Activation of the Lime-Flyash Reaction By Trace Chemicals

D. T. DAVIDSON, MANUEL MATEOS and R. K. KATTI¹, respectively, Professor of Civil Engineering, Graduate Assistant, and Research Associate. Iowa Engineering Experiment Station, Iowa State College, Ames, Iowa.

The results of an investigation of the effect of small amounts of forty-seven different chemicals on the strength of Ottawa sandlime-flyash mixtures are presented. An explanation is offered for the mechanism of strength improvement by the different groups of chemicals studied.

●ROAD BASES stabilized with lime and flyash may not gain sufficient strength in 7 or 28 days to satisfactorily carry heavy traffic or withstand repeated freeze-thaw cycles. This prolongs the period that the road must be closed to traffic or reduces the construction season in northern climates. Thus, an economical method of speeding up the rate-of-strength gain of lime-flyash stabilized soil would extend its usefulness in road construction.

Heat is known to be a good activator for the lime-flyash (pozzolanic) reaction; 7-day strengths of over 1,000 psi may result from curing compacted specimens of soil-lime-flyash at 140 F in sealed containers. But since high temperature curing of road bases is not economical with presently available fuels, a more practical alternative for activation of the lime-flyash reaction would be with trace chemical additives.

This paper presents the findings of a search for trace chemical activators.

MATERIALS

Soil

Natural monomineralic silica sand from Ottawa, Ill., was used as the soil component of mixtures to eliminate variables due to the complex mineral composition of natural soil. The gradation of the sand met the requirements (ASTM Designation: C 109-56) for graded standard sand:

SIEVE SIZE	PERCENT PASSING
No. 16 (1190-micro	on) 100
No. 30 (590-micror	n) 98 + 2
No. 50 (297-micror	28 + 5
No. 100 (149-micror	2 ± 2
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Flyash

The flyash was from the Detroit Edison Company St. Clair Power Plant, St. Clair, Michigan. The composition and physical properties of the sample used are:

Silicon dioxide (SiO ₂), percent	41.9
Magnesium oxide (MgO), percent	1.0
Calcium oxide (CaO), percent	2.7
Aluminum oxide (Al_2O_3) , percent	22.5
Iron oxide (Fe ₂ O ₃), percent	25.8
Sulphur trioxide (SO ₃), percent	0.8

¹ Presently Assistant Professor of Civil Engineering, Indian Institute of Technology, Bombay, India.

Available alkalies (as Na ₂ O), percent	0.3
Loss on ignition, percent	3.6
Moisture content, percent	0.2
Specific gravity	2.61
Fineness (percent passing No. 325 sieve)	88.7
Specific surface (sq cm/g)	2720

Lime

The lime was calcium hydroxide, reagent grade, from the Allied Chemical and Dye Corporation.

Chemicals

Forty-seven chemicals were evaluated. The selection included chemicals known or suspected to improve the pozzolanic reaction as well as chemicals whose effect on the reaction was unknown (1, 2, 3, 4, 5, 6). The chemicals were reagent, technical or purified grade. They are grouped in Table 1, primarily on the basis of their reactions —basic, neutral or acid. 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 solution to varying extents. Neutral salts in water solution do not upset the natural balance of hydrogen and hydroxyl ions. Unclassified chemicals are in the miscellaneous group.

METHODS

Mix Proportions

Lime-flyash mortars were composed of 75 percent Ottawa sand and 25 percent lime and flyash, with the ratio of lime to flyash either 1:9 or 1:4. (75:2.5:22.5 or 75:5:20 Ottawa sand-lime-flyash.) The trace chemical additive was 0.5 and/or 1 percent, based on the dry weight of the mortar. Chemicals were added to the dry mortar as a powder or as a component of the mix water which was close to standard Proctor optimum moisture (ASTM Designation: D698).

Mixing and Molding

Mixing of batches for preparing test specimens was done in a Hobart kitchen mixer, model C-100, at low speed. The dry ingredients were mixed 25 sec; then the mix water was added and mixing continued for 4 minutes.

Molding was started immediately after a batch was mixed. A double plunger drophammer apparatus was used to mold 2 in. diameter by 2 in. high specimens to approximate standard Proctor density.

