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GEOLOGICAL ALTERATIONS AND CHEMICAL TREATMENT OF A POLLUTED LIMESTONE FOUNDATION

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ABSTRACT

A large factory for the production of concentrated sulphuric acid is constructed in 1977 and located in the west of Iraq near Al-Kaim city. The footings carrying the installations rest on calcareous rocks which extend deep into the ground. For many years, about 1.5 tons per day of acid seeped and percolated into the ground apart from frequent accidents when larger amounts took their path down into the ground. A record of the footings movement revealed that the footings experienced significant heave and settlement indicating a cyclic movement which depends on the frequency of seepage. The results of the past geotechnical and geochemical investigations have been carefully studied in order to trace the geological alterations occurring in the ground due to the percolation of sulphuric acid over years. It appeared that at certain depths the limestone rock has been almost converted to dough and that a significant amount of dolomitization has taken place in the factory ground. Contaminated samples have been obtained from boreholes executed in the factory site. Many chemical materials have been chosen to treat the contaminated samples. Among these materials are sodium silicate, sodium carbonate, sodium silicate plus calcium chloride, barium sulfate, aluminum oxide, ferric oxide and bentonite. Unconfined compression, ultrasonic wave, physical, wet chemical and XRD tests were performed on intact, contaminated and treated specimens. The results proved that sodium silicate is the best alternative to be used for chemical grouting of the ground. The use of calcium chloride with sodium silicate did not show an additional advantage. Samples contaminated to the degree of having the form of dough have almost regained their original solid state strength when treated with sodium silicate.

INTRODUCTION

A Phosphate Fertilizer Complex is located in Al-Kaim city 380 km west of Baghdad, close to the border line with Syria, as shown in the map of Iraq presented in Fig. 1. The elevation of this area is about 250 meter above sea level. A large sulphuric acid unit is located within this complex which involves processing towers, economizers, heat exchangers, filters, stacks and storage tanks; they are all supported by isolated footings and spreading over an area of about 7000 m².

The rocks underlying the foundations are of Euphrates formation composed mainly of chalky limestone, sandy limestone, dolomite and dolomitic limestone (Buday, 1980 and Sybetra, 1977).

Due to the lack of maintenance and the occurrence of several accidents, the acid was seeping from many installations, connections and pipes. This continued for more than ten years and the acid percolated into the ground with different rates which amounted some times to 1.5 ton/day. As a result, the footings experienced continuous significant movement. This situation caused many operational problems.

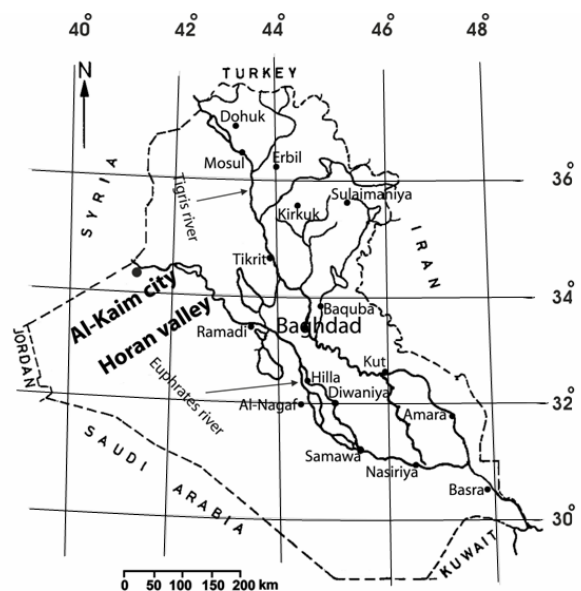


Fig. 1. A general map of Iraq showing Al-Kaim city.

Such problems can not be solved using the conventional concepts of soil and rock mechanics as it involves chemical reactions between the effluent and the different minerals that make up the soil or rock.

