

Effect of Sulphuric and Phosphoric Acids on the Behaviour of a Limestone Foundation

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Introduction

Industrial chemicals often leak into soil or rocks resulting in changes in their material properties. These changes may induce movements in the footings supporting the equipment and consequently cause disturbance to the production process. This problem cannot be solved using the conventional concepts of soil mechanics as it involves chemical reactions between the effluent and the different minerals that make up the soil or rocks. In addition, the findings derived from one site cannot be extended to other problems as the response of the foundation depends on the particular chemical present and the composition of the underlying strata.

Lukas et al. (1972) documented foundation failures in three industrial buildings due to dissolution of subsoil materials in the chemical contaminants. In one of the sites, the subsoil contained a significant amount of limestone and dolomite, and the spillage was mainly acetic acid. Sridharan et al. (1981) reported distress to floors, pavements and foundations in a fertilizer plant due to heaving of clayey soils contaminated by phosphoric acid. Kumapley and Ishola (1985) studied the effect of caustic soda contamination on the undrained shear strength of three types of clays.

The Phosphate Fertilizer Complex in the western Iraqi city of Al-Kaim, where the limestone dominates the ground composition, includes two large factories for the production of sulphuric and phosphoric acids. These factories include many processing towers, economizers, heat exchangers, filters and storage tanks, and are all supported by isolated footings. The actual contact pressures were relatively small compared to the allowable pressure on the intact rocks, ranging from 80 kN/m² to 120 kN/m² for the economizers and processing towers respectively, and up to 300 kN/m² for the stack foundation.

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The footings were seated directly on the chalk, which had been overlain by 0.5 m to 1.5 m of top soil. The sublayers, up to 10 m in depth, consist of chalk, marl, sandstone, and shelly limestone (Sybetra 1977).

The factories were badly damaged in the 1991 war, especially the sulphuric acid factory, where about 5000 tons of concentrated acid spilled over, as a result. Five months later, geotechnical and geophysical investigations were carried out by the National Center for Construction Laboratories (NCCL 1991a and b). The pH values at some places were reported to vary from 1.5, for the surface soil, to 7, at 4.5 m depth. The corresponding average pH value over that depth in 1977 was 7.8.

Although the factories were then summarily repaired and production restarted, the leakage of acids through pipes, fittings, processing towers and storage tanks continued and the acids percolated into the limestone foundation. The concrete footings experienced continuous movements causing more operational problems.

This paper presents the field movement of some footings in the sulphuric acid factory, in conjunction with a comprehensive deformation test program using both the sulphuric and phosphoric acids. The field wave velocities in the sulphuric acid factory are presented and then compared with past records in order to assess the effect of continuous acid leakage. A detailed laboratory study presented in this paper, demonstrates the continuous degradation in the strength and dynamic elastic moduli of limestone, which is due primarily to the percolation of each acid. The field bearing capacity is evaluated and a method of ground treatment is offered.

Site Geology

The city of Al-Kaim is located in North-Western Iraq, close to the border with Syria as shown on the map of Iraq, Figure 1. The soils and rocks in this area are part of the Euphrates Formation, and is considered to be of lower Miocene age. The Euphrates limestone formation was deposited under shallow marine, reef and lagoonal conditions. It has a relatively large surface extension on the stable shelf to the south and southwest of the Euphrates River.

Limestones are sedimentary-bedded rocks often containing many fossils. They are essentially composed of calcium carbonate with which there is generally some magnesium carbonate and siliceous matter such as quartz grains. Limestone may be composed of four minerals, namely, Calcite (CaCO_3), Aragonite (CaCO_3), Dolomite ($\text{CaMg}(\text{CO}_3)_2$), and Magnesite (MgCO_3). The Euphrates limestone Formation, although composed mainly of limestones, contains several beds of greenish marls, marly sands, breccias and conglomerates, including conglomeratic limestone. The limestones may be found in different forms: recrystallized, siliceous, oolitic, shelly and chalky limestones. This lithological variability led to the introduction of three lithologically different members (Buday 1980):

- Cavernous and conglomeratic limestone member lying at the bottom of the formation,
- Shelly limestone member,
- Marly and chalky limestone member.

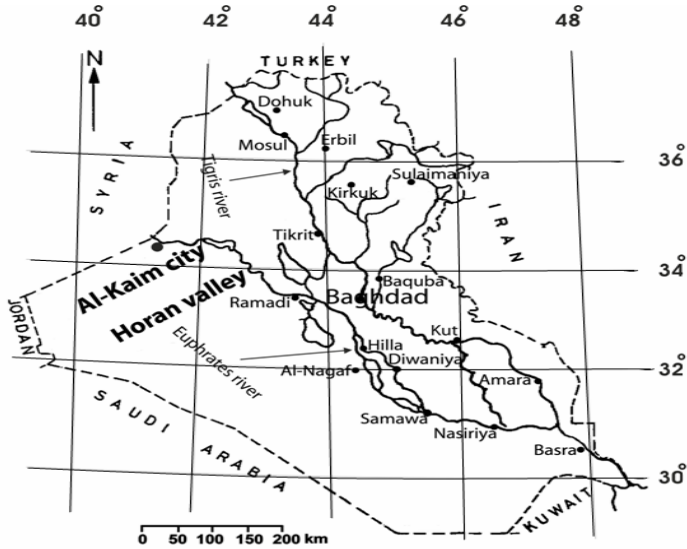


Fig. 1 A General Map of Iraq Showing Al-Kaim City and Horan Valley

Chalk is an organically formed soft white limestone largely made up of finely divided calcium carbonate, CaCO_3 , which was probably formed at moderate depths. Shelly limestone is an organically formed rock in which fossil shells form a large part of its bulk. Calcareous shaly clay is known as marl. A typical ground profile in the complex area is shown in Figure 2.