Curing

Specimens of each batch were moist cured at near 70 F and 100 percent relative humidity for 7 days, 28 days and 4 months. To better preserve moisture and reduce entry of carbon dioxide from the air, all specimens were wrapped in wax paper sealed with cellophane tape.

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 0.10 in. per minute. Tests were run in triplicate and the average strengths are reported.

Free-Thaw Testing

Twenty-eight day cured 2- x 2-in. specimens of selected mixtures were subjected to cycles of freezing and thawing. Specimens on water saturated felt pads were frozen

TABLE 1					
CHEMICALS	EVALUATED	AS	ADDI	TIV	ES

Group and Chemical	Formula	Manufacturer
BASES		
Potassium hydroxide	КОН	J.T. Baker Chem. Co.
Sodium hydroxide	NaOH	11 11 11 11 11
BASIC SALTS		
Lithium carbonate	Li ₂ CO ₃	Fisher Scientific Co.
Potassium bicarbonate	KHCO ₃	Mallinckrodt Chem. Works
Potassium carbonate	K ₂ CO ₃	J.T. Baker Chem. Co.
Sodium bicarbonate	NaHCO ₃	11 11 11 11 11
Sodium borate	Na ₂ B ₄ O ₇ · 10H ₂ O	Fisher Scientific Co.
Sodium carbonate	Na ₂ CO ₃	J.T. Baker Chem. Co.
Sodium sulfite	$Na_2SO_3 \cdot 7H_2O$	11 11 17 TT TT
NEUTRAL SALTS		
Lithium chloride	LiCl	J.T. Baker Chem. Co.
Lithium fluoride	LiF	Fisher Scientific Co.
Lithium nitrate	LiNO ₃	11 11 11
Lithium sulfate	Li2SO4 · H2O	** ** **
Potassium chlorate ^a	KClO ₃	J.T. Baker Chem. Co.
Potassium chloride	KCl	11 11 11 11 11
Potassium dichromate ^a	K ₂ Cr ₂ O ₇	Fisher Scientific Co.
Potassium permanganate ^a	KMnO₄	J. T. Baker Chem. Co.
Sodium chloride	NaCl	11 11 11 11 11
Sodium dichromate ^a	Na ₂ Cr ₂ · 3H ₂ O	Fisher Scientific Co.
Sodium hypochlorite ^a	NaOC1 b	11 11 11
Sodium nitrate	NaNO ₃	J.T. Baker Chem. Co.
Sodium pemanganate ^a	NaMnO ₄ ·3H ₂ O	Fisher Scientific Co.
Sodium sulfate	Na ₂ SO ₄	J.T. Baker Chem. Co.
ACID SALTS		
Aluminum chloride	AlCl ₃ · 6H ₂ O	J.T. Baker Chem. Co.
Ammonium chloride	NH ₄ Cl	Allied Chem. & Dye Corp.
Calcium chloride	CaCl	J.T. Baker Chem. Co.
Calcium hypochlorite ^a	Ca(OCl)	Fisher Scientific Co.
Calcium sulfate	CaSO ₄ · 2H ₂ O	J.T. Fisher Chem. Co.
Chromic chloride	CrCl ₃ · vH ₂ O	Fisher Scientific Co.
Cobaltous chloride	CoCl ₂ · 6H ₂ O	11 11 11
Cupric chloride	CuCl	** ** **
Ferric chloride	FeCla	** **
Ferric sulfate	$Fe_2(SO_4)_3 \cdot xH_2O$	Allied Chem. & Dve Corp.
Ferrous chloride	FeCl ₂ · 4H ₂ O	Fisher Scientific Co.
Ferrous sulfate	FeSO ₄ · 7H ₂ O	J.T. Baker Chem. Co.
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	Allied Chem. & Dye Corp.
Manganous chloride	MnCla · 4HaO	Fisher Scientific Co.
Nickel chloride	NiCla 6H2O	tt ty ty
Stannous chloride	SnCl ₂ · 2H ₂ O	11 17 11
Titanium tetrachloride	TiCl₄	** ** **
Zinc chloride	ZnCl ₂	PT PT 11
MISCELLANEOUS		
Ethylene glycol	CH₂OHOH₂OH	Wilkens-Anderson Co.
Magnesium oxide	MgO	Allied Chem. & Dye Corp.
Portland cement	_	Hawkeye Portland Cement Co.
Potassium_biphthalate	KHC8H4O4	J.T. Baker Chem. Co.
Quadrafos ^c	—	Rumford Chem. Co.
Vanadyl dichloride	VO Cla	Fisher Scientific Co.

