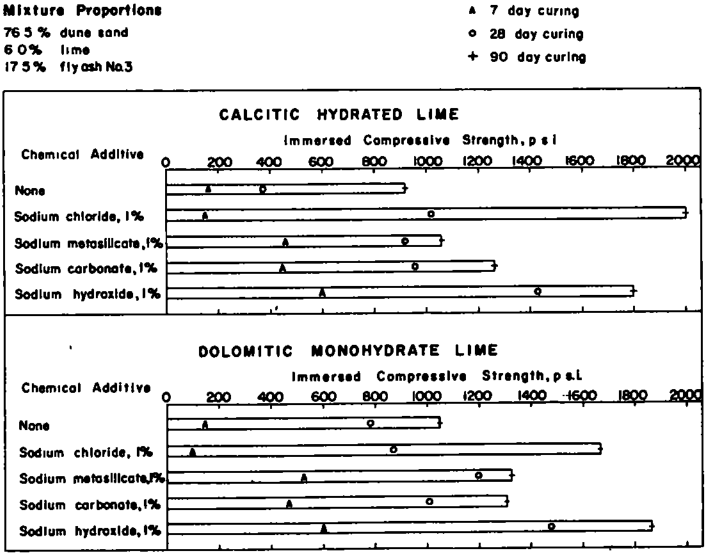


Figure 5. Effect of 1.0 percent chemical additive on strength of a 76.5:6:17.5 mixture of dune sand-lime-fly ash No. 3.

except for 90-day strength of specimens made with sodium metasilicate and fly ash No. 2 (Figs. 6 through 8). Loess-dolomitic lime-fly ash mixtures were not appreciably benefited by the addition of the chemicals.

The use of sodium chloride, sodium carbonate or sodium hydroxide in mixtures of friable loess, calcitic hydrated lime and fly ash No. 1 or No. 3 could be recommended. The strengths produced by the addition of these chemicals in mixtures containing calcitic hydrated lime surpassed that of the similarly proportioned mixtures containing dolomitic monohydrate lime, with or without chemicals.

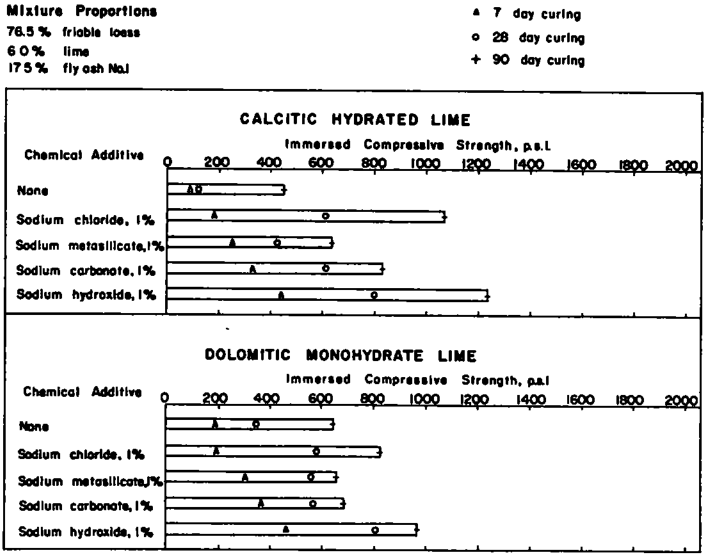


Figure 6. Effect of 1.0 percent chemical additive on strength of a 76.5:6:17.5 mixture of friable loess-lime-fly ash No. 1.