Lukas and Gnaedinger (1972) documented foundation failures in three industrial buildings due to dissolution of subsoil materials in the chemical contaminants. Sridharan *et al.* (1981) reported distress to floors, pavements and foundations in a fertilizer plant due to contamination by phosphoric acid. Kumapley and Ishola (1985) studied the effect of caustic soda contamination on the strength of clay. Slewa (1997) investigated the effect of sulphuric acid solutions on some properties of limestone using the ultrasonic technique. Mohammed (1998) studied the effect of sulphuric acid on the deformation and strength of undisturbed limestone specimens.

The State Company for Phosphate sought for a solution to this problem. There are two phases for the solution; the first is to treat the polluted limestone where as the second is to structurally enhance the foundation like the use of underpinning techniques.

In reference to the second phase of the solution, Al-Marsoomi (2006) conducted a finite element analysis of a proposed rehabilitated foundation subjected to a chemical attack. This proposed foundation is based on surrounding the existing footing by piles and the employment of a floating steel pile cap.

The first phase of the solution is investigated in the present work. A laboratory investigation is carried out using many chemical materials in order to find out the most suitable material to be used in a proposed chemical grouting of the site. Also, the results of the recent subsurface investigations are compared with the original rock condition in order to draw a picture of the geological alterations occurring in the site of the sulphuric acid unit.

SITE GEOLOGY

The site ground is part of the Euphrates formation. A review of the stratigraphy and lithology of this formation is available in Buday (1980) and Al-Ghreri (1985). The type locality of Euphrates formation is located near Wadi Fuhaimi at Lat. 34° 15' 58" N, Long. 42° 08' 09" E.

This formation is composed of shelly, chalky, well bedded recrystallized and dolomitized limestone, and brecciated part that consists of limestone and dolomitic limestone with lenses of green marl, and undulated limestone that consists of thinly well bedded, light brown and grey, recrystallized, very hard, slightly fossiliferous limestone.

The Euphrates formation is of a lagoonal facies. The age of the formation has been determined as early Lower Miocene to early Middle Miocene. The term "Euphrates limestone" is not

because the deposition had anything to do with the river Euphrates. It is that the limestone crops out along the river.

Limestone is a sedimentary rock consisting mainly of calcium carbonate (CaCO₃) primarily in the form of the mineral calcite, and with or without magnesium carbonate. Common minor constituents include silica, feldspar, clays, pyrite and siderite. Calcium carbonate occurs as two minerals, Aragonite and Calcite. Aragonite crystallizes in the orthorhombic crystal system, while calcite is rhombohedral. Dolomite is calcium magnesium carbonate Ca.Mg(CO₃)₂. A comprehensive review on limestone and dolomites is available in Pettijohn (1957). The chemistry and properties of limestones are given in Boynton (1980).

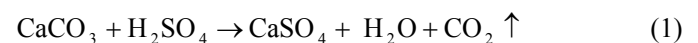
Many parameters are often used to classify carbonate rocks; these include chemical composition, grain size, particle type, degree of crystallinity and quantity of mud. From an engineering point of view and according to Stapledon (1968) the rocks may be classified according to the value of the unconfined compressive strength. Another classification is based on the modulus ratio which is the ratio of elasticity modulus to the uniaxial compressive strength (Roberts, 1977).

Boynton (1980) reported some data on the physical properties of limestone. The hardness of pure calcite is standardized on Moh's scale at 3 whereas aragonite is harder, ranging between 3.5 and 4.0. The unconfined compressive strength of limestones varies widely, the values of the modulus of elasticity ranged between 19×10⁶ and 41.2×10⁶ kN/m² while Poisson's ratio ranged between 0.07 and 0.35.

CHEMICAL REACTIONS

The limestone group is among the most basic alkalies with pH values of 8-9; sulphur is the most basic acid. High calcium limestone dissolves and effervesces readily in most strong acids. It even effervesces freely in cold, very dilute hydrochloric acid but dolomitic limestone will not effervesces unless the weak HCl is heated, since it is not nearly as reactive as high calcium limestone.