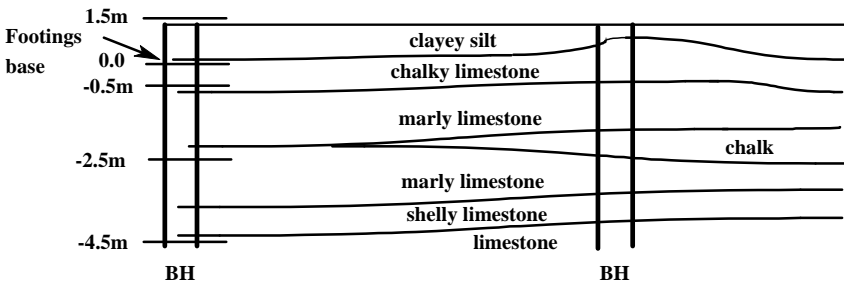


Fig. 2 A Typical Geological Stratification at the Place of the Sulphuric and Phosphoric Acid Factories in Al-Kaim (after Sybetra 1977)

The porosity of limestone ranges generally between 0.3% and 25%, whereas it may be as low as 0.1% for marble. The specific gravity is estimated to be 1.4-2 for chalk, 2.71 for calcite, 2.75-2.9 for dolomite and 2.929 for aragonite.

Details on limestone are available in Boynton (1980) and Blyth (1963). More information and web sites on limestone can be found in Al-Marsoomi (2006).

Field Monitoring

Settlement

Each installation in the sulphuric acid factory is fixed on an isolated rigid footing, and the installations are joined together by pipes and ducts. The movements in the footings caused failure in the connections and some of the installations. The acid that was seeping or splashing from different places caused the ground to be covered with a sulphate skin that was frequently replaced by an intact limestone layer.

Careful field monitoring of the disposition of some of the towers' footings in the sulphuric acid factory was conducted during the period February to November, 1995. Similar data was available for a longer period that is for the period February, 1995 to August, 1999. The typical shape and dimensions of a footing is given in Figure 3. The applied pressure is 120 kN/m^2 . The allowable pressure on the intact rocks was 1000 kN/m^2 as given in Sybetra (1977). Figure 4 demonstrates typical variations in the levels of the corners of five arbitrarily selected footings with time. The reference footings elevation in each case was that obtained in February 1995.

The movement is of the heave-settlement cyclic form, and is a result of the chemical reactions involved, as will be discussed in a section later. No field monitoring of the footings in the phosphoric acid factory was carried out.

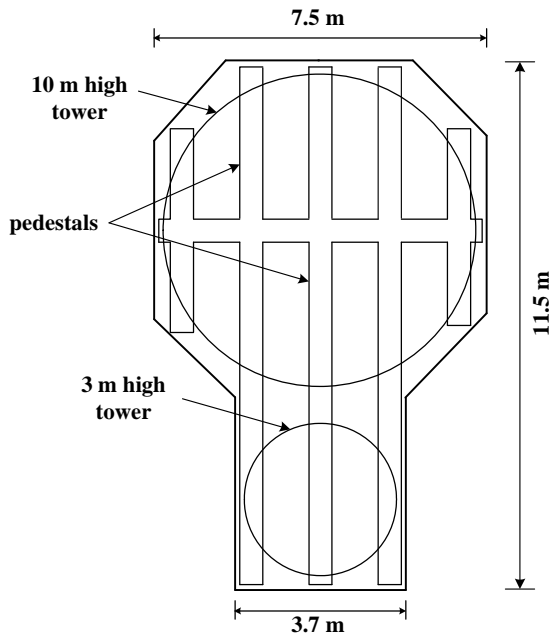


Fig. 3 A Typical Plan of an Isolated Footing Carrying Towers

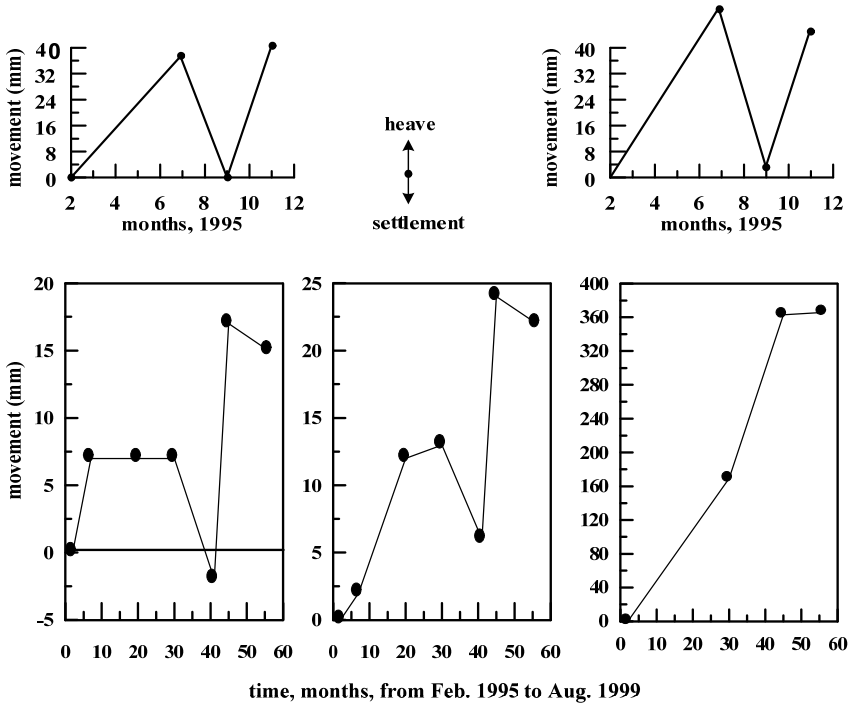


Fig. 4 Vertical Movement of Some of the Tower Footings as the Average Measured Values at Two Corners of the Same Side

Seismic Velocities

Based on the principles of wave propagation in an elastic medium, the compression wave velocity, v_p , and the shear wave velocity, v_s , are known to increase with the increase in the modulus of elasticity, E_d , and the shear modulus, G_d , respectively. These wave velocities are correlated to the type of rock. Such correlations are available elsewhere.