^a Strong oxidizing agent. ^b In solution with 5 to 6 percent available chlorine. ^c Tradename for sodium tetraphosphate (P₂O₅, 63.5 percent; Na₂O, 36.0 percent; H₂O, 0.5 percent). at -10 F for 23 hr; then they were removed from the freezer and allowed to thaw in open air for 2 hr and in a moisture (near 100 percent RH) room for 23 hr. This was one cycle. Specimens were tested for unconfined compressive strength after 0, 1, 4, 5, 7, 9 and 12 cycles, (zero cycle specimens were immersed in water for 2 hr before testing for strength). Strengths reported are the average for three specimens.

GENERAL COMPARISON OF CHEMICALS

The first study of the investigation was a general comparison of the chemicals to determine their relative effects on 7-day, 28-day and 4-month strengths. The amount of each chemical treatment was 0.5 percent, based on the dry weight of the 75 percent

No additive Lithium carbonate (suspension) Potassium hydroxide (solution) Sodium hydroxide (solution) Sodium permanganate (suspension) Quadrafos (solution) Sodium carbonate (solution) Sodium sulfite (solution) Potassium permanganate (suspension) Potassium bicarbonate (solution) Lithium sulfate (solution) Potassium carbonate (solution) Sodium bicarbonate (solution) Lithium fluoride (suspension) Lithium nitrate (solution) Sodium nitrate (solution) Sodium chloride (solution) Sodium sulfate (solution) Potassium chloride (solution) Manganous chloride (solution) Potassium dichromate (solution) Magnesium chloride (solution) Ferric chloride (solution) Ammonium chloride (solution) Potassium chlorate (solution) Vanadyl chloride (suspension) Calcium chloride (solution) Nickel chloride (solution) Stannous choride (solution) Ferrous chloride (solution) Cobaltous chloride (solution) Ferrous sulfate (solution) Amm chloride + sodium chl (sol) Sodium dichromate (solution) Chromic chloride (solution) Lithium chloride (solution) Aluminum chloride (solution) Portland cement (powder) Ferric sulfate (suspension) Calciúm sulfate (suspension) Sodium hypochlorite (solution) Calcium hypochlorite (solution) Magnesium oxide (solution) Ethylene glycol (solution) Zinc chloride (solution) Potassium biphthalate (solution) Cupric chloride (solution) Sodium borate (suspension) Titanium tetrachloride (solution) No additive



Unconfined compressive strength after one day immersion, psi

Figure 1. Immersed strengths after 7-day, 28-day, and 4-month normal moist curing of 2 in. diameter by 2 in. specimens prepared at standard Proctor density from 75:2.5:22.5 Ottawa sand-lime-flyash mortar treated with 0.5 percent of each chemical listed. Chemicals are listed fr m top to bottom in decreasing order of benefit to 7-day strength. All chemicals were added to the mortar dissolved or suspended in the mix water.

Ottawa sand: 2.5 percent lime: 22.5 percent flyash mortar. The chemicals were added dissolved or suspended in the mix water.

Test results are shown by bar graphs in Figure 1. Starting at the top of the figure chemicals are listed in order of decreasing benefit to 7-day strength.

7-Day Strength

The 7-day strength of a soil-lime-flyash road base is of much practical significance. Seven days is about as long as newly constructed roads can be kept closed to traffic, and to avoid rutting, base course strength, as measured by the unconfined compression test, may have to reach 100 to 300 psi, depending on soil type stabilized, road usage and thickness of bituminous surfacing. Since the strength gain of soil-lime-flyash road bases is greatly reduced or even halted when the temperature drops to near freezing, 7 days of curing in northern climates may represent the maximum obtainable in late season construction. For adequate freeze-thaw resistance, soil-lime-flyash bases may need a strength of 300 to 500 psi, depending on soil type stabilized, thickness of bituminous surfacing and severity of the climate.