When an amount of dibasic acid, like sulphuric acid, reaches the limestone, the reaction result will be calcium sulfate and water accompanied by the liberation of CO₂ gas. After a period of time, the calcium sulfate will gain two molecules of water to form the gypsum as in the following equations:



The mineral framework of gypsum crystals and the molecular volume are larger than the original limestone therefore; the

reaction will be accompanied by increasing in volume and decreasing in the hardness of the reactive limestone. Dolomitic limestone reacts to some extent with the acids, forming magnesium salts; its rate of reactivity is slower.

FIELD AND LABORATORY OBSERVATIONS

The main reason which made the State Company for Phosphate to seek the help of consultants and researchers is the movement of footings carrying the installations. These movements cracked many of the connections and increased the amount of the spilled acid and consequently caused many operational problems.

It was decided to monitor the movement of the nine footings carrying the processing towers. The length of each footing is 11.5 m while the width is 3.7 m at an end and 7.5 m at the other end. An area on the surface of the corner of each footing had been prepared and preserved and a bench mark was used to monitor the footings level. Typical results for a footing are given in Fig. 2, where the measurement period is from February 1995 to November 1995, full details are available in Al-Omari (1996). Cyclic heave and settlement was noticed. The heave occurs when the percolated acid reacts with some of the calcium carbonate. A reaction pressure develops and the resulting material, gypsum, possesses a molecular volume larger than the original material. This causes the underlying rock to swell against the footings. When the reaction ceases during the shut down period, the footing settles because the gypsum is softer than the original calcium carbonate. Thus, the non-steady percolation of the acid causes the movement pattern to be cyclic.

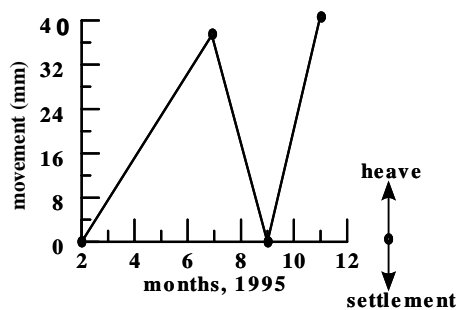


Fig. 2. Vertical movement of a tower footing.

Mohammed (1998) conducted a laboratory investigation on contaminated specimens from the sulphuric acid unit. In the deformation tests, the acid was allowed in portions in order to simulate the field non-steady percolation of acid. The same cyclic pattern of deformations was obtained. A constant but different value of surcharge was applied on the sample in each test. The maximum recorded deformation was plotted against the surcharge. The value of surcharge which corresponds to zero deformation is considered to be equal to the pressure developed during the reaction and causes the swell of the sample. This value is termed the "reaction pressure" and was found to be 430 kN/m².

GEOLOGICAL ALTERATIONS

The purpose of this section is to demonstrate the geological alterations which had taken place in the ground of the sulphuric acid unit since 1977, the date of construction of the complex. It should be mentioned that there are many other facilities in the complex which produce different chemical materials. These materials may have also reached the ground of the studied location in a later time.

According to Sybeta (1977) the upper 7 m profile indicates that the top soil, 1-1.5 m, was clayey silt followed subsequently by layers of chalky limestone, marly limestone, chalk and shelly limestone. A borehole executed by Andrea (1980) showed that the top soil contained limestone fragments increasing with depth. The top soil overlies subsequent layers of chalky limestone, marl, white limestone and a shelly limestone layer. Those two lithological descriptions of the stratigraphy of the intact formation are similar.

A geotechnical investigation was carried out in 1991 (NCCL, 1991), six months after an accident in the storage tanks which caused the spillage of large amounts of acid into the ground. Eight boreholes, BH, were executed and no core samples could be recovered giving a rock quality designation, RQD, of almost zero. This investigation revealed that the top soil is silty sand to silty marl sometimes containing limestone fragments while the rest of the ground down to 7.5 m depth is marly limestone with little gypsum.

Similar rock description was reported in 1996 when seven boreholes were drilled in the same site (NCCL, 1996). However, the average RQD for the site was 35% indicating that the rock has restored some of its strength because the rate of acid percolation was reduced. This regain of strength was also obtained in the laboratory (Mohammed, 1998).

