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VOLUME CHANGE IN CALCAREOUS SOILS DUE TO PHOSPHORIC ACID CONTAMINATION

CHANGEMENT DE VOLUME EN TERRAIN CALCLAIR A CAUSE DE LA CONTAMINATION DE ACIDE PHOSPHORIQUE

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Synopsis: Results of a laboratory investigation to evaluate the effect of phosphoric acid on volume change characteristics of silty clay soils are presented. In-situ soil samples contaminated with phosphoric acid were analyzed for reaction products and mechanism to evaluate volume change characteristics. The subsoils at the site of an industrial building were calcareous in nature and contained large amount of calcite and dolomite. Test results revealed that calcium hydrogen phosphate hydrate or brushite had formed as the reaction product between phosphoric acid and calcium carbonate. The results of the study suggest that the formation of brushite caused volume changes in the in-situ soils as well as the differential movements in the foundations of the supported structures. The test data also indicated that the high solubility of brushite in concentrated acid solution would affect the volume stability of the contaminated in-situ soils and thus cause varying degree of uplift of structures supported on such soils.

INTRODUCTION

Majority of the research in the area of environmental geotechnology is related to the land disposal of waste and hazardous chemicals. The detrimental effect of accidental spillage or leakage of highly aggressive industrial effluents on properties of soils has also received attention but less than it deserves. The leakage of industrial effluent into subsoil directly affects the use and stability of the supported structure. Results of some studies indicate that the detrimental effect of seepage of acids and bases into subsoils can cause severe foundation failures. Lukas et al(1972) reported foundation failures of three industrial buildings as a result of spillage. The dissolution of either the limestone in glacial till or the high silica sand subsoils in the chemical contaminants was found to be the cause of large settlement in each case. Extensive cracking damage to the floors, pavements and foundations of a light industrial building in a fertilizer plant in Kerala State in India was reported by Sridharan et al(1981). In this case, the leakage of phosphoric acid from cracked open drains was the source of contamination which resulted in heaving of the subsoil. The authors gave the possible mechanisms of reaction between subsoil and phosphoric acid as (1) reaction of adsorbed cations with phosphate, (2) reaction of phosphate with sesquioxide, (3) exchange of phosphate ion with hydroxyl ion present in the clays of the subsoil. A similar case of accidental seepage of highly concentrated sodium hydroxide solution as a result of spillage from cracked drains in an industrial establishment in Tema, Ghana caused considerable structural damage to a light industrial building in the factory, in addition to localized subsidence of the affected area (Kumaplay and Ishola, 1985). The undrained shear strength of the contaminated soil was drastically reduced.

Severe damage occurred to the interconnecting piping of a phosphoric acid storage tank in particular and also to the adjacent buildings due to differential movements between pump and acid tank foundations of a fertilizer plant in Calgary, Canada. An average ground heaving of about 15 cm was measured at and near the acid storage tank. The pH value of the subsoil below tank foundation varied from 2.4 to 4.7 with the sampling depths ranging from 30 cm to 150 cm. The pH of the effluent from the tank was about 1.1. Therefore, the damage due to the differential movement and uplifting of the acid storage tank and adjacent buildings was suspected to be caused by the leakage of phosphoric acid into the subsoils.

This paper presents results of a laboratory investigation on the effect of phosphoric acid contamination of in-situ soils at the subject site which might cause uplifting and subsequent failure of the supported structures.

MATERIALS AND TEST METHODS

Three soils were studied in this laboratory investigation. Two of the soils were from the contaminated site and are designated as in-situ soil-1 and in-situ soil-2. In-situ soil-1 which was from location away from the phosphoric acid tank, was relatively less contaminated than the in-situ soil-2 which was located below the acid tank. The third soil was from a construction site on the campus of the University of Calgary(UC soil), which had a very similar mineral composition and geological origin as the in-situ contaminated soils. As the uncontaminated soil was not available from the in-situ site, the UC soil was considered as a representative of the in-situ uncontaminated soil.

The soils were air dried, pulverized and passed through a ASTM #40 sieve before testing. The sieved soils were stored separately in plastic bags for experimental use. All the three soils, as per Unified Classification System, were low plastic silty clays.

