

# Introductory Remarks

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● SEVERAL REPORTS on the use of phosphoric acids and phosphates in soil stabilization were offered to the Department of Soils, Geology and Foundations after the deadline for acceptance of papers for the 1960 Annual Meeting of the Highway Research Board. Because it was too late for their inclusion in the already established program, and in view of the apparent renewal of interest in the use of such compounds in soil stabilization, it was decided that a symposium be organized on this topic for the 1961 meeting of the Board. J.W. Lyons, of the Monsanto Chemical Company, was asked to collect and organize papers for this symposium. This he did diligently and effectively, and it is deemed no more than fair that he take the chair during presentation of those papers due to his efforts.

This should not indicate a lack of interest in this area on the part of the committee chairman. On the contrary, in 1933 he was conducting field experiments for the Missouri State Highway Department on the soil stabilizing effect of soluble phosphates (1); subsequently, in the early 1940's, in work for the Civil Aeronautics Administration and the Air Force, and again in the later forties, in work for the Navy Department, he directed laboratory and field experiments on the soil stabilizing power of phosphoric acids and acid, neutral and basic phosphates, by themselves or in combination with organic amines, amine-aldehyde condensation products, partially neutralized resinous fatty and lignin acids, and other chemicals. A number of the soil systems thus treated could be considered as stabilized; however, the stringent requirements set up by the Government for that program, requiring that less than 2 percent of stabilizer had to provide effective stabilization under war construction conditions, and the vagaries encountered with phosphate stabilization, forced him to follow other more promising lines of research. Though much of this work was originally confidential, it has long since become declassified. In 1945, still under war-time restrictions, he wrote "So far, none of the soil treatments based on the formation of an insoluble silicate, phosphate, borate, or other inorganic salt in the soil has been successful in shallow soil stabilization, within an economical range of material employed. Winterkorn believes that no formation of an insoluble compound will result in satisfactory soil stabilization for road and airport bases, if such formation involves also the formation of a soluble salt, which may increase the water affinity of the soil system." (2) The obvious inference was that best results had been obtained by reaction between the phosphoric acids and aluminum and iron components of the solid soil minerals.

Such reactions, occurring at normal temperatures between soil constituents and phosphoric acids, as well as acid salts, had long been known and studied, mainly because of their undesirability in the manufacture of super- and double super-phosphate fertilizers (3) and in the fertilizing of soils possessing clay minerals of low silica-sesquioxide ratios. A good deal of research in agricultural chemistry has been and still is being devoted to the elucidation of this complex field. The complexity is, of course, one of the main reasons for the vagaries so often encountered in phosphate-soil stabilization.

With respect to the development of cementing power as a result of such reactions, a considerable body of knowledge was already available to the chemical art, by 1931. Proof of this can be found in practically every old-time chemical formulary or book of chemical recipes. A typical recipe (4) reads as follows:

<u>Dental Cement:</u>	Lithium phosphate	1/2 oz
	Phosphoric acid	5 oz
	Zinc phosphate	1/2 oz
	Aluminum phosphate	1/3 oz

The above is added to a ground porcelain of the following composition:

Alumina	30 - 50 oz
Feldspar	10 - 20 oz
Sand	25 - 40 oz
Zinc oxide	1 - 10 oz

The bearing of this recipe on phosphate soil stabilization is apparent from the composition of the ground solids to be cemented. It is also apparent that this "empirical" recipe is quite scientific insofar that the chemicals first mixed with phosphoric acid show the latter's molecules what type of reaction is expected from them.

An ever-present problem in producing either crystals of appreciable size, coherent coatings, or cementing substances by the interaction of two solutions is the formation of too many crystal nuclei deriving from too high a concentration or activity of the reagents. This often results in pulverulent, noncementing systems. Thus, Henin, in attempting to synthesize montmorillonite in an aqueous medium, obtained nothing but amorphous floccules when he added the soluble silicate even in very low concentrations. The desired synthesis occurred, however, by itself when the reagent-catalyst solution without the soluble silicate was stored for an extended period of time in a glass vessel. The rate of solution of silicate from the glass was slow enough to permit its orderly incorporation into a structure that proved to be montmorillonite.