The distribution of pick up units, geophones, may be horizontal, (surface seismic method), or vertical, (down-hole method). Readings at certain depths between two boreholes may be recorded. This is known as the cross-hole method (Prakash 1981).

The range of v_p values determined for the subsurface layers in the sulphuric acid factory is about 1300-2500 m/s whereas that for v_s is about 800-1475 m/s (NCCL 1996). These correspond to the chalk type of rocks.

In order to properly assess the deterioration in the limestone, it would be essential to obtain the previous records of velocity measurements. Unfortunately no geophysical investigation was carried out during the erection of the complex in 1977. However, a down-hole survey was conducted in the same site in 1990 before the spilling of the 5000 tons of acid (NCCL 1990). Another geophysical investigation was performed later as reported in NCCL (1991b). Table 1 shows the range of v_p values obtained in 1990, 1991, and 1995.

Table 1: Representative Range of Field Compression Wave Velocities (V_p) During Six Years

Year	Range of v_p (m/s)
90 ^a	770-2620
91 ^b	1000-2000
95 ^b	1300-2500
95 ^a	391-514

^a down-hole method ^b surface seismic lines

The results obtained depend on the method employed. It is obvious that a serious degradation has taken place in the profile after 1990 as indicated by the results of the down-hole method. However, this great reduction in v_p values may not be totally due to the deterioration in the quality of rock because the compression wave velocity is very sensitive to moisture. When the rock is fully saturated, it reflects the properties of the fluid rather than that of the rock. The acid present moistens the limestone; this may have contributed to the reduction in v_p values in addition to the degradation in the rock quality.

Table 1 also indicates that the rock condition during 1995 is better than that of 1991. This is compatible with the geotechnical results of unconfined compressive tests and the rock quality designation tests as reported in NCCL (1991a, 1996).

Laboratory Testing

Time-Dependent Deformations

The purpose of the laboratory deformation tests was to determine the heave and/or settlement of loaded limestone attacked by acids. The surcharge load should be varied in order to determine the minimum pressure required to prevent heave, referred to as "the reaction pressure". The conventional oedometer apparatus has been used in this work.

Several pilot tests were performed using both sulphuric and phosphoric acids and it has been found that the interaction of either acid with calcium carbonate leads to the formation of a soft dough which plugs the pores of the conventional porous stone and gradually hardens.

Therefore, the porous disc of the standard consolidation cell was replaced successfully by a new element made of a relatively anti-acid mineral and essentially has the same features as the porous disc, but with relatively large openings to ease the passage of acid without plugging.

A geotechnical site investigation was performed by the National Center for Construction Laboratories (NCCL 1996) at the site of the sulphuric acid factory. Core samples of partially contaminated limestone were recovered and used in the deformation study. In the experiments using sulphuric acid, a series of tests was also conducted using limestone of the Horan Valley located in western Iraq (Figure 1) in order to investigate the effect of the porosity on the

results. In the experiments using phosphoric acid, the limestone used in the tests was uncontaminated and recovered from an area near the factory. Table 2 presents the porosity and the CaCO_3 content of the used specimens.

Table 2: Source and Properties of Limestone Specimens Used in the Deformation Tests

Tests using sulphuric acid				Tests using phosphoric acid	
Contaminated limestone from Al-Kaim		Intact limestone from Horan Valley		Intact limestone from Al-Kaim	
Porosity %	CaCO_3 %	Porosity %	CaCO_3 %	Porosity %	CaCO_3 %
16.77	79	0.46	94.5	12.34	96.3

The concentrations of the acids used are 98% for the sulphuric acid and 53% for the orthophosphoric acid. All the limestone specimens were subjected to the carving process in order to suit the standard consolidation ring with a diameter of 75 mm and a height of 20 mm. Each sample was then gently depressed inside the testing ring and made to adhere to the inner wall of the ring, in order to keep a one-dimensional deformation.

A quantity of either acid that is chemically calculated to be sufficient for reacting with all CaCO_3 present in the sample was gradually allowed. The acid was allowed into the top of the cell using a 50 ml capacity medical enema and a plastic joining tube whose inner diameter is 3 mm. In the experiments using sulphuric acid, this amount was allowed in three equal portions. Each successive portion was released at the end of the deformation caused by the previous portion. This procedure is expected to simulate the field monitoring, as the seepage was not steady. Full experimental details may be found in Mohammed (1998) and Kasseer (2000).

Figure 5 demonstrates the time-deformation relationships of specimens impregnated by sulphuric acid. In the free heave tests (surcharge = 7 kN/m^2), the maximum expansion was 44% and 53% for Al-Kaim and Horan Valley samples respectively.

Examination of the obtained curves reveals that when the surcharge is relatively not large ($\leq 100 \text{ kN/m}^2$), the size of the sample will continue increasing until the reaction ceases. The size decreases at the end of the reaction if the surcharge is between 200 kN/m^2 and 400 kN/m^2 . The sample then rises again with the addition of another amount of acid. This is due to the fact that the reaction product, gypsum, results in a softer deposit. When the surcharge is 400 kN/m^2 , the deformation-time mode is cyclic heave and settlement. For surcharge values greater than 400 kN/m^2 , the specimens always contract whenever a new amount of acid is added. This leads to the deduction that the reaction pressure should be less than 500 kN/m^2 .

Figure 6 demonstrates the deformation behavior of loaded limestone when impregnated by phosphoric acid. The general trend is similar to that of sulphuric acid. However, a slight volume decrease was noticed once the acid is allowed to the sample, even for small-applied loads. This small contraction is perhaps due to an instant softening in the sample surface on arrival of the phosphoric acid prior to the chemical reaction.