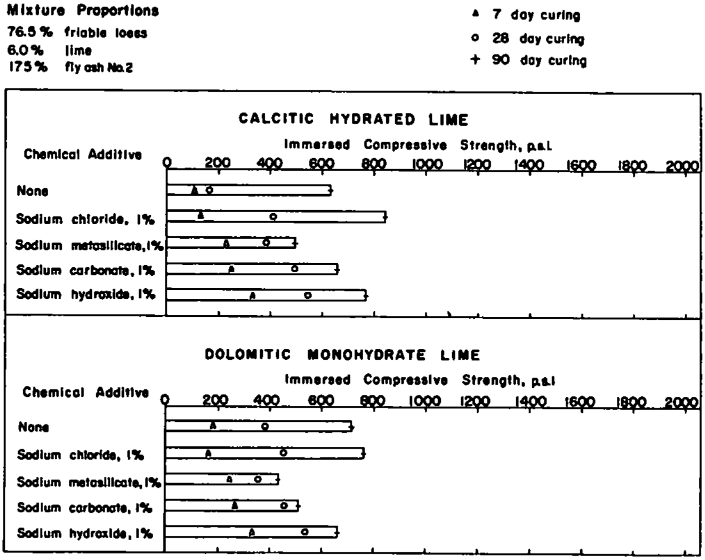


Figure 7. Effect of 1.0 percent chemical additive on strength of a 76.5:6:17.5 mixture of friable loess-lime-fly ash No. 2.

## Alluvial Clay and Gumbotil

The effect of chemical additives on these clayey soils stabilized with lime and fly ash was nil and sometimes detrimental; consequently the results are not graphed. Specimens treated with sodium carbonate, sodium hydroxide or sodium metasilicate and cured for 90 days were so weakened during the 24-hr immersion period that strength testing was impossible, or strengths were much lower than the strengths of specimens made without treatment or with sodium chloride as the additive. Sodium carbonate, sodium hydroxide and sodium metasilicate are therefore not recommended for use as additives to montmorillonitic clay soils stabilized with lime and fly ash. Sodium chloride was neither harmful nor beneficial; so there appears no reason to use it as an additive.

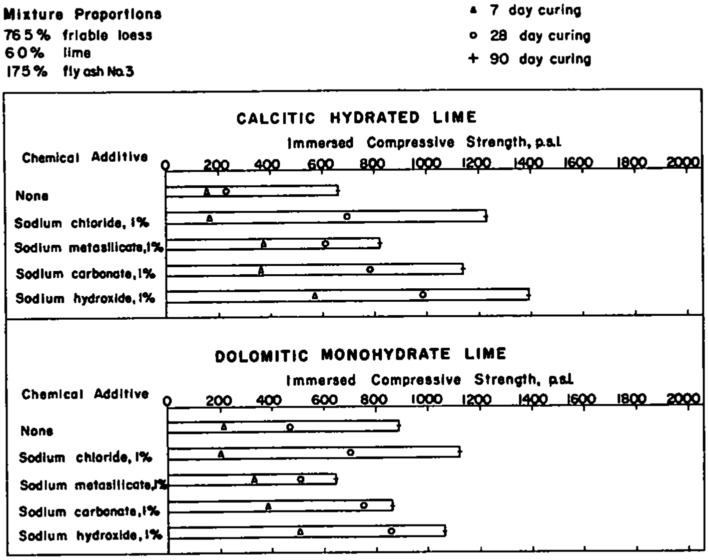


Figure 8. Effect of 1.0 percent chemical additive on strength of a 76.5:6:17.5 mixture of friable loess-lime-fly ash No. 3.

## Sodium Carbonate

This chemical is very effective in the improvement of 7- and 28-day strengths of sandy soil-lime-fly ash mixtures, regardless of the kind of hydrated lime used. Ninety-day strengths are also benefited, but to a lesser extent. Sodium carbonate also improved the early strength of friable loess-lime-fly ash mixtures containing calcitic hydrated lime, but it did not improve the early strength of mixtures containing dolomitic monohydrate lime.

Owing to its relatively low cost, sodium carbonate in amounts of 0.5 to 1.0 percent is a most promising additive for sandy soils stabilized with lime and fly ash.

Neither sodium carbonate, nor sodium hydroxide or sodium metasilicate, are recommended as additives to montmorillonitic clay soil-lime-fly ash mixtures because they reduce the long-term immersed strength, and do not affect early strength.

## Sodium Hydroxide

This chemical greatly improved the strength of sand and friable loess stabilized with hydrated lime and fly ash. The over-all effectiveness is greater with calcitic hydrated lime than with dolomitic monohydrate lime. As an example of the strength increases possible, dune sand stabilized with calcitic hydrated lime and fly ash No. 1

showed the following strength improvements by the addition of 1.0 percent of sodium hydroxide:

| Curing Period | Untreated Mixture | Treated with 1.0% NaOH | Increase |
|---|---|---|---|
| 7 days | 42 psi | 443 psi | 10.5 times |
| 28 days | 74 psi | 1,291 psi | 17.4 times |
| 90 days | 241 psi | 1,493 psi | 6.2 times |

Its use is therefore recommended with these types of soils.