After an increase in the footings movement another geotechnical investigation was conducted in 2001 (Al-Omari, 2001). Eight boreholes were executed to a depth of about 8m.

Table 1. Range of depths at which limestone was converted to dough (Al-Omari, 2001)

BH No.	1	2	3	4	5	7	8
depth (m)	4-7	5.5-8	4-8	4-8	4-8	3-8	4.5-6

The rock description of marly limestone was also reported but at a depth generally deeper than 4 m the limestone was converted to dough. Table 1 shows the range of depths at which this condition was encountered in all the holes except borehole number 6 which was located outside the plant area to serve as a reference.

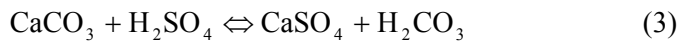
Table 2. The CaCO₃ content obtained in two investigations with 10 years time lapse.

Investigation date	Borehole arbitrary Number											
	1		2		3		4		5		6	
	depth (m)	CaCO ₃ %	depth (m)	CaCO ₃ %	depth (m)	CaCO ₃ %	depth (m)	CaCO ₃ %	depth (m)	CaCO ₃ %	depth (m)	CaCO ₃ %
1991	4.5-6	90.4	1.3-1.5	53.4	6-7.5	81.08	1.5-3	83.6	1.5-3	80.3	3-4.5	73
2001	4-5.5	83.9	1-2	61.5	7-8	87.5	1-2.5	41.3	1-2.5	72.6	4.5-6	52.4

Actually the low design load on the various footings, 80-300 kN/m², compared to the allowable pressure on the intact rocks of 1000 kN/m² prevented the sinking of footings, moreover the reaction pressure continued to uplift the footings.

Equation 1 gives rise to the expectation that CaCO₃ should have been almost diminished or significantly reduced during these years of acid percolation. Table 2 presents the percent CaCO₃ obtained from two investigations with 10 years time lapse.

It is surprising that generally there is no significant reduction in the CaCO₃ content. Therefore, it is thought that equation 1 is suitable for a laboratory reaction but due to the overburden pressure inside the ground which does not allow the release of CO₂, reversible reaction controls according to equation 3 and the CaCO₃ content remains almost unchanged.



All the prescribed investigations were within the discipline of geotechnique. Therefore, it has been recommended to conduct a geochemical investigation. This program was executed by Mosul University in 2002 under the auspices of the consultant. In geochemical investigations the rock identification and description is carried out using tests like, wet chemical, X-ray diffraction, infra red, atomic absorption and petrographic analysis.

The plane of the factory foundation is given in Fig. 3, a grid is set up and the location of boreholes is marked on the intersections of the orthogonal axis.

A petrographic study on specimens from different depths is summarized in Table 3 (Mosul University, 2002). It was concluded that most of the underlying medium is, at present, composed of dolomite or dolomitic limestone with little gypsum. This highlighted the possibility of the occurrence of dolomitization. Dolomitization is the process by which limestone is wholly or partly converted to dolomite rock or dolomitic limestone by the replacement of the original calcium carbonate (calcite) by magnesium carbonate (mineral dolomite), usually through the action of magnesium-bearing water. As a result, magnesium-bearing effluents may have migrated from other facilities in the complex to the ground of the sulphuric acid unit and caused this lithological alteration.