Reagent grade ortho-phosphoric acid (86% H_3PO_4) was used as the contaminant in this study. Normal ammonium acetate solution at pH 7.0 and 1N sodium chloride solution were used for exchangeable cations and cation exchange capacity (CEC) analyses of the soils.

The mineralogical analyses of the soils were carried out using a Philips PW 1710 diffractometer with $Co-K\alpha$ radiation. Both the clay and silt fractions were tested. The clay fraction separated by sedimentation under gravity was syphoned off, air dried and pulverized for analysis. The silt fraction was air dried before testing. The X-ray diffraction patterns were recorded and analyzed.

Fractions of the soils finer than $75\mu m$ were analyzed for exchangeable cations and cation exchange capacity using methods similar to those described by Dunn(1983), Hesse (1972) and McClure(1980). Four grams of soil were first washed three times in 95% ethanol to remove

Table 1 Chemical and Mineralogical Characteristics of the Soils

Soil Specimen	Location	pH*	Exchangeable Cations (meq/100g)				CEC meq/100g	Mineralogy
			Na	K	Ca**	Mg		
In-Situ Soil-1	near acid tank brown	6.59	0.2	0.4	30.2	3.6	16.5	Main: quartz, dolomite, calcite, brushite Minor: illite, kao. [#] , mont. ^{##} , feldspar
In-Situ Soil-2	below acid tank brown	6.15	0.6	0.7	32.2	6.2	17.2	Main: quartz, dolomite, calcite Minor: illite, kao., mont., feldspar
UC Soil	UC campus brown	8.30	0.2	0.3	31.2	4.8	11.2	Main: quartz, dolomite, calcite Minor: illite, kao., mont., feldspar

* measured in 1:2 water suspension by weight
 ** may include soluble calcium from calcite and dolomite

kao.- kaolinite
 ## mont.- montmorillonite

Table 2 Physical Properties of the Soils

Soil Specimen	Particle Size Distribution			W ₁ (%)	W _p (%)	PI (%)	Loss on Ignition (%)	OMC (%)	Max. Dry Density (kg/m ³)
	sand(%)	silt(%)	clay(%)						
In-Situ Soil-1	45	37	18	30.5	17.0	13.5	4.5	18.0	1720
In-Situ Soil-2	42	41	17	28.0	14.2	13.8	3.6	15.3	1750
UC Soil	41	39	20	31.2	16.4	14.8	2.5	14.8	1810

soluble salts, then the adsorbed cations were replaced by ammonium ion with three washings in 33 ml 1N ammonium acetate solution at pH of 7.0. After each washing, the soil suspension was centrifuged and the supernatant liquid was collected in a 100ml flask diluted to the mark using deionized water. After the first extraction, the sample was washed 5 times using 1N sodium chloride solution to saturate the exchange complex with Na⁺. The excess Na⁺ was removed by washing three times with ethanol, and the adsorbed Na⁺ was then replaced by ammonium ion again by washing with 1N ammonium acetate solution at pH 7.0 for three times. The supernatant was collected in another 100 ml flask and diluted to the mark. The first extraction was analyzed for sodium, potassium, calcium, and magnesium. The second extraction was tested only for sodium. The CECs of the soils were obtained from the test results of second extractions. A Perkin Elmer atomic adsorption spectrometer was used for the analyses. The mineralogical and chemical characteristics of the soils are presented in Table 1.

Particle size distributions of the soils were determined by hydrometer analysis (ASTM, D442-63). Liquid and plastic limits of the soils were obtained by ASTM procedures D4318-84. Moisture-density relationships were determined according to ASTM D558. Ignition loss of soil was measured at a temperature of 500°C on basis of oven dry soil. The results of tests on physical properties of the soils are presented in Table 2.