Sodium Chloride

This chemical used as an additive increased the 90-day strength of dune sand-lime-fly ash mixtures, in some cases to a considerable extent. Seven-day strength was slightly reduced, and 28-day strength was sometimes greatly improved and sometimes was even reduced. All 90-day strengths were increased by the addition of sodium chloride. The same trends were observed in mixtures with friable loess as a soil. Thus sodium chloride may be a promising additive to friable soils stabilized with lime and fly ash when long-term strengths are desired. The strength of montmorillonitic clay soil-lime-fly ash mixtures was not affected by adding sodium chloride.

Sodium Metasilicate

Sodium metasilicate in the amount of 1.0 percent increased the strength of the dune sand-lime-fly ash mixtures. It can also improve friable loess-lime-fly ash mixtures containing some fly ashes. For the percentage used, this chemical rates lower than sodium carbonate or sodium hydroxide. Greater amounts are suspected to improve greatly the strength of friable soils; they were not tried here for economic reasons.

Calcitic Hydrated and Dolomitic Monohydrate Limes

The dolomitic monohydrate lime used produced better strengths than the calcitic hydrated lime when the mixtures were not treated with chemicals. However, the calcitic lime responded better to chemical treatments, surpassing in most instances the strength of mixtures made with dolomitic lime, treated or not.

## EFFECTS OF ADDITIVES AT LOW CURING TEMPERATURES

The strengths obtained with lime-fly ash mixtures depend greatly on curing temperatures. When soils are stabilized with lime and fly ash in the late part of the summer in temperate climates, they may not develop sufficient strength to withstand the imposed stresses of the colder seasons. This may lead to failure of the pavement.

The effect of chemical additives at low temperatures was investigated. Dune sand and fly ash No. 1 were used with both calcitic hydrated and dolomitic monohydrate limes. The curing temperature was 43 ± 1 F. Results for 7- and 28-day strengths are given in Figure 9.

Calcitic Lime

The mixture of dune sand, calcitic hydrated lime and fly ash No. 1 without additive, cured for 7 days, failed during the period of immersion in water. The same happened with the mixture with 1.0 percent sodium chloride as additive. Additions of 1.0 percent sodium metasilicate, sodium carbonate or sodium hydroxide, however, gave strengths of about 100 psi.

After 28 days curing, the mixture without additive showed some immersed strength, 41 psi. This strength was increased five- or sixfold by additions of 1.0 percent sodium metasilicate, sodium carbonate or sodium hydroxide. Sodium chloride produced a slight strength improvement.

Dolomitic Lime

The untreated dune sand-dolomitic lime-fly ash mixture did not show any immersed strength after 7 days curing. Additions of 1.0 percent sodium metasilicate gave a 7-day strength of 107 psi; 1.0 percent sodium carbonate gave 57 psi; and 1.0 percent sodium hydroxide gave 76 psi. Sodium chloride was not beneficial.

After 28 days, the untreated mixture had a strength of 111 psi. Additions of 1.0 percent sodium metasilicate or sodium carbonate increased the strength more than two times. One percent sodium hydroxide increased the strength almost three times, to 298 psi. Specimens with sodium chloride did not show any immersed strength.

## Discussion

The beneficial effects of some additives to the lime-fly ash pozzolanic reaction are very important when low temperatures are expected during the curing period. Addition of promising chemicals may lengthen the working season for stabilization of soils with lime and fly ash.