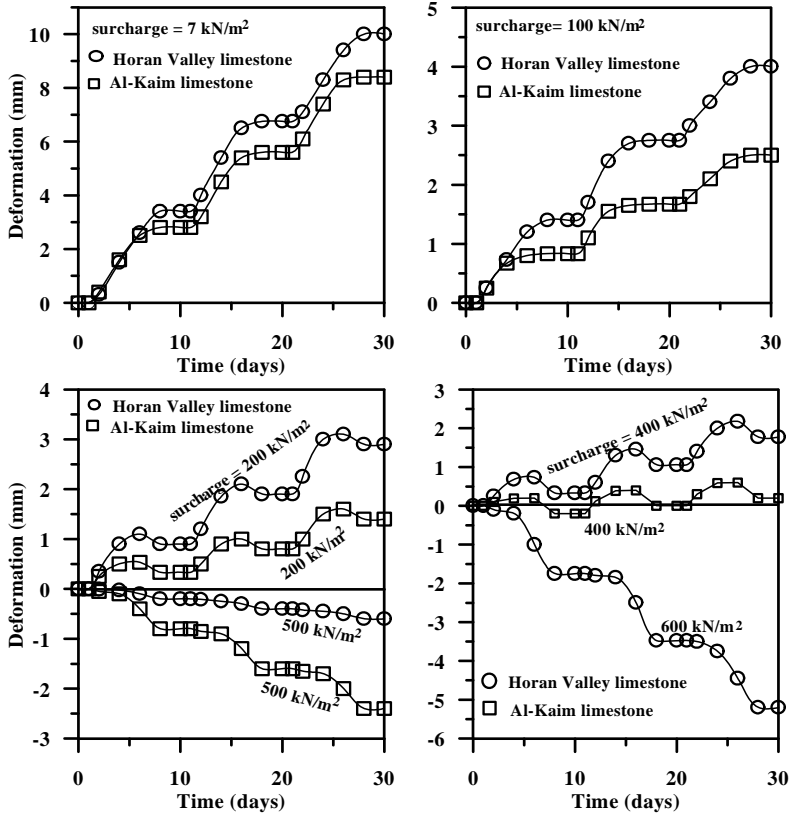


Fig. 5 Time–deformation Relationships of Limestone Subjected to Percolation of Sulphuric Acid

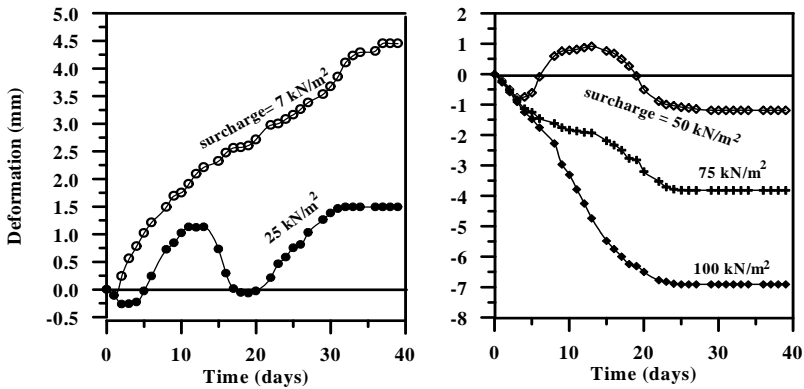


Fig. 6 Time –deformation Behavior of Limestone Subjected to Percolation of Phosphoric Acid

In the free heave test the maximum expansion was 23.4%. The heave-settlement pattern is also noticeable when the surcharge is 25 and 50 kN/m², since the reaction product, brushite, is softer than the original material. Heave commences again when an amount of acid starts reacting with the remaining CaCO₃.

Strength and Elastic Moduli

Experimental work

The effect of acids on the strength and elastic moduli was determined in the laboratory using uncontaminated specimens. Limestone of the Horan Valley and Al-Kaim regions were employed in the experiments related to sulphuric and phosphoric acids respectively. The factory-produced sulphuric and orthophosphoric acids were 98% and 53% in concentration respectively.

Core samples were extracted from the same parent rock using an extruder that cut samples in the shape of cylinders 30 mm diameter. The height of the sample was twice its diameter. The samples were subjected to a polishing process at their ends using a grinding machine.

The unconfined compression test was used to measure the strength. The test was conducted according to the standard of ASTM D 2938-79 (1983). Ultrasonic tests were employed to measure the shear wave velocity, v_s , and the compression wave velocity, v_p . The tests were carried out according to ASTM D 2845-69 (1983). The dynamic modulus of elasticity, E_d , and the dynamic modulus of rigidity, G_d , was then calculated according to the relationships given in Prakash (1981).

The aim of these tests was to assess the effect of acids on the stiffness and strength of limestone. This includes the effect of acid when the samples are immediately tested after variable time of exposure and the effect when the samples have been tested many weeks after exposure. This rheological behavior would substantiate the field findings.

Accordingly nine samples were soaked in the sulphuric acid for different periods. They were then removed and allowed to cure for also different periods before ultrasonic testing. The same samples were then subjected to the unconfined compression test. Similarly twenty samples were subjected to the same test conditions, using phosphoric acid. Pilot tests were required to fix the soaking and curing periods. In each case three intact samples were tested so that their average behavior will represent the reference or control results.

Effect of acids on strength

The value of the unconfined compressive strength, q_u , for the Horan Valley limestone is rather high, being 76814 kN/m². It is thus classified as a strong rock (Stapledon 1968). After 84 days of soaking in sulphuric acid, the value of q_u dropped to 13827 kN/m², giving a strength decrement of 82%, changing the classification to a weak rock. Figure 7a presents the variation of q_u with the soaking period. The strength degradation is obviously attributed to the chemical reaction between CaCO₃ and the acid. Unfortunately due to time limitation, the soaking time could not be extended to the period when the strength reaches a steady value. Figure 7b shows the gain in strength when the samples were left to cure before testing. When the soaking period was 84 days,

the gain in strength after 28 days was about 25%. Again the time limitation did not allow a curing time long enough to reach a steady value.