The sedimentation volumes of the soils in 0.01N CaSO₄, referred as standard ground water solution (Olson and Deniel, 1981), and in various concentrations of phosphoric acid solutions were studied. Ten grams of air dried specimens passing ASTM #200 sieve were submerged in 50 ml of 0.01N CaSO₄ solution, 0.1M, 0.5M, and 1.0M phosphoric acid solutions in 100 ml graduated glass cylinders. The suspensions were repeatedly stirred and allowed to stand for four hours to ensure wetting of the soil particles. The suspensions were then made up to 100 ml mark with respective salt and acid solutions. The cylinders were then shaken for five minutes and left undisturbed for sedimentation volume measurement. The volumes occupied by settled soil particles were recorded with time until constant sedimentation volumes or equilibrium sedimentation volumes were attained.

SEM pictures were taken from samples of selected sedimentation tests. To minimize the disturbance of the samples, specimen stubs were previously suspended in duplicated cylinders for two and half months before they were taken out. The samples were freeze dried and gold coated for SEM study, as per procedure described by Gillott(1975).

X-ray analyses were performed on the samples from sedimentation tests. Samples taken from the cylinders were first washed four times in distilled water to remove excess acid solution. The prepared samples were then air dried and pulverized for X-ray analysis.

TEST RESULTS AND DISCUSSION

The results of sedimentation tests are presented in Table 3. The time needed to attain equilibrium sedimentation volumes varied from one month to two and half months. It was found that the equilibrium sedimentation volumes were not equal to the smallest sedimentation volumes in some cases. There was a volume increase after the smallest volume was reached particularly for the soil samples settled in 0.5M acid solutions. It was also observed that large quantity of carbon dioxide was evolved from the samples upon inundation in acid solutions. However no gases were observed from similar tests on pure clay samples. An examination of the X-ray diffraction patterns of the soils confirmed that the in-situ soil-1 and UC soil contained calcite and dolomite in abundance, which would react with phosphoric acid to release CO₂. However the in-situ soil-2 contained less amount of these acid reactive minerals, possibly for the reason that it had already reacted with phosphoric acid.

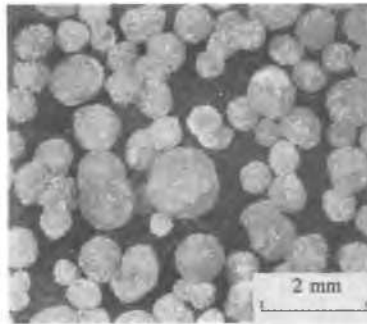
After two and half months, the sediments were taken out and washed with distilled water to remove excess acid solution. During the washing, some brown pellets varying from 0.5 mm to 2 mm in size were noticed in the samples which had been suspended in 0.5M acid solutions. A magnified picture of these pellets is shown in figure 1. Obviously, These pellets were the product of reaction between the soils and phosphoric acid. Electromicroscopic examination of this reaction product revealed a well crystallized narrow platy structure growing in all directions. The etching and

Table 3 Sedimentation Volume Tests on the SoMs

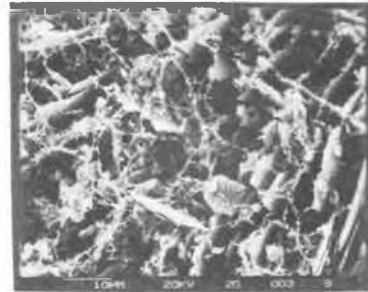
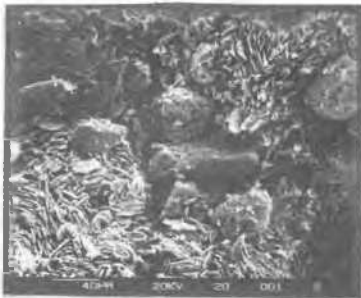
Specimen	Sedimentation Volume (cm ³ /per 10g dry soil)							
	0.01N CaSO ₄		0.1M H ₃ PO ₄		0.5M H ₃ PO ₄		1.0M H ₃ PO ₄	
	Small.*	Equil.**	Small.	Equil.	Small.	Equil.	Small.	Equil.
In-Situ Soil-1	10.5	10.5	11.5	11.5	11.0	12.0	10.0	10.0
In-Situ Soil-2	10.0	10.0	10.5	10.5	10.5	11.0	10.2	10.2
UC Soil	9.5	9.5	10.8	10.8	9.9	11.0	9.9	10.2