The strengths obtained with dune sand-lime-fly ash No. 1 mixtures cured at 43 ± 1 F may be of the order of 200 to 300 psi by the addition of a small amount of sodium

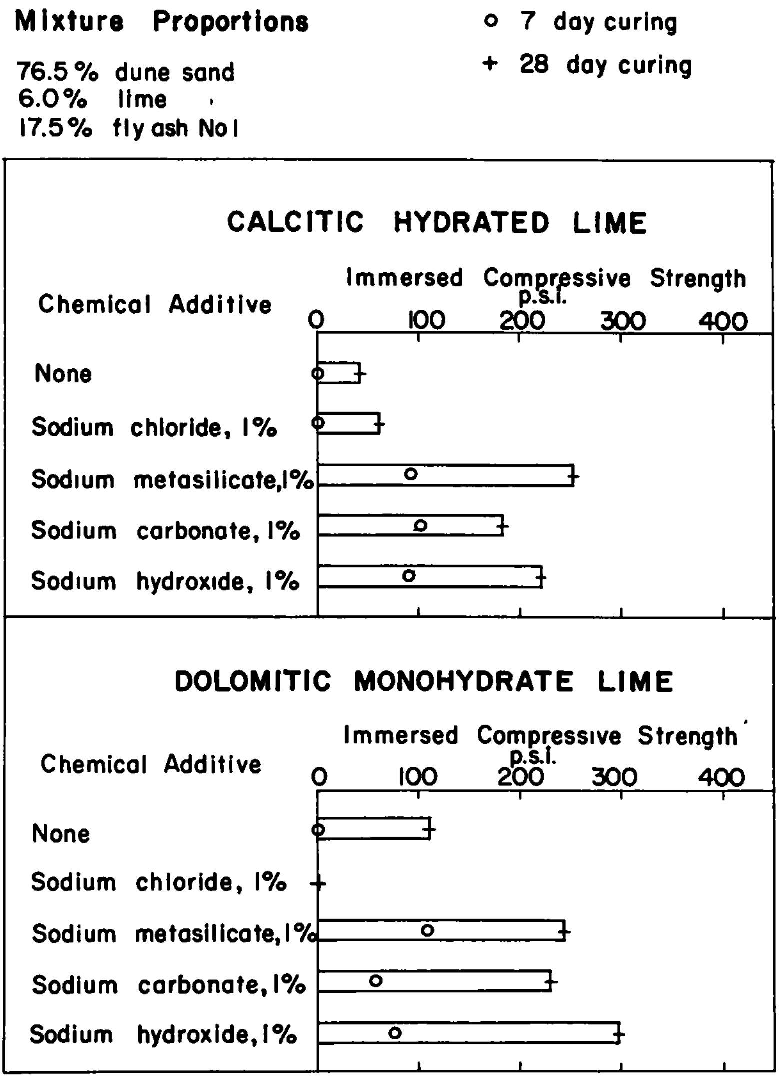


Figure 9. Effect of 1.0 percent chemical additives on strength of a 76.5:6:17.5 mixture of dune sand-lime-fly ash No. 1 cured at a temperature of 43 F.

metasilicate, sodium carbonate or sodium hydroxide. Those strengths may be sufficient in a base course to withstand the adverse effects of traffic and lower winter temperatures. Untreated sand-lime-fly ash No. 1 mixtures showed strengths of 100 psi or less after 28 days curing, which are insufficient for a base course. The same beneficial effects may be expected with other fly ashes. Sand-lime-fly ash mixtures made with either calcitic hydrated or dolomitic monohydrate lime increased in strength by the addition of sodium metasilicate, sodium carbonate or sodium hydroxide, but the data obtained herein were not sufficient to indicate which lime is more beneficial.

The chemical additives, as salts, also assist by lowering the freezing point of the free water in stabilized soil mixtures. By depressing the temperature at which the free soil water freezes, more time is allowed to gain strength; and the stabilized soil is exposed for shorter periods to the damaging effects caused by ice formation.

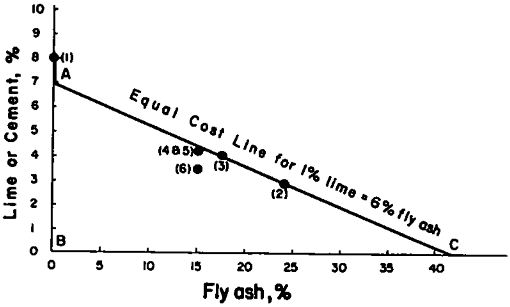


Figure 10. Equal-cost-line chart for dune sand stabilized with selected admixtures of lime-fly ash or lime-fly ash-chemical compared with dune sand-cement.