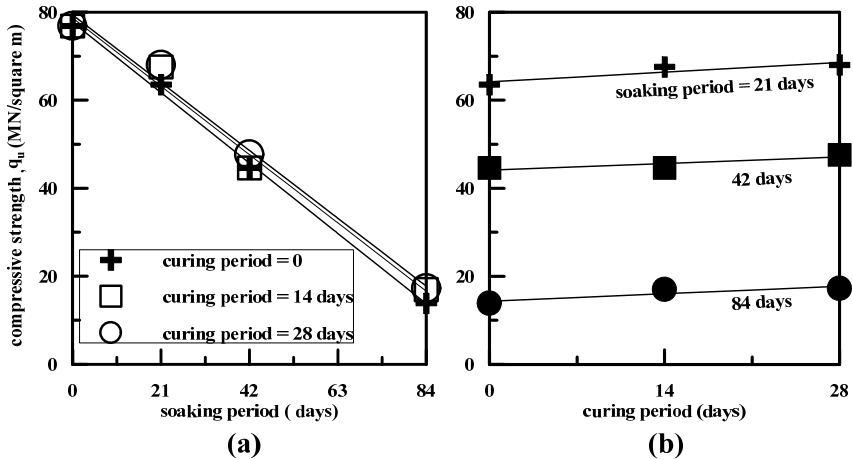


Fig. 7 Effect of Sulphuric Acid on Strength of Limestone

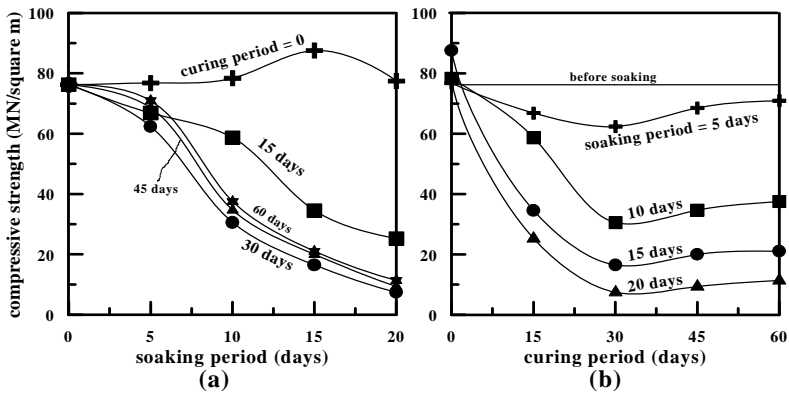


Fig. 8 Effect of Phosphoric Acid on Strength of Limestone.

The strength degradation due to phosphoric acid has been found to be faster than that due to sulphuric acid. A sample left to cure for 30 days, suffered a strength decrement of 90% after only 20 days of soaking. Figure 8a demonstrates the effect of the soaking period on strength. Generally, and except in the case of a zero curing period, the strength deterioration is fast and the rate starts to decrease after the 15 days of soaking. However the behavior at the zero curing periods is ambiguous. The strength is enhanced with increasing the soaking period until a peak is reached at 15 days, after which it decreases. Thus, five new samples were prepared, and tested using a zero curing period in order to verify such behavior. The same trend has been obtained in this second series. The strength significantly decreases when samples are left to cure for a

period of 30 days, as given in Figure 8b. This behavior contradicts that of the samples soaked in sulphuric acid.

Effect of acids on elastic moduli

The values of the dynamic modulus of elasticity, E_d , and the modulus of rigidity, G_d , of intact specimens from the Horan Valley limestone have been measured to be 99.48 GN/m^2 and 39.96 GN/m^2 respectively. When tested immediately after 84 days of soaking in sulphuric acid, these values dropped to 52.19 GN/m^2 and 21.53 GN/m^2 , giving dramatic moduli decrements of 47.5% and 46.1% respectively.

Figure 9a exhibits the deterioration in the elastic moduli with the increase in the soaking period. Again the specimens harden with the increase in curing time before testing. The gain in stiffness due to 28 days of curing was 7.6% and 6.7% for E_d and G_d respectively.

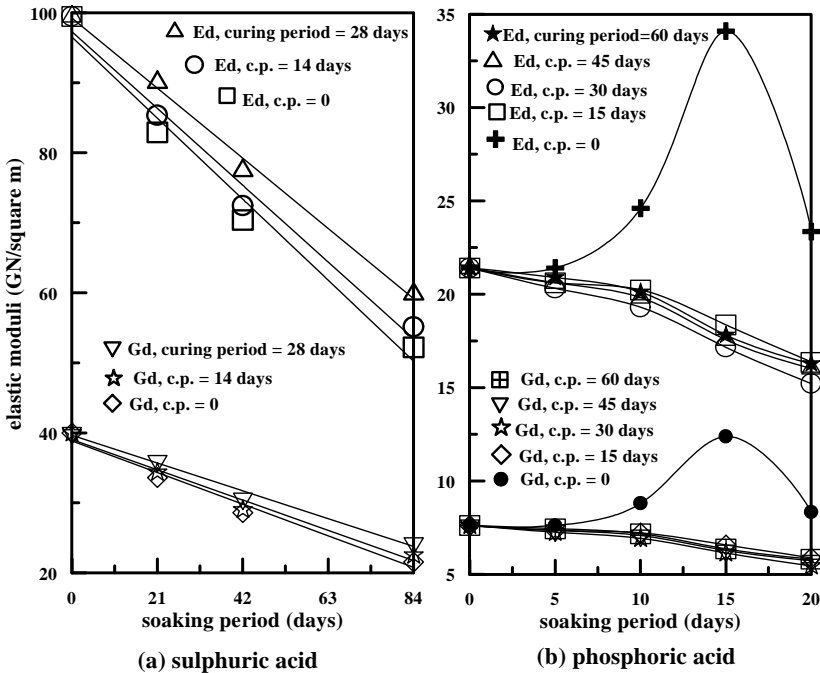


Fig. 9 Effect of Acid on the Dynamic Moduli of Elasticity, E_d , and Rigidity, G_d .