* Small: smallest sedimentation volume

** Equil: Equilibrium sedimentation volume



a) crystalline brushite



b) SEM picture of brushite



c) etching and breakdown of calcite

Fig.1 Optical and SEM pictures of brushite formed and acid etching of calcite

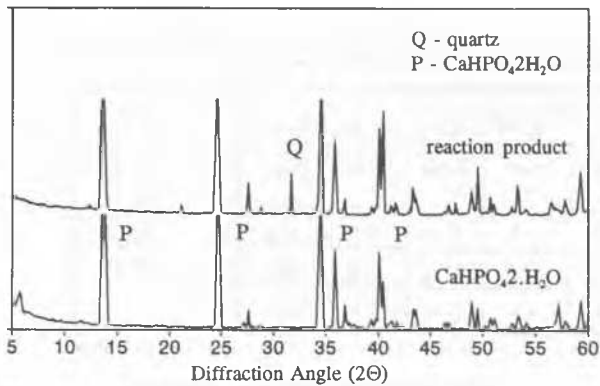


Fig.2 X-ray diffraction patterns of the reaction product - calcium hydrogen phosphate hydrate

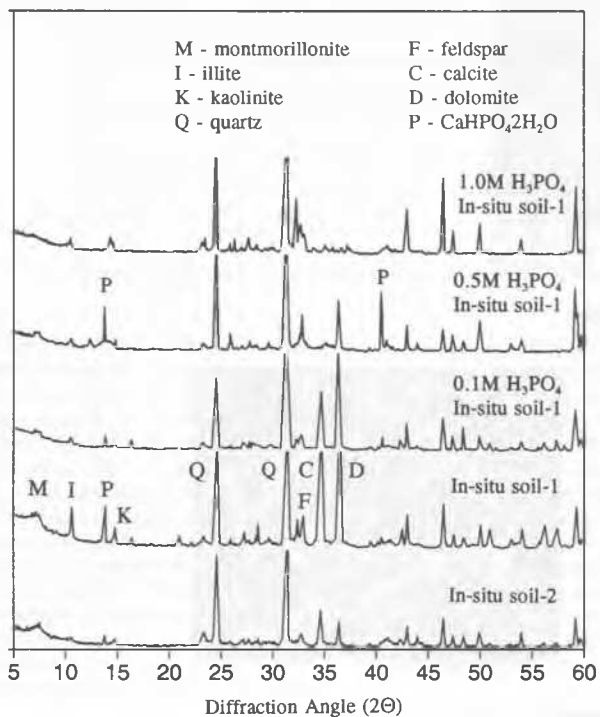


Fig.3 X-ray diffraction patterns of in-situ soils before and after reaction with phosphoric acid of different concentrations

break down of the calcite or dolomite were evident from the SEM pictures as shown in Figure 1.

X-ray diffraction analysis of the pulverized pellets indicated that major and minor peaks of the reaction product had very good correlation with the peaks of calcium hydrogen phosphate hydrate (CaHPO₄.2.H₂O), also called brushite. Refer to Figure 2. A comparison between the diffraction patterns of the reaction product and of a pure chemical substance of the reaction between calcium carbonate and 0.5M phosphoric acid solution further confirmed that the product was calcium hydrogen phosphate hydrate, as shown in Figure 2. An examination of the X-ray diffraction pattern of the in-situ soils also revealed the diffraction peak at 7.49Å which proved the presence of this crystalline product in the in-situ contaminated soils.

The X-ray diffraction patterns of the in-situ soils and of the specimens from the sedimentation tests on the in-situ soil-1 are shown in Figure 3. From the high intensities of the strongest diffraction peaks of calcite and dolomite, it can be noted that the in-situ soil-1 still contains large amount of these minerals which possibly originated from the adjacent Rocky Mountains. With increasing concentration of acid solution, however, the intensities of the peaks of calcite and dolomite gradually decreased to almost zero in two and half months time, indicating the fast consumption of these minerals by concentrated acid. A further look at the diffraction peaks of the reaction product revealed that the formation of brushite was not proportional to the concentration of the acid solution. The intensity of the major peak of brushite formed in 0.5M acid solution is higher than that formed in 0.1M and 1.0M acid solutions. As a matter of fact, more pellets were observed in the specimen settled in 0.5M solution, while few were found in 1.0M and 0.1M acid solutions. This does not imply that the reaction is slow or incomplete in strong acid solution but manifests that the product dissolves in strong acid solution. Repeated tests indicated that even the originally formed brushite in the in-situ contaminated soil-1 dissolved in 1.0M acid solution as evidenced by the lack of a diffraction peak at 7.49Å.