The 7-day strength, after 24 hr immersion, of untreated Ottawa sand-lime-flyash specimens averaged only 9 psi (Fig. 1), illustrating the slowness of the pozzolanic reaction under normal curing conditions. Many of the chemicals greatly increased 7-day strength; these may be classed as accelerators for the lime-flyash reaction. The primary purpose of this investigation was to discover such chemicals.

Best strength acceleration was with lithium carbonate which gave an average 7-day strength of 226 psi, over 47 times the strength of the untreated reference specimens. Potassium hydroxide, sodium hydroxide, sodium permanganate and Quadrafos gave 7-day strengths near or above 300 psi. Sodium carbonate, sodium sulfite, potassium permanganate, potassium bicarbonate, lithium sulfate, potassium carbonate, sodium bicarbonate, lithium nitrate also are worthy of special mention, all giving 7-day strengths near or over 200 psi.

A look at the classification of chemicals in Table 1 shows that the two bases were good activators for the pozzolanic reaction. The basic salts, with the exception of sodium borate, gave 7-day strengths over 150 psi. The neutral salts produced variable results; best were the strong oxidizing agents potassium permanganate and sodium permanganate, both giving strengths over 200 psi. The acid salts did not appreciably improve 7-day strength. Of the chemicals in the miscellaneous group, only Quadrafos gave good 7-day strength.

28-Day Strength

Twenty-eight days of curing can usually be counted on in late summer or early fall construction and ideally soil-lime-flyash should reach adequate strength before the first freeze. The untreated lime-flyash mortar specimens did not gain adequate strength in 28 days (Fig. 1), the average being only 34 psi.

The chemicals cited as most beneficial to 7-day strength also greatly improved 28-day strength, but it will be noted that the order of merit is somewhat changed. Also, a number of chemicals which did not look promising on the bais of 7-day strength improvement, showed up well in the 28-day tests. Chemicals which gave 28-day strengths near or above 600 psi (about 18 times the 28-day untreated strength) are: potassium hydroxide, sodium hydroxide, potassium permanganate, potassium carbonate, sodium carbonate, calcium chloride, sodium bicarbonate and potassium bicarbonate, listed in order of decreasing merit. Many of the other chemicals gave 28-day strengths of 400 to 500 psi or higher. Among the most promising of this group are: lithium carbonate, sodium permanganate, sodium sulfite, sodium chloride, and the 50:50 combination of ammonium chloride and sodium chloride.

The bases and the basic salts, except sodium borate, again gave best results. The neutral salts, except sodium hypochlorite, gave 28-day strengths over 300 psi. Among the acid salts, calcium chloride, ammonium chloride, magnesium chloride and manganous chloride gave strengths over 300 psi, but as a whole the chemicals in this group rated low. Quadrafos and the 50:50 combination of ammonium chloride and sodium chloride were the most promising in the miscellaneous group.

4-Month Strength

The average 4-month strength of the untreated Ottawa sand-lime-flyash specimens was 589 psi, which is very adequate, and demonstrates that the long-term strength of lime-flyash stabilized soil is not a problem. In northern climates, spring or early summer construction is necessary to obtain 4 months of curing. But even when this is possible, sufficient early strength to carry traffic is necessary.

Figure 1 shows that most of the chemicals cited as being very beneficial to 7 and/or 28-day strengths caused little or no improvement of 4-month strength, or even decreased it. The greates benefit to 4-month strength was obtained with calcium chloride (855 psi) and manganous chloride (852 psi). Both of these chemicals were beneficial to 28-day strength, particularly calcium chloride, but they rated low on the basis of 7-day



Figure 2. Relationship between strength and pH of 75:2.5:22.5 Ottawa sand-lime-flyash mortar treated with 0.5 percent of the different chemicals.

strength improvement. Calcium hypochlorite gave a 4-month strength of 789 psi, but 7 and 28-day strengths with this chemical were very low. On the basis of strength improvement at all three ages, potassium permanganate might be rated highest. Other chemicals giving 4-month strengths above 700 psi, and which were also noteworthy for 7 and 28-day strength improvements, were: sodium permanganate, lithium fluoride and lithium nitrate. Potassium dichromate and sodium dichromate gave 4-month strengths over 700 psi and also gave good 28-day strengths, but both rated low at 7-days.