Slow reactions of this kind are important in many types of soil stabilization. For quicker formation of cementing substances, one normally chooses an aqueous phase of elevated viscosity. This viscosity is supposed to slow down the movement of the reacting ions or molecules to a sufficient extent to permit the development of a structure that possesses the desired cementing properties. This argument possesses validity as far as true viscosity is concerned. It breaks down, however, in the many cases of structural viscosity in which essentially the same molecular and ionic mobility may obtain, irrespective of whether the solvent is in the form of a free liquid or has become enmeshed within a gel structure. It may well be, though, that such gels or similar systems, which owe their high integral flow resistance to a secondary structure, induce the reactants to build themselves into this structure or at least to follow its pattern. Keeping in mind that silicates, phosphates, borates, and similar compounds are essentially oxygen structures, with positive ions built in whenever geometry and electric neutralization requirements call for it, and that the water molecule itself is volumetrically mostly oxygen, the importance of a reaction-directing gel or related structure should be apparent. Such a role is easily played by many hydrophilic organic substances such as carbohydrates and proteins, and their intimate interaction with phosphates both within and outside of living bodies is well known. The bearing of this on cementing action is also well illustrated by the following old recipe (4, 1:9).

#### Casein Glue, Water Resistant

Casein	39	Add the solids slowly to the water while stirring with an efficient stirrer. Continue until smooth and free from lumps. Allow to stand 20-30 minutes and add a mixture of aldol $\frac{1}{2}$ , water 1, and 50 per cent copper nitrate 2. Stir for 5 minutes then it is ready for use.
Peanut meal	39	
Hydrated lime	11	
Trisodium phosphate	4	
Sodium fluoride	7	
Water	225-235	

Before denouncing a formula of this type as "creeping empiricism", a second look had better be taken. This reveals an ingenious use of the following:

1. Interaction with water of the casein and peanut meal, on one hand, and of the inorganic ions, especially  $\text{PO}_4^{---}$ , on the other, with formation of specific hydration structures;
2. Interaction between  $\text{PO}_4^{---}$ ,  $\text{Ca}^{++}$ , and  $\text{F}^-$ , influenced by their respective hydration structures and also by that of the organic components of the system;
3. Denaturation of the proteins by the excess of the inorganic ions over the amounts

required for apatite formation and sorptive binding of these excess ions by the organic matter.

4. Waterproofing treatment by reaction of the proteins with the aldol.

5. Utilization of the fungicidal and bactericidal properties of fluorine and copper ions.

With similar combinations, but employing aniline-furfural in small amounts, as more effective waterproofing and germicidal agents, beach sands have effectively been stabilized in the laboratory and in small field tests.

This composition may be viewed from another angle, namely, the stabilization of the very hydrophilic casein and peanut meal by means of a calcium phosphate compound. In stabilization of soils with phosphoric acid, calcium in the soil has been found quite detrimental. Are there not some valuable lessons to be learned from this formula for the potential phosphate stabilization of such soils and also from the fact that calcium-rich soils usually contain in their organic matter a goodly portion of proteins?

At the present time there are on the market several well-established cementing and waterproofing materials that are of lower cost than phosphoric acid with or without ancillary additives. To gain field experience for cementing phosphate stabilization, similar in extent and dependability to that accumulated in the past for bituminous, portland cement and lime stabilization, for example, would require investments of a magnitude that no single chemical company could justify to its stockholders. Nor could any state highway department, singly or in combination with others, justify such expense or even in this time of shortage of highway engineering personnel justify assignment of the necessary trained men to such a development.

As far as cementing stabilization with the various phosphoric acids and phosphates is concerned, the limited available resources need to be directed to possible stabilization of such soils or soil conditions for which stabilization by presently available means and materials has definitely been proven ineffectual or uneconomical. Personnel from the chemical industry and from universities and research institutes that would follow this line, must add to their arsenal of so-called purer chemical and physical weapons those of colloid chemistry and even of allegedly "crude" empiricism if they want to succeed. With growing familiarity with the intrinsic complexity and dynamism of natural and stabilized soil systems under actual service conditions, they will be better prepared to utilize the knowledge accumulated over the years by the many devoted and excellently qualified material and soils engineers in the highway departments.

Cementing stabilization, however, may hardly be considered as the most significant, potential contribution of phosphate and polyphosphate compounds to highway engineering. Rather, more important possibilities are presented by the effect of the respective anions on the structure of the water contained in soil pores and adsorbed on the surfaces of soil mineral and organic constituents. One consequence of such change in water structure is the repression of frost heave in normally susceptible soils. The last paper on the program treats of this subject.

Before concluding these introductory remarks, reference might be made to a case of naturally occurring phosphate-soil stabilization observed and excellently described by Tschebotarioff (5) under the title "An Unusual Case of Accidental Underwater Stabilization of a Natural Clay Deposit and Its Implications."

#### REFERENCES

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4. Bennet, H., "Chemical Formulary." Van Nostrand, 3:15 (1936).
5. Tschebotarioff, G. P., "Soil Mechanics, Foundations and Earth Structures." pp. 325-327.