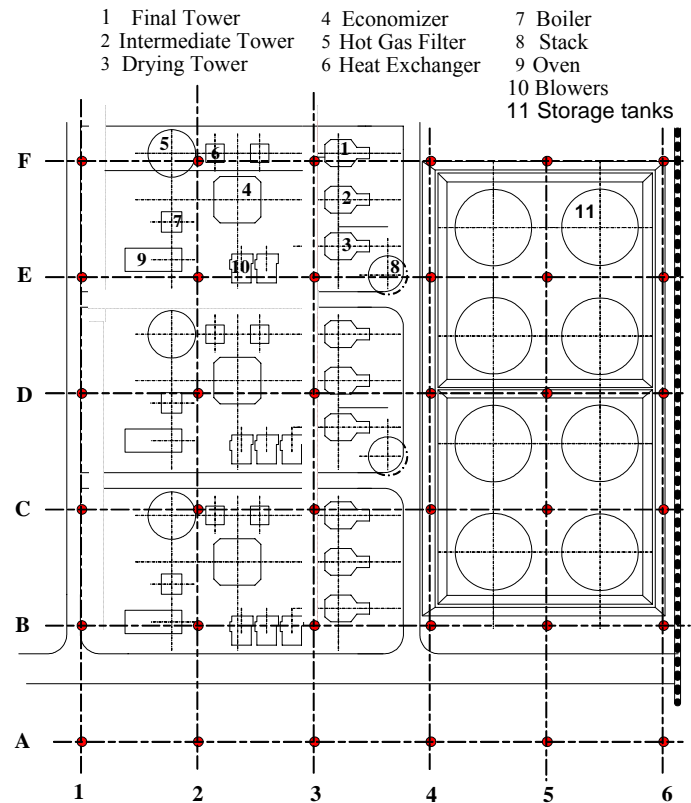


Fig. 3. Foundation plane of the sulphuric acid factory in Al-Kaim.

The porosity was noted to be high apparently due to the dissolution and internal reactions with the effluents. Porosity values of some samples are shown in Table 4 compared with that of intact and contaminated specimens obtained from the same site but in 1995.

The X-ray diffraction analysis revealed, for certain, the availability of dolomite, calcite, gypsum and quartz with an indication of the existence of some other minerals. The acid broke-up the basic structural units of the available clay liberating some aluminum, iron, potassium and magnesium, and resulting in the formation of minerals like alunite and jarosite.

The chemical analysis gave a similar picture for the mineral constituents of the different specimens. Table 5 illustrates the percent of MgO and CaO present in different specimens. In general, the contents of these two oxides are not significantly different giving rise to the relatively significant amount of magnesium which may have contributed to the phenomenon

Table 3. Petrographic description of some soil samples (Mosul University, 2002)

BH No.	A3	B1	B2	B3	B5	B5	C2
Specimen depth(m)	2.7-3	3.5-4	5.5-5.7	3.5-4	1-1.5	3.5-4	8.75-9.35
Petrographic description	Dolomitic calcite	Dolomite with quartz	Gypsum with dolomite	Dolomitic carbonate clay	Calcite partially dolomitized	Calcite-dolomite	Dolomite-microspar

Table 4. The porosity of contaminated samples obtained in 2002 compared with previous cases

BH No.	A3	D2	D3	D4	D5	C2	C4	Intact specimen	Contaminated specimen, 1995
Specimen depth (m)	8.7-9	4.5-4.7	13-13.5	3-4.5	1.5-2	1.2-1.5	12-12.5	-	-
Porosity%	24.76	44.96	31.05	18.79	32.86	56.58	47.33	12.34	16.77

Table 5. The percent of MgO and CaO present in different contaminated specimens (Mosul University, 2002)

BH No.	B1	B2	B3	B4	B5	A3	A3	A4	C2	C2
Specimen depth (m)	2.7-4	2.7-3	3.5-4	5.5-6	5.5-6	2.7-3	7.2-7.5	4-4.5	4.2-4.5	8.75-9.35
CaO%	19.67	15.89	18.93	24.61	25.44	23.72	30.56	22.73	33.30	32.33
MgO%	16.57	7.97	19.32	19.53	20.03	22.03	20.26	18.29	19.79	20.49

of dolomitization. In addition to the effluents seeping from other facilities in the complex the source of magnesium may also be from the break-up of the basic structural units of the clay present in the form of Marl.