The bases and the basic salts did not contribute much to the 4-month mortar strength indicating that the chemicals in these groups act mainly as activators of the lime-flyash reaction. The three chemicals which gave the highest 4-month strengths are acid salts, but several neutral salts also were beneficial; other chemicals in these two groups reduced 4-month strength. Several of the better neutral and acid salts are strong oxidizing agents (Table 1). In the miscellaneous group, vanadyl dichloride and the 50:50 combination of ammonium chloride and sodium chloride were slightly beneficial.

Density Variations

Some of the chemical additives influenced the compaction characteristics of the 75:2.5:22.5 Ottawa sand-lime-flyash mortar as evidenced by variations in the dry density of test specimens. The maximum variation from the compacted density of the untreated mortar was plus 6.4 or minus 2.6 pcf. However the variations in density do not correlate with the improvements in strength.

pН

Determinations of pH were made on material from specimens tested for unconfined compressive strength. (The electrometric method was used, employing 15 grams of sample in 30 mm of distilled water.) The object was to find a relationship between strength and pH after each curing period. A significant correlation is not evident to the authors from the data plotted in Fig. 2 although it is seen that mixtures containing the bases and basic salts maintained a relatively constant and high pH during the three curing periods.



Figure 3. Comparison of powder vs mix water application of chemical additives. The amount of chemical was 0.5 percent; the mortar was 75:2.5:22.5 Ottawa sand-lime-flyash.

All pH values were in the alkaline range due to the presence of calcium hydroxide. The amount of lime present in the mixtures was greater than the maximum solubility (1.2 grams per liter) of calcium hydroxide at 25 C. Enough lime was present to counterbalance the influence of the acid salts used as additives. Decreases of the pH of mixtures with time is presumably due to the lime being used up in the pozzolanic reaction.

POWDERED VS LIQUID APPLICATION OF CHEMICALS

Since some of the chemicals could be used in powdered form, and dry mixed with the lime-flyash mortar prior to adding the mix water, a check was made to fine out what effect powdered application would have on mortar strengths. Test results in Fig. 3 show that most of the chemicals gave better results when mixed as a powder. Most noteworthy is powdered sodium carbonate which produce 7-day, 28-day and 4-month



Figure 4. Effect of amount of chemical additive on strength of 75:2.5:22.5 Ottawa sand-lime-flyash mortar.

strengths that are, respectively, 71, 28 and 18 percent higher than the comparable strengths produced by liquid application of sodium carbonate.

AMOUNT OF CHEMICAL

The use of more chemical additive than 1 percent may not be economical; 0.5 percent represents a more desirable treatment level. A comparison of strength benefits from 1 and 0.5 percent chemical treatments of 75:2.5:22.5 and 75:5:20 mortars are shown in Figs. 4 and 5. It appears that there is little advantage and perhaps a disadvantage in using more than 0.5 percent chemical, particularly of the more promising additives such as sodium carbonate, sodium hydroxide, potassium hydroxide, calcium chloride, aluminum chloride, potassium permanganate and magnesium oxide.

INFLUENCE OF LIME TO FLYASH RATIO

The ratio of lime to flyash may be an important factor affecting the strength attained by soil-lime-flyash mixtures. In the present investigation the influence of the ratio was studied by comparing the strength gains of chemically treated 75:2.5:22.5 (ratio 1:9) and 75:5:20 (ratio 2:8) Ottawa sand-lime-flyash mortars. The results obtained from 1 and 0.5 percent chemical treatments are shown in Figures 6 and 7 respectively.