## DURABILITY EVALUATION

To evaluate the effectiveness of lime-fly ash stabilization with and without chemical additives, a few mixes were prepared and compared with soil-cement mixtures. These selected mixtures were submitted to a severe freeze-thaw test.

Based on the previous investigation the selected mixes should include dune sand, fly ash No. 3, and dolomitic monohydrate lime when no chemicals are added. The lime should preferably be calcitic hydrated when chemicals are added. Sodium carbonate and sodium chloride were chosen as additives based on strength improvements, cost of the chemicals, and practicability of their use in field construction.

Given the desired components of the mixes, the proportions were calculated to compete with the required amount of cement needed to stabilize the same soil. Use was made of the Iowa State equal-cost-line method for soil-lime-pozzolan mix design (12, pp. 21-102).

It was assumed that:

1. Eight percent portland cement is required to stabilize the dune sand.
2. The cost of handling two materials (lime and fly ash) instead of one (if stabilized with cement), is equal to the cost of one percent of cement.
3. The costs of lime and cement are the same, about $22 a ton.
4. The cost of the fly ash is one-sixth that of lime or cement.
5. The cost of sodium carbonate and handling this extra material is 2.5 times that of an equal amount of cement, and that sodium chloride costs the same as cement.

From these assumptions, all the sand-lime-fly ash mixes that are within the triangle ABC of Figure 10 compete economically with soil-cement. The mixes selected (Table 4) all have the same cost or are cheaper than soil-cement.

All five selected sand-lime-fly ash mixtures gave 28-day strengths equal or greater than sand-cement for the same curing period. It has been estimated that after freezing and thawing, the stabilized soil specimens should yield a minimum of 250 psi (4). This value was surpassed by all mixtures; see column $p_f$ of Table 4. It is desirable that soil-stabilized specimens show an index of resistance ($R_f$) of at least 80 percent to withstand the Iowa climatic conditions. Only mixes Nos. 4 and 6 gave an index of resistance lower than 80 percent; nevertheless they still show $R_f$ values of 78 percent which may be adequate as the values of $p_f$ and $p_c$ are more than 400 psi.

Some mixtures continued gaining strength during the freezing-and-thawing tests and/

or during wetting. None of the mixtures showed any visual detriment by freezing, neither did they show any expansion.

The as-molded dry density of the several mixes changed by as much as 12 pcf, but there is no relation whatsoever between density and strength values.

The principal consequence that can be derived from these tests is that, based on 28-day strength requirements, lime and fly ash may be economically used to stabilize sandy soils. Either straight lime and fly ash mixtures or lime and fly ash mixtures with additives withstood the severity of freezing and thawing tests and had enough residual strength to be considered as good stabilizers. A good quality fly ash (No. 3) was used in these tests; these results may not be reproduced with all kinds of fly ash.

TABLE 4

DURABILITY EVALUATION OF SELECTED MIXES

| Mix No. | Proportions | As-Molded Dry Density, pcf | Unconfined Compressive Strength, psi | | | |
|---|---|---|---|---|---|---|
| | | | 28 Day[a] | $P_f$[b] | $P_c$[c] | $R_f$, %[d] |
| 1 | 92% sand, 8% p. cement | 112.6 | 474 | 507 | 517 | 98 |
| 2 | 73% sand, 3% dol lime, 24% fly ash No. 3 | 124.3 | 792 | 821 | 966 | 85 |
| 3 | 76% sand, 4% dol lime, 17.5% fly ash No. 3 | 124.4 | 646 | 634 | 674 | 94 |
| 4 | 82% sand, 3% dol lime, 15% fly ash No. 3 + 0.5% sodium carbonate | 117.2 | 554 | 452 | 583 | 78 |
| 4A | 82% sand, 3% dol lime, 15% fly ash No. 3 | 123.8 | 390 | ND[e] | ND | ND |
| 5 | 82% sand, 3% calc lime, 15% fly ash No. 3 + 0.5% sodium carbonate | 116.1 | 644 | 596 | 570 | 104 |
| 6 | 82% sand, 3% calc lime, 15% fly ash No. 3 + 0.5% sodium chloride | 124.1 | 453 | 414 | 454 | 78 |
| 5A-6A | 82% sand, 3% calc lime, 15% fly ash No. 3 | 123.1 | 120 | ND | ND | ND |

[a] After 28 days curing and 24-hr immersion in distilled water.