The X-ray diffraction patterns of UC campus soil before and after reaction with phosphoric acid are shown in Figure 4. From the diffraction pattern of the raw soil sample, it is evident that the mineral composition of the UC soil is very similar to that of the in-situ contaminated soils. The only difference is that the UC soil is uncontaminated by phosphoric acid. The data in Figure 4 show that there is the gradual disappearance of the strongest diffraction peaks of calcite and dolomite with increasing concentration of phosphoric acid solution. Moreover, the formation of the reaction product almost followed the same pattern as that observed in in-situ soil specimens. However brushite formed this time did not totally dissolve in 1.0M acid solution. This might be attributed to a higher final pH of the pore water system since the breakdown of calcite and dolomite would neutralize quite a bit of phosphoric acid.

A possible reaction between calcite and phosphoric acid is as follow:



Relevant data on the reactant(calcite) and the reaction product are presented in Table 4. A theoretical volume increase of about 120% will occur upon total reaction. Brushite has a very low solubility in water (0.0316), but it dissolves in acid (Weast, 1987). To find out the relative solubility of this product in different concentration of acid solution, an equal amount of pulverized CaHPO₄.2H₂O was put into 0.1M, 0.5M and 1.0M phosphoric acid solution separately and stirred. After ten minutes the powder in 1.0M acid solution (pH = 1.35) dissolved entirely. The powder in 0.5M (pH = 1.69) solution also dissolved but in thirty minutes time. Only the powder in 0.1M (pH = 2.02) acid solution remained undissolved.

Table 4 Data Related to Reaction between Calcite and Phosphoric Acid

Property	Reactant - Calcite (CaCO ₃)	Reaction Product - Brushite (CaHPO ₄ .2H ₂ O)
Molecular weight (g/mol)	100.09	172.09
Specific Gravity	2.93	2.306
Volume (cm ³ /mol)	34.18	74.62

It is reasonable to hypothesise that intermittent leakage or spillage of phosphoric acid will alter the concentration of pore fluid; and the formation and/or dissolution of brushite will cause differential movements of the structures supported on calcareous silty clays.

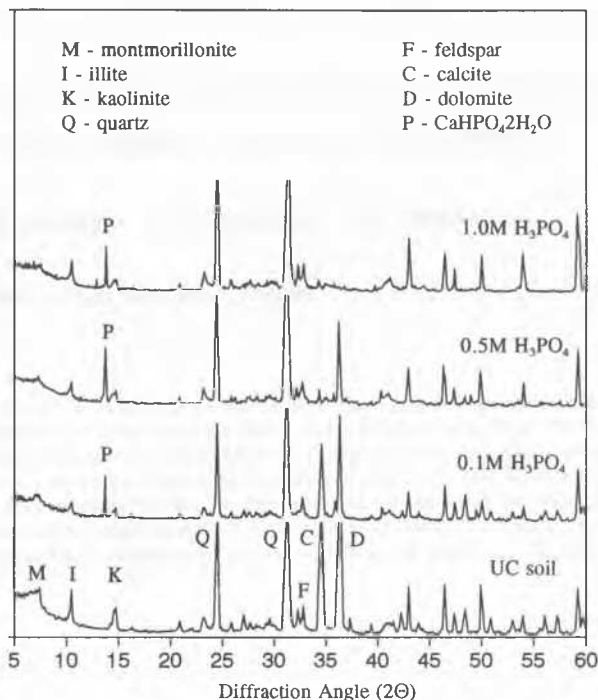


Fig.4 X-ray diffraction patterns of UC soil before and after reaction with phosphoric acid of different concentrations