When specimens of the Al-Kaim limestone were soaked in phosphoric acid, the maximum drop in E_d and G_d was 28.94% and 28.59% respectively. Figure 9b demonstrates the variation of E_d and G_d with the soaking period. Similar to the results of compressive strength, the stiffness has been enhanced when the curing period was zero up to the peak reached at 15 days of soaking. The effect of curing period became insignificant when this period exceeded 15 days. When the curing period was greater than zero, the specimens softened.

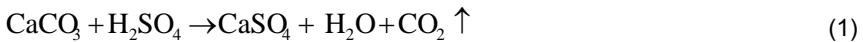
Discussion

Reaction of Limestone with Acids

An understanding of the fundamental chemical reactions is the basic key for the interpretation of the above presented results.

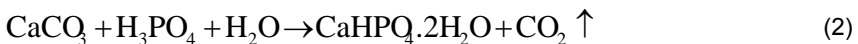
The limestone group is of the most basic alkalies with pH values of generally 8-9; sulfur, being at the other end of the pH scale, is the most basic acid. High calcium limestone readily dissolves in most strong acids, and is accompanied by the liberation of CO₂ gas. It freely effervesces in cold and very dilute hydrochloric acid, but dolomitic stones will not effervesce unless the weak HCl is heated.

When calcium carbonate reacts with sulphuric acid, the known reaction product is calcium sulfate and water, accompanied by the liberation of CO₂ gas as in the following:



The reaction of CaCO₃ with phosphoric acid is relatively complex. This acid may be orthophosphoric acid (H₃PO₄), pyrophosphoric acid (H₄P₂O₇), and polyphosphoric acid (H_{n+2}P_nO_{3n+1}).

Joshi et al. (1994) reported differential movement in the foundations of a fertilizer plant in Calgary, Canada, due to the leakage of phosphoric acid into the calcareous subsoil. They investigated the problem using X-ray diffraction analysis of uncontaminated and contaminated samples. Reagent grade orthophosphoric acid (86% H₃PO₄) was used as the contaminant. The analysis indicated that the major and minor peaks of the reaction product had a very good correlation with the peak of calcium hydrogen phosphate hydrate (CaHPO₄.2H₂O), also called brushite. Brushite has a very low solubility in water but it dissolves in acids. They stated that a possible reaction between calcite and phosphoric acid is as follows:



The volume of the reactant (calcite) in cm³/mol is 34.18 whereas it is 74.62 for the reaction product (brushite), thereby inducing a certain total volume increase of the material upon reaction.

This reaction is irreversible with apparently a very high equilibrium constant. It seems that both kinetic and thermodynamic factors favor the reaction of CaCO₃ with phosphoric acid over that with sulphuric acid. To obtain a complete picture, one must consider the enthalpy of formation of products in each case and determine the order of the reaction rate-law. These measures are certainly beyond the scope of the present work.

Deformation Behavior

When an amount of acid reaches the limestone underlying the footing base, the material will effervesce. The reaction will result in calcium sulfate accompanied by the liberation of CO₂ gas according to equation 1. After a certain period of time, the calcium sulfate may gain two molecules of water to form the gypsum, as in the following equation:



An increase in volume and a decrease in the hardness of the reactive limestone will accompany this reaction. The resulting gypsum may gradually gain strength if no additional amount of acid percolates.

The increase in volume during the reaction would be resisted by the weight of footing and the applied load. If the reaction pressure is greater, heave will initiate, with the amount of heave depending on the difference between the reaction pressure and the total applied pressure. After the end of the reaction and the formation of gypsum, the footing may return to its original position. It is also possible for the footing to settle lower than its original position. This process will continue cyclically, depending on the frequency of acid leakage, which in turn depends on the operation hours and the shutdown periods.

It should be mentioned that the actual design pressure on the towers footings was 120 kN/m^2 ; therefore, the reaction pressure of sulphuric acid is expected to be much greater than this value

In order to compare the present laboratory results with the field observations, the maximum and minimum deformations after the addition of each portion of acid are drawn against time in conjunction with a field observation, as presented in Figure 10. The two patterns of deformation are similar and they represent a cyclic behavior.

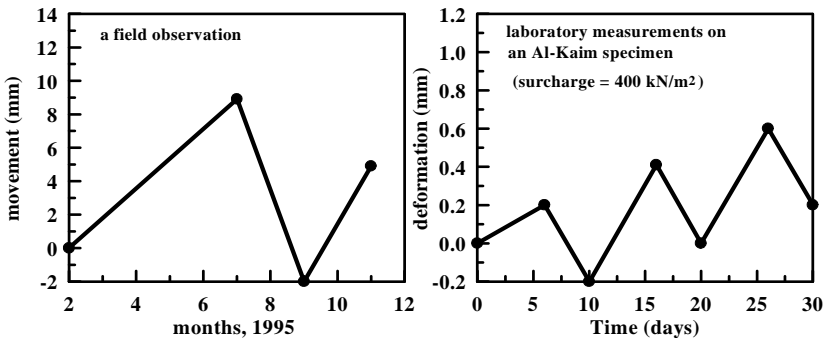


Fig. 10 Field and Laboratory Heave – Settlement Behavior of Limestone Subjected to Frequent Amounts of Sulphuric Acid

Actually, this trend of cyclic heave–settlement of loaded limestone subjected to frequent ingress of sulphuric acid may be similar to the trend of cyclic swell–shrink of expansive clay subjected to frequent ingress of water as reported in Al-Omari and Oraibi (2000), although the causes are different. After a number of cycles, the clay will reach a fatigue state. In the present case, this corresponds to the condition when CaCO_3 gradually diminishes, the footing then will either not move with continuous seepage of acid or will merely settle. Similarly the reaction pressure will correspond to the swelling pressure. It depends on the amount of restraint to volume expansion. The maximum pressure will be reached when expansion is completely prohibited.