7-Day Strength

The 7-day strengths, with a few exceptions, were similar for both ratios. The exceptions are of interest because they involve three of the most promising activators: potassium hydroxide, sodium hydroxide and sodium carbonate. One percent powdered sodium carbonate gave highest strength with the 2:8 ratio mortar, the increase being





144 psi; with 0.5 percent sodium carbonate the 7-day strength difference between the two mortars was negligible. One-half percent sodium hydroxide gave best results with the 1:9 ratio mortar by about 100 psi, whereas little strength difference was observed for the 1 percent treatment. Potassium hydroxide likewise favored the 1:9 ratio mortar, the strength increase being about 100 psi for the 0.5 percent treatment.

28-Day Strength

It is difficult to conclude which lime to flyash ratio gave the best 28-day strength. With the better chemicals previously cited, good strengths were obtained with both ratios. Examples of chemical treatments most sensitive to the ratio are: 0.5 and 1 percent calcium chloride, which gave best results with the 1:9 ratio mortar by about 150 to 230 psi; 1 percent potassium permanganate, which was best with the 2:8 ratio mortar by about 260 psi; and 0.5 and 1 percent sodium carbonate, which produced best strengths with the 2:8 ratio mortar by about 250 to 390 psi.

4-Month Strength

The best 4-month strengths without exception were obtained using the 2:8 lime to flyash ratio; in some cases the strength was two or more times that obtained when the ratio was 1:9. The following chemicals produced 4-month strengths above 1,000 psi: aluminum chloride, calcium chloride, potassium permanganate, sodium carbonate and magnesium oxide. Of these, only magnesium oxide was appreciably less effective when the amount used was 0.5 percent.



Figure 6. Effect of lime to flyash ratio on strength benefits from 1.0 percent chemical treatments. The mortars were composed of 75 percent Ottawa sand and 25 percent lime and flyash.

The strength retention through 12 cycles of alternate freezing and thawing of 28-day cured 2-in. diameter x 2-in. specimens provides an indication of relative durability. The effects of 0.5 percent of any one of four chemicals on the durability of the 75:2.5: 22.5 mortar are shown in Figure 8.

The mortar specimens with no chemical additive showed high strength retention, but initial strength was less than 200 psi. Specimens containing sodium carbonate (added as a powder) had a marked decrease in strength, but after 12 cycles the strength retained was more than 600 psi. Potassium permanganate treated specimens, after a decrease in strength through 4 cycles, showed an abrupt increase to over 600 psi which was retained with little reduction through the last 8 cycles. Specimens containing calcium chloride and sodium chloride failed after the fifth cycle.

SUMMARY DISCUSSION

Evaluation of Chemicals by Groups

Classification of the chemical additives as in Table 1 permits some generalized statements concerning the effects of each group on the lime-flyash (pozzolanic) reaction. The bases and the basic salts, except sodium borate, greatly improved early strength, but did not improve long-term strength to a proportionate degree. Thus most chemicals in these two groups appear to be good activators (accelerators) of the pozzolanic reaction. One of the basic salts, sodium carbonate (soda ash), is considered the most promising trace chemical evaluated.



Figure 7. Effect of lime to flyash ratio on strength benefits from 0.5 percent chemical treatments. The mortars were composed of 75 percent Ottawa sand and 25 percent lime and flyash.

The neutral salts produced very good 28-day strengths, which were further improved after 4 months curing. With only two exceptions 4-month strengths were close to or higher than the untreated mortar strength. Seven-day strengths with neutral salt additives were higher than the corresponding untreated mortar strength, but the improvement was not always exceptional. The most promising activators in this group are potassium permanganate, sodium permanganate, lithium sulfate, lithium fluoride, lithium nitrate, sodium nitrate and sodium chloride (because it is cheap).

The acid salts did not appreciably improve 7-day strength, but some gave marked improvement to 28-day and 4-month strengths. The most promising chemicals in this



Figure 8. Effect of freezing and thawing on strength of 28-day cured 2 in. diameter by 2 in. specimens of 75:2.5:22.5 Ottawa sand-lime-flyash mortar treated with 0.5 percent each of sodium carbonate, potassium permanganate, calcium chloride and sodium chloride. Sodium carbonate was added to the mortar in powdered form; the other chemicals were added in the mix water.

group are the chlorides, particularly calcium chloride and manganous chloride. Calcium hypochlorite gave very good 4-month strength but 7- and 28-day strengths were low with this chemical.