[b] After 28 days curing, 24-hr immersion in distilled water and ten freeze-thaw cycles.

[c] After 28 days curing and 11 days immersion in distilled water.

[d] $R_f = \frac{100 P_f}{P_c}$.

[e] Not determined.

## MECHANISM

A complete evaluation of the mechanism of the effects of chemical additives in lime-fly ash mixtures must involve extensive chemical analysis. Based on the strength data and on the assumption that strength is indicative of the extent of the pozzolanic reaction, an explanation of the mechanism is given herein.

The effects of chemical additives on lime-fly ash may be grouped in one or more of the three following categories:

1. Speeding up of the pozzolanic reaction,
2. Production of secondary cementitious products, and
3. Combination with the primary, or pozzolanic, cementitious products.

The first should probably be of a catalitic nature. It may show up particularly in the curve for 7-day strength versus additive content, with a sharp increase in strength for small amounts of chemical added.

In the second category, the chemicals combine or react with lime to form cementitious products like $CaCO_3$, $Ca(PO_4)_2$, $Al(OH)_3$, etc.

In the third category are included those chemicals that may combine or react with the pozzolanic cement produced, with the pozzolanic materials in fly ash or with the soil. This combination or reaction may be a complex one producing better cementitious materials or speeding up the reaction or be a reaction that activates some of the materials, increasing their pozzolanic value.

For a separate evaluation of the different chemicals, they may be grouped on the basis of their reactions—basic, neutral or acidic. Bases and basic salts, also known as alkalies and alkaline salts, produce hydroxyl ions in water solution to varying extents. Acid salts produce hydrogen ions in water solutions to varying extents. Neutral salts in water solution do not upset the natural balance of hydrogen and hydroxyl ions. Another group is formed with phosphoric acid, and magnesium oxide is in a miscellaneous group.

This evaluation is made based on the results obtained with mixtures with Ottawa sand as a soil in this and in a previous paper (6). The characteristics of this sand make it, supposedly, an inert material in the lime-fly ash or lime-fly ash-chemical reactions.

## Bases and Basic Salts

Alkaline additives increase the amount of available hydroxyl ions in the moistened Ottawa sand-lime-fly ash system, and as a result the pozzolanic reaction may be accelerated by the increased solubility of the siliceous material caused by the alkalinity (9).

The base, sodium hydroxide, acts as a catalyst supposedly in the following way:

1. It first reacts with the siliceous material to produce intermediate sodium silicates.
2. The over-all reaction goes to completion when the intermediate sodium silicates subsequently react with lime (calcium hydroxide) to form sodium hydroxide and cementitious insoluble calcium silicates.
3. The sodium hydroxide is then free for further reaction with unreacted siliceous material.

In the alkaline salts, sodium carbonate very likely reacts with lime in the moist Ottawa sand-lime-fly ash mixture to form calcium carbonate and sodium hydroxide in the following way,

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH$$

The precipitated calcium carbonate contributes cementation to the system, and, as hypothesized in the preceding paragraph, the sodium hydroxide acts as a catalyst.

The other alkaline salts used, sodium phosphate, sodium metasilicate and lithium carbonate, may act in a way similar to sodium carbonate. Sodium phosphate reacts with lime to form calcium phosphate, which may be cementitious, and sodium hydroxide, which acts as a catalyst. Sodium metasilicate forms highly cementitious calcium silicates with lime and releases also sodium hydroxide. Lithium carbonate reacts with lime and precipitates calcium carbonate releasing lithium hydroxide, an alkali that produces the same catalitic effects as sodium hydroxide in the lime-fly ash reaction.

## Acid Salts

Acid salts undergo a hydrolysis reaction with the precipitation of weak bases (hydroxides). With calcium hydroxide (lime) and aluminum chloride this reaction proceeds as follows:

$$2AlCl_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3CaCl_2$$

The weak base formed, $Al(OH)_3$, has some cementing properties that may be beneficial. The calcium chloride formed may also benefit through complex effects of the third category.