CHEMICAL TREATMENT

The Engineering Office of the Phosphate Complex demanded a treatment method for the ground which does not necessitate the shut down of the factory for a long time. Furthermore, they demanded the treated ground to withstand future leakage of acid. This is because the country at that time was in desperate need for the fertilizers and permission for a long shut down will not be granted. Therefore it has been recommended to adopt chemical grouting of the ground after choosing the proper material. Chemical grouts are valuable in solving site problems. Their major advantages are low cost, time saving, simplicity, obviating of danger to the structure by under pining excavation and reduction in design cost as well as in field problems and subsequent foundation construction (Bowen, 1981).

Sampling

Intact, non-spoiled, blocks of rock were brought from the factory site. Core samples were extracted from the parent rock using an extruder which cuts samples in the shape of cylinders 30 mm diameter. The height of the sample is twice the

diameter. Core samples were used for physical, non-destructive and destructive testing while rock pieces left after cylindrical specimens preparation were used for X-ray diffraction and wet chemical analyses.

Contaminated samples were obtained from boreholes A2 and D5 (Fig. 3) which were drilled up to 15 m in the factory site during the work of Mosul University (2002). The samples were almost in the form of dough due to the action of acid. They were treated using chemical materials and then molded into cylindrical shapes using plastic moulds.

Tests

In order to assess the effect of chemical treatment, the following tests were conducted:

- 1) Ultrasonic test
In this test the wave velocities of compression, v_p , and shear, v_s , were determined according to ASTM D 2845-69 (1983). The values of v_p and v_s are used to calculate the dynamic moduli of elasticity, E_d , and rigidity, G_d (Prakash, 1981).
- 2) Unconfined compression test
This test was conducted according to ASTM D 2938-79. It is used to classify the rock (Stapledon, 1968) and to estimate the strength.
- 3) Physical tests
These include the bulk density, porosity and specific gravity.

Table 6. The unconfined compressive strength of the chemically treated samples

BH No.	depth (m)	Type of grout					
		Sodium silicate		Sodium carbonate		Sodium silicate +calcium chloride + retarder	
		% Na ₂ SiO ₃ of total sample	q _u (MN/m ²)	% Na ₂ CO ₃ of total sample	q _u (MN/m ²)	% Na ₂ SiO ₃ + CaCl ₂ + retarder respectively of total sample	q _u (MN/m ²)
A2	1.5-2	-	-	-	-	20+10+3.33	4.112
	2-3	33	1.605	-	-	-	-
			1.615 1.605				
	2-3	50	9.362	-	-	-	32.6+17.34+6.5
			9.364				
			9.463				
	4.5-5	-	-	33	0.802 0.823 0.806	-	-
6-7	33	4.021	25	-	-	-	
		4.021 4.022					
10.5-11	33	9.364	-	-	-	-	
		9.346 9.363					
10.5-11	25	8.024	-	-	-	-	
		8.026 8.025					
D5	0-1.0	-	-	-	-	23.53+11.67+6	4.110
	2-3.25	33	2.407	33	0.805	-	-
			2.047		0.815		
			2.047		0.804		
3.25-3.5	-	-	50	0.857 0.855 0.888	-	-	
7.5-10	-	-	-	-	26.87+13.34+6.67	5.140	

4) Wet chemical analysis

As the limestone and dolomite are composed of many major and minor constituents, this test includes determinations like loss on ignition, impure silica or insoluble matter, combined oxides, calcium oxide, magnesium oxide, carbon dioxide and insoluble silicate (Vogel, 1982).

5) X-ray diffraction analysis

This instrumental procedure is used to determine the mineralogical composition of the samples.

toxic, non-corrosive, non-explosive and able to withstand appreciable dilution with ground water.

According to the study performed in this research, the following solutions are proposed;

1) Sodium silicate

Sodium silicate, Na₂SiO₃, is a syrupy liquid, the viscosity of which varies with water content and the ratio between silica and sodium oxide.