In the miscellaneous group of chemicals, Quadrafos was most beneficial to 7-day strength; magnesium oxide was beneficial to 28-day and 4-month strengths.

Mechanism of Benefits

An explanation of the mechanism of the beneficial effects obtained with the different chemicals is difficult because each chemical or narrow range of chemicals may act in a completely different way. A chemical may act as a catalyst or as an inhibitor or as a component of the pozzolanic reaction, and also may go into side reactions other than the pozzolanic reaction and produce either cementing or inert materials.

<u>Bases and Basic Salts.</u> —Alkaline additives increase the amount of available hydroxyl ions in the moistened Ottawa sand-lime-flyash system, and as a result the pozzolanic reaction may be accelerated by the increased solubility of the siliceous material (4). For example sodium hydroxide may act as a catalyst in which: (a) it first reacts with the siliceous material to produce intermediate sodium silicates, (b) 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, (c) the sodium hydroxide is then free for further reaction with unreacted siliceous material.

The most promising of the alkaline additives, sodium carbonate, very likely reacts with lime in the moist Ottawa sand-lime-flyash mixture to form calcium carbonate and sodium hydroxide. The precipitated calcium carbonate contributes cementation to the system, and, as hypothesized in the preceding paragraph, the sodium hydroxide acts as a catalyst. The formation of calcium carbonate from the lime obviously decreases the amount of lime available for the pozzolanic reaction. The hypothesis is apparently consistent with the experimental data: with a 1:9 ratio of lime to flyash better strength results were obtained with 0.5 percent sodium carbonate than with 1 percent, whereas the opposite results were obtained with a 2:8 ratio. This indicates the possibility of an optimum amount of sodium carbonate for a given amount of lime.

Acid Salts. — Acid salts undergo a hydrolysis reaction with the precipitation of weak bases (hydroxides). This may be summarized as follows:

$$R_n X_m + nm H OH \vec{\leftarrow} nR(OH)_m + mH_n X_2$$

With calcium hydroxide this reaction proceeds as follows:

$$2R_n X_m + nm Ca (OH)_2 \stackrel{\checkmark}{\leftarrow} 2n R (OH)_m + m Ca_n X_2.$$

With aluminum chloride as the acid salt, a weak base is precipitated and an equivalent amount of lime is withdrawn from the reaction,

$$2 \operatorname{AlCl}_3 + 3 \operatorname{Ca(OH)}_2 \rightarrow 2\operatorname{Al(OH)}_3 + 3 \operatorname{CaCl}_2.$$

weak base

The removal of lime results in a reduction of the lime to flyash ratio. Thus acid salts may impede the development of strength when the ratio of lime to flyash is 1:9. For example when aluminum chloride was used in mixtures having a 1:9 ratio of lime to flyash, strengths were much lower than when the ratio was 2:8. In mixtures with a 1:9 ratio 1 percent aluminum chloride gave lower strengths than 0.5 percent aluminum chloride.

Some of the weak bases formed, such as Al $(OH)_3$ and $Fe(OH)_3$, have some cementing and water-proofing properties which may be beneficial. Such weak bases may also affect the long-term formation of hydrated calcium silicates and thus increase long-term strength.

Although calcium chloride is an acid salt, the principal long-term strength benefits

obtained with this chemical are thought due to a different type of chemical mechanism than discussed above. Calcium chloride being highly hygroscopic and deliquescent ensures a relatively high concentration of calcium ions over a long period of time by providing moisture for a solution. Since lime has a lower ionization constant than calcium chloride, the concentration of calcium ions from lime is lower than that from calcium chloride. Also lime is subject to conversion to calcium carbonate during long curing periods; when this takes place pozzolanic action ceases. The experimental data tend to support this line of reasoning: calcium chloride was found to be very beneficial to 4-month strength, whereas it only slightly improved 7-day strength.