It appears that the reaction pressure is not yet known. Therefore it was worthwhile conducting the present laboratory investigation using a device similar

to the oedometer in order to determine the value of this pressure. Knowledge of this value is important in the design of foundations for such factories.

Figure 11 presents the relationship between maximum deformation and the applied load. The intersection of each curve with the line of zero deformation gives an estimate of the magnitude of the reaction pressure. Accordingly the magnitude of this pressure is estimated to be 430 kN/m^2 for the Al-Kaim samples and 480 kN/m^2 for the Horan Valley samples. This difference is obviously due to the difference in porosity and the variation in the initial content of CaCO_3 . It is interesting to note that the case of the Al-Kaim limestone subjected to a load of 400 kN/m^2 is very close to the reaction pressure, as shown in Figure 5. A footing loaded to this pressure will almost keep oscillating around its original level when the ground is subjected to frequent amount of acid percolation.

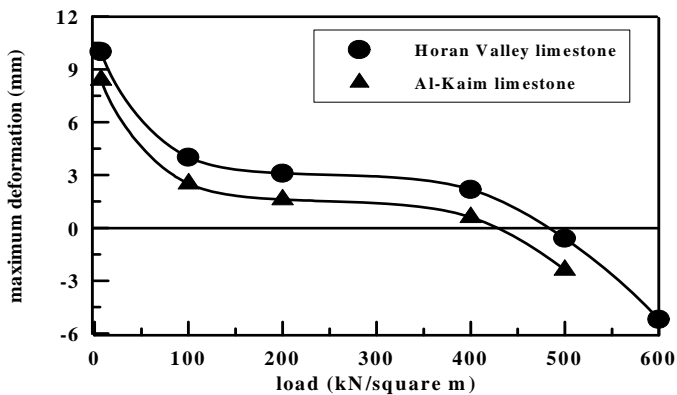


Fig. 11 Effect of Applied Load on the Maximum Deformation of Limestone Specimens Impregnated by Sulphuric Acid

The above discussion holds qualitatively true for the case of phosphoric acid. The relationship between maximum heave and the applied load is shown in Figure 12, to illustrate the load of zero heave. The authors suggest a value of 65 kN/m^2 for the reaction pressure. Thus, if the design footing load is around this value, no significant field heave will take place. However, if the calcium carbonate diminishes while the seepage of acid continues, then a significant settlement may commence. It is worth noticing that the reaction pressure due to sulphuric acid is more than sevenfold that due to phosphoric acid.

Some structural changes because of acid interaction were noticed. Slewa (1997) conducted a scanning electron microscope analysis on Al-Kaim non-contaminated chalky limestone before and after 15 days of treatment, with 50% concentration of sulphuric acid. It was reported that this treatment caused an increase in surface roughness, an increase in porosity and a replacement of calcite mineral by gypsum. An analysis on the marly limestone showed that the increase in porosity reflects an increase in both number and size of pores. In the present deformation tests using a surcharge of 400 kN/m^2 and after a test period of 30 days, the porosity slightly increased from 0.46 to 0.47% for the Horan

Valley samples and from 16.77 to 17.91% for the Al-Kaim samples. Twenty days of soaking in phosphoric acid also caused a slight increase in the porosity from 12.12 to 12.59%.

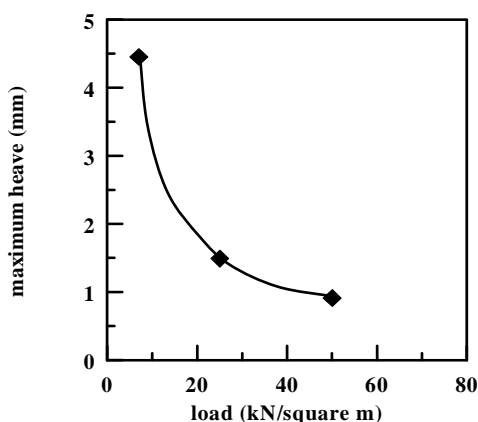


Fig. 12 Effect of Applied Load on the Maximum Heave of Limestone Specimens Impregnated by Phosphoric Acid

Strength and Stiffness Behavior

Figure 7a demonstrates the rapid deterioration in the strength of limestone, in proportion to the increase in the soaking period in sulphuric acid, whereas there is a gradual gain in strength with the increase in the curing period, as given in Fig. 7b. In fact the immediate loss of strength of gypsum due to wetting by water was already established in Sirwan et al. (1989). Therefore, the reverse process may be anticipated, i.e., gypsum left to dry would harden. Using samples from the Iraqi city of Baiji, they reported a drastic reduction of 11° in the angle of internal friction of dry gypsiferous soils upon wetting. This overrides the factor of safety of 3, normally adopted for design of footings. Gumusoglu and Ulker (1982) using pure gypsum samples from Anatolia in Turkey reported a drop in the compressive strength of gypsum from 204 kg/cm^2 in the natural state, to 81 kg/cm^2 after being 40 days in water.

The results of Figure 9a indicate that the elastic stiffness of gypsum is much smaller than that of CaCO_3 . This fact has clearly appeared in the results of deformation tests given in Figure 5. When the applied surcharge is higher than the reaction pressure, the elastic settlements were significant in these laterally confined tests. Since the added amount of acid in the deformation tests was compatible with the amount of CaCO_3 present in the sample, this settlement is a reflection of the stiffness of the produced gypsum, rather than dissolution of gypsum in extra amount of acid. Actually the straight lines obtained in Figures 7a and 9a, where the specimens were soaked in sulphuric acid, indicate that the dissolution of the already produced gypsum in the extra amount of acid is not dominant until the 84th days of soaking.

It should be recalled here that most of the natural gypsum and anhydrite rock were formed by precipitation from aqueous supersaturated solutions, which is due to the evaporation of water in shallow inland areas (Wirsching 1978). This

type of gypsum is stiff when dry; however, it significantly softens when subjected to wetness.