With calcium chloride, the principal long-term strength benefits obtained are thought due to a different type of chemical mechanism than previously discussed, and that are included in the third category of effects. Calcium chloride being highly hygroscopic and deliquescent insures a relatively high concentration of calcium ions over a long period of time by providing moisture for a solution. Because lime has a low solubility and a lower ionization constant than calcium chloride, the concentration of calcium ions from lime is lower than that from calcium chloride.

The other acid salt used, manganese chloride, is suspected to produce effects analogous to those of calcium chloride.

### Neutral Salts

Sodium chloride, although a neutral salt, may act similarly to calcium chloride, but it gives less benefit to long-term strength perhaps because sodium chloride is less hygroscopic and deliquescent than calcium chloride.

The mechanism of the action of potassium permanganate in lime-fly ash mixtures is also included in the third category. Potassium permanganate, a strong oxidizing agent, may oxidize the carbon in the fly ash with subsequent production of potassium carbonate and the precipitation of manganese dioxide. The potassium carbonate formed may then give rise to further reactions, of the first and second category, similar to those of sodium carbonate, previously discussed, which are beneficial to strength. Potassium permanganate may also clean the surface of fly ash by oxidation of possible organic matter present on it; this may make the fly ash more reactive with lime.

### Acid

Very small amounts of phosphoric acid somewhat improved the strength. This may be brought about by the formation of complex calcium phosphates or by the activation of fly ash (1). Increased amounts of acid caused a decrease in strength, which is due to the neutralization caused by the acid which reduced the alkalinity and subsequently the silica release.

### Miscellaneous Chemical

Magnesium oxide is supposed to react with lime and fly ash producing effects of the third category. It may enter into the pozzolanic reaction and form complex silicates of calcium and magnesium. The effectiveness of magnesium oxide, a component of dolomitic monohydrate lime, in calcium hydroxide-fly ash mixtures corresponds to the findings of previous research which indicated that dolomitic monohydrate lime gives better strengths than calcitic hydrated lime in soil-lime-fly ash mixtures cured at ambient temperatures.

### Chemical Additives in Soil-Lime-Fly Ash Mixtures

Four chemicals were evaluated with soils: sodium carbonate, sodium hydroxide, sodium metasilicate and sodium chloride. The greater benefits were obtained with the sandy soil and the benefits decreased with the increase in the amount of clay in the soil.

With the data at hand it is difficult to evaluate the influence of the soil factor in soil-lime-fly ash-chemical mixtures. The chemical additives used were beneficial in mixtures with friable soils and detrimental in mixtures with montmorillonitic clay soils. It is supposed that the decrease in strength in the clayey soils is brought about by the excess of sodium ions and high alkalinity present in the pore fluid of the soil-lime-fly ash mixtures. Both factors introduce disruptive forces in the clay structures that are not overcome by the cementitious bond of the pozzolanic reaction.

## SUMMARY AND CONCLUSIONS

Twelve chemicals were evaluated as additives to Ottawa sand-lime-fly ash mixtures. It was found that the immersed strength of the mixtures may be increased several times by the addition of small amounts of some chemicals. Sodium carbonate, sodium metasilicate and sodium hydroxide appear to be the most promising ones among those evaluated.

The immersed strength of friable soils stabilized with lime and fly ash may also be increased by the addition of small amounts of sodium carbonate, sodium metasilicate, sodium hydroxide, and in some instances sodium chloride.

The benefit in strength increase takes place at ordinary temperatures. The strength increase brought by the addition of chemicals is very critical at temperatures close to freezing because it may permit the use of soil-lime-fly ash stabilization under cold climatic conditions, thus extending the working season.

Using selected compositions of lime and fly ash, or lime, fly ash and chemicals to stabilize a dune sand, it was found that they can compete in strength, freeze-thaw resistance and costs with mixtures of the same soil stabilized with portland cement.

Sodium carbonate is the chemical recommended for use in sandy or even silty soils stabilized with lime and fly ash. Addition of 0.5 percent sodium carbonate permits a reduction of the amounts of lime and fly ash needed to obtain the same strength obtained with larger amounts of lime and fly ash.

## ACKNOWLEDGMENTS

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