Sodium chloride may act similarly to calcium chloride but there appears to be less benefit to long-term strength, perhaps because sodium chloride is less hygroscopic and deliquescent than calcium chloride. Another difference is that some sodium hydroxide is probably formed, and thus a small amount of catalysis would be expected. This may explain why sodium chloride gave slightly higher 7-day strength than calcium chloride.

<u>Neutral Salts.</u>—The reactions of neutral salts with the Ottawa sand-lime-flyash mixtures are somewhat more complicated than those of the other groups. The most promising neutral salts, potassium permanganate and sodium permanganate, are strong oxidizing agents. It is believed that these chemicals oxidize the carbon in the flyash with the consequent production of potassium carbonate or sodium carbonate, and the precipitation of manganese dioxide. These carbonates, as discussed previously, then give rise to further reactions which are benficial to strength. It is also believed that the permanganates, and other strong oxidizing agents, benefit strength by reacting with grains of flyash, cleaning the surfaces and making them more available for chemical reactions with lime. As already mentioned, several of the better neutral and acid salts were strong oxidizing agents.

<u>Miscellaneous Chemicals</u>. —Quadrafos (sodium tetraphosphate), the only chemical in the miscellaneous group that greatly benefited early strength, may react with lime to produce complex phosphate cementation products which supplement those produced by the pozzolanic reaction. The availability of sodium ions to form sodium hydroxide may improve the pozzolanic reaction as previously discussed under bases and basic salts.

The beneficial effect of magnesium oxide, another miscellaneous chemical, is an agreement with the findings of previous research that dolomitic monohydrate (Type N) lime gives greater strengths than high-calcium lime (6). The present data show that magnesium oxide was most effective when added as a powder, when the amount was 1 percent, and when the lime to flyash ratio was 2:8. The mechanism of the benefit can only be guessed at. Perhaps cementation by calcium magnesium silicates is better than by calcium silicates?

<u>Powdered vs Liquid Application of Chemicals.</u>—All chemicals tried gave best results when used in powdered form, rather than when added in the mix water as a solution or suspension. This may be due to consumption of the chemical by side reactions that take place more rapidly in solution or suspension than in a semi-dry system. Another possibility is that lesser amounts of chemicals than were studied are needed for optimum benefits when the chemicals are added in water.

The greatest benefit from use of a powdered chemical was with sodium carbonate. The reaction of this chemical with lime in the mortar is responsible for the previously discussed precipitation of calcium carbonate cement. Calcium carbonate is thought to be more effective as a cement when precipitated after the mortar has been compacted, because then the carbonate crystals are formed on the sand (and flyash) grains. This is more apt to occur when sodium carbonate is added in powdered form since when added in the mix water, the calcium carbonate may be prematurely precipitated before compaction is completed. Perhaps another advantage in using powdered sodium carbonate is that a slower production of sodium hydroxide may be more favorable to the sustained formation of pozzolanic cementing products.

CONCLUSION

Several of the forty-seven chemicals evaluated in lime-flyash mortars greatly in-

crease early strength. Other chemicals benefit long-term strength more than early strength; calcium chloride is one of the most promising chemicals in this group.

All factors considered, sodium carbonate (soda ash) is considered the most promising trace chemical activator investigated. Best results are obtained when it is mixed in powdered form. The use of 0.5 percent powdered sodium carbonate in a mixture of 75 percent Ottawa sand: 5 percent lime: 20 percent flyash increased 7-day strength about sixty times, and 28-day and 4-month strengths about two times.

ACKNOWLEDGMENTS

The subject matter of this report was obtained as part of the research being done under Project 283-S of the Engineering Experiment Station of Iowa State College. This project, entitled "The Loess and Glacial Till Materials of Iowa; An Investigation of Their Physical and Chemical Properties and Techniques for Processing Them to Increase Their All-Weather Stability for Road Construction," is being carried on under contract with the Iowa State Highway Commission and under the sponsorship of the Iowa Highway Research Board and is supported by funds supplied by the Commission.

Thanks are given to Dr. R. L. Handy, Dr. J. B. Sheeler, Mr. T. Demirel and other members of the Engineering Experiment Station for contributions to this investigation.

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