The smallest sedimentation volumes of both the in-situ contaminated soils and the UC campus soil in 0.5M acid solution were attained in four to seven days. But the equilibrium sedimentation volumes were reached after two and half months. During the first four to seven days, the reaction between calcite, dolomite and phosphoric acid was rapid and released large quantity of carbon dioxide. During this time calcite and dolomite were broken down, as a result, Ca^{+2} and Mg^{+2} were released into the solution. As the calcite and dolomite were dissolved into the acid solution, the sedimentation volumes of these soils decreased until the smallest sedimentation volumes were attained. The breaking down of calcite and dolomite marked the beginning of nucleation and formation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals. The crystallization process was accompanied by volume increase which would contribute to a larger sedimentation volume obtained as long as the pH of the pore water solution was not low enough to dissolve the already formed brushite. This was exactly what happened in 0.5M acid solution. One may argue that the reaction product will dissolve in 0.5M acid solution as stated above. But in the soil acid system, the consumption of phosphoric acid by the dissolution of calcite and dolomite would increase the final pH value of the pore water solution so that the brushite formed would remain undissolved.

Table 3 also gives the sedimentation volumes of in-situ soils and UC campus soil in 1.0M acid solution. The smallest sedimentation volume of the in-situ soil-1 was equal to its equilibrium sedimentation volume. The reason for this can be ascribed to the high solubility of the reaction product in concentrated acid solution. This can be explained by the disappearance of the strongest diffraction peak of brushite at 7.49\AA from the sample in 1.0M acid solution. Refer to Figure 3. Even the originally present brushite in the soil was dissolved in the 1.0M acid solution together with the calcite and dolomite. As a result the equilibrium sedimentation volume in 1.0M acid solution was even smaller than that in 0.01N CaSO_4 solution. Differing from that of in-situ soils the equilibrium sedimentation volume of UC soil in 1.0M acid solution was larger than the smallest volume. An examination of the X-ray diffraction pattern of the UC soil sample after being submerged in 1.0M acid solution for two and half months shows the existence of brushite in the

sample which would contribute to the larger equilibrium sedimentation volume.

No volume changes for the in-situ soils and UC campus soil were noticed in 0.1M acid solution after five days. The rate of evolution of carbon dioxide in 0.1M acid solution was relatively slower than that in 0.5M and 1.0M acid solution. This indicated that the reaction between calcite, dolomite and phosphoric acid was slow. X-ray diffraction patterns of samples inundated in 0.1M acid solution for two and half months still show high intensity of the diffraction peaks of calcite and dolomite. This indicated that the reaction was incomplete. More phosphoric acid was needed to consume the remaining calcite and dolomite.

Severe damage to the interconnecting piping observed at the phosphoric acid storage tank site can therefore be attributed to leakage and subsequent contamination of the in-situ soils by phosphoric acid. The subsoils at the site contain large amount of acid reactive minerals such as calcite and dolomite. Upon phosphoric acid attack, the particles of these minerals break down and a crystalline product of calcium hydrogen phosphate hydrate is formed. This chemical reaction process is accompanied by a volume increase of 120% on the basis of equivalent calcium carbonate volume. The amount of the reaction product formed, however, depends on the pH of the pore water solution because of the high solubility of calcium hydrogen phosphate hydrate in concentrated acid solution.

CONCLUSIONS

The results of the study suggest that the in-situ soils contained large amount of calcite and dolomite. The test data further suggest that calcite and dolomite in the soils reacted with phosphoric acid and formed calcium hydrogen phosphate hydrate also known as brushite. Gases were also evolved during the formation of brushite. The resultant increase in molecular volume of the reaction product in phosphoric acid contaminated soils was responsible for subsoil heave and differential movement and resultant damage to structures seated on such soils.

The results of sedimentation tests and X-ray diffraction analyses show that the formation of brushite is rapid and complete in 0.5M phosphoric acid solution. The reaction in 1.0M phosphoric acid solution is rapid but the formation of crystalline product is less than that in 0.5M solution due to the lower final pH of the pore water solution. The reaction in 0.1M phosphoric acid solution is relatively slow and incomplete but continuous. The changing solubility of the reaction product in different pore water pH causes volume instability in phosphoric acid contaminated calcareous soils.

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