In reference to the effect of phosphoric acid on limestone, Figures. 8a and 9b indicated that the strength and elastic moduli increase in a certain pattern instead of decreasing when the curing period is zero. It is very difficult to explain this ambiguity. However, it is most likely related to the progressive mobilization of the chemical reaction inside the sample, combined with the time required to complete the reaction. For a completed reaction, the resulted brushite is known to be weaker than the original material. However, the condition is different during the reaction. This was modeled in the deformation test under a small load of 50 kN/m^2 (Figure 6), where the specimen expanded against the load during the reaction, and then settled down below the original level after the end of the reaction. At any instant three zones may be present in the sample: (a) a zone in which the reaction is completed, (b) a zone where the reaction is started but not completed, and (c) the third zone where the material is yet intact. When the second zone forms a significant portion of the specimen, an apparent strength enhancement may be anticipated. This may explain the results shown in Figure 8b, where the strength is increased at zero curing periods, and then decreased until it reaches an approximately stable value, when the reaction at every location is completed.

X-ray diffraction analyses on powdered specimens before and after treatment with phosphoric acid have been carried out. The treatment with acid was for 2 and 6 days only. The results revealed that the calcite completely disappears after 2 days of treatment whereas the dolomite disappears after 6 days. Hydrate and anhydrate calcium hydrogen phosphate was formed. Thus, the reaction is rapid, which agrees with the findings of Joshi et al. (1994). These findings also reported that the produced brushite dissolves in phosphoric acid. This may be a reason of the softening of the samples with the increase in the curing period. The acid remained in the pores, and began to dissolve the brushite, causing the elastic moduli to decrease, until this amount of acid is completely consumed.

It is known that the elastic settlement is inversely proportional to the modulus of elasticity. Therefore, if the applied load on the footings is higher than the reaction pressure, significant settlements may be expected. After a long period of time when all the CaCO_3 diminishes, settlements may commence, even if the applied load is small.

Remedial Strategy for Foundation Material

Unconfined compressive testing of many field samples was previously carried out (Sybeta 1977; NCCL 1996). Based on the results, Al-Omari (1996) estimated that the allowable pressure in the site of the sulphuric acid factory has degraded to half its original value, due to the long period of acid percolation. Rock strengthening had been recommended. However, no type of treatment was conducted. In 2001, a soil investigation in the sulphuric acid factory revealed that the rock has been converted to acidic dough (Al-Omari 2001).

Further leakage of acid below foundation has to be prevented using special drains. Considering the nature of the medium and for a post construction improvement, grouting is a convenient method of treatment. It was

recommended to use a two-shot injection of sodium silicate and calcium chloride. The reaction, which forms a gel, is virtually instantaneous. This method has been reported to yield successful results in conventional improvements (Singh 1993). However, laboratory tests verified that the chemical gelling remains instant even in an acidic medium, which is the present underground condition. Commercial sodium silicate is suitable and economically available.

The resulting material, which is calcium silicate, is relatively hard, resistant to acids, and serves the purpose of handling several years of continuous leakage. The hardness of calcium silicate is 4.5-5 on the Mohs' scale. Karol (1983) reported that sufficient contact between the two grouts occurs to provide a continuous gel network through stabilized soil. Soil strength of 6.9 MN/m^2 has been attained using this method (Bowen 1981). Laboratory results using different proposed injection materials strongly support the employment of sodium silicate to treat the contaminated limestone (Sagman, 2004). Nevertheless, field trials remain necessary in order to obtain the best results. More details on this problem may be found in reports by Al-Omari (1996; 2001).

Conclusions

Layers of a limestone foundation supporting rigid isolated footings in a fertilizer plant were subjected to percolations of sulphuric and phosphoric acids over a long period of time causing serious movements in the footings. Comprehensive laboratory investigations were conducted in order to understand the engineering behavior of limestone upon exposure to both acids in conjunction with a field study in the case of sulphuric acid. The following conclusions may be drawn:

A volume increase accompanies the reaction between acids and limestone. The presence of a restraint to this volume change, like an applied load, produces a reaction pressure that increases with increasing the applied restraint.

Laboratory tests showed that the minimum applied pressure sufficient to completely prevent the volume increase upon reaction is 430 to 480 kN/m^2 in the case of sulphuric acid. This reaction pressure is around 65 kN/m^2 in the case of phosphoric acid.

Upon exposure to acids and until the end of reaction, the height of chalk samples increased by 44% and 23.4% in the free heave tests, due to sulphuric and phosphoric acids respectively.

When the rate of percolation is not steady, the movement of footings in the sulphuric acid factory was cyclic heave and settlement. The heave is due to the expansion of foundation. The subsequent settlement occurs because the reaction product, gypsum, formed in place of original rock is softer. This mechanism may continue for years until no further carbonates remain. This behavior matches the laboratory behavior at certain values of the applied surcharge. When the applied surcharge is slightly less than the reaction pressure the height of the sample appears to be oscillating about its original position.

Significant degradation in the strength of limestone takes place due to the percolation of acids. In certain circumstances, this degradation amounted to 82% and 90% due to sulphuric and phosphoric acids respectively.

Wave velocity measurements in the field confirmed the degradation in the quality of rock, due to the percolation of sulphuric acid.

The values of the dynamic moduli of elasticity and rigidity suffered a drop of 47.5% and 46.1% respectively, due to sulphuric acid. The corresponding drop due to phosphoric acid was 28.94% and 28.59%, respectively.

When samples were left to cure after removal from the sulphuric acid, the strength and stiffness of limestone were both enhanced with time. In the case of phosphoric acid and for curing periods greater than zero, the samples suffered deterioration instead of enhancement in the strength and stiffness.

Chemical grouting using a two-shot injection of sodium silicate and calcium chloride is recommended in order to improve the properties of the contaminated limestone.

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Notations

q_u	Unconfined compressive strength
E_d	Dynamic modulus of elasticity
G_d	Shear modulus of elasticity (modulus of rigidity)
v_p	Compression wave velocity
v_s	Shear wave velocity

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