As the present contaminated medium contains plenty of calcium ions and an excess sulphuric acid, sodium silicate may function in two directions. First, sodium silicate can in certain conditions exchange the sodium ion with the calcium ion to form calcium silicate, CaSiO₃, and the latter is a solid material and resistant to acids. Second, sodium silicate reacts with the excess sulphuric acid to form new solid material, silica gel, which is thought to be a tangled mass of polymeric

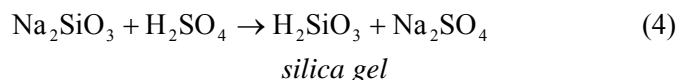
The Possible Grouting Materials

The basic types of grouts are suspensions, solutions and emulsions. In the present problem the suitable grouts are solutions. According to Karol (1983) the grout solution should be of low viscosity, stable under all normal temperatures, non-

Table 7. Physical test results

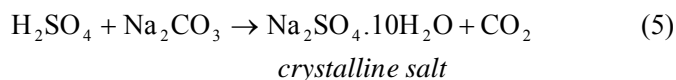
Type of sample	Bulk density (g/cm ³)			Porosity %			Specific gravity		
	mean value	(σ_n)	n	mean value	(σ_n)	n	mean value	(σ_n)	n
Intact	2.492	0.055	9	16.707	0.081	9	2.615	0.043	9
Treated with Na ₂ SiO ₃	1.846	0.174	18	18.483	2.337	18	2.352	0.040	18
Treated with Na ₂ SiO ₃ +CaCl ₂ + retarder	1.377	0.055	4	39.654	0.381	4	2.419	0.024	4

silicic acid. A small quantity of sodium sulphate, Na₂SO₄, is also produced according to the equation:



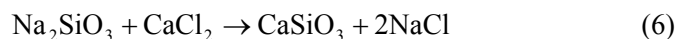
2) Sodium carbonate

Treatment with sodium carbonate, Na₂CO₃, is thought to give a solid crystalline sodium sulphate according to the equation:



3) Sodium silicate + Calcium chloride

The two-shot injection of sodium silicate and calcium chloride has been successfully used world wide (Xanthakos *et al.* 1994). The silica and chloride meet in the ground and react instantaneously. The reaction product is calcium silicate, equation 6, which is hard and resists temperature changes, salinity and sulphate attack.



In the one-shot method retarders are added, organic esters (ethyl acetate) proved to be appropriate (Bowen, 1981).

4) Other materials

Different other materials were proposed to treat the contaminated limestone such as barium sulfate, aluminum oxide, ferric oxide and natural aluminosilicate materials such as bentonite, ironstone and kaolinite. These materials have been primarily tested using limestone samples obtained from the contaminated site but they gave unsatisfied results because they are non-reactive and non-absorbable materials for the excess sulphuric acid. Furthermore, the oxides and aluminosilicate materials react only at high temperatures with sulphuric acid to form solid salts.

Results and Discussion

It was decided to start with the ultrasonic and unconfined compressive tests since they are not expensive so that the wet chemical and X-ray diffraction tests can be restricted to the specimens treated with the most successful grouts.

Wave velocity tests were conducted on nine intact samples. The averages values of E_d and G_d were 29.91×10⁶ and 11.75×10⁶ kN/m² respectively. Considering the chemically treated samples, unfortunately the ultrasonic test could not be carried out successfully due to the presence of foreign chemical matters and the high degree of heterogeneity which made the compression and shear waves transmission registration not reliable.

Nine intact samples were subjected to the unconfined compressive test giving an average strength, q_u, of 7.672 MN/m² with a standard deviation of 0.0227. It should be recalled here that the average q_u obtained in the preconstruction investigation was 7.85 MN/m² over the depth investigated. The q_u values for the chemically treated samples are given in Table 6. It appears that the sodium carbonate did not help the samples to regain their original strength not even a reasonable value.

However, after treating the samples with sodium silicate, a hard unbreakable rock was formed perhaps due to the intrusion of sodium silicate into the internal parts of the sample. Fifty percent of the treated samples gained strength higher than that of the intact samples. It should be appreciated that such high values have been obtained from samples which were originally in dough state. During the immersion of treated samples in concentrated sulphuric acid, effervescence has either not occurred or slightly occurred on the surface. This is thought to be due to the intrusion of the silicate by capillary tension or the absorption of calcium ions from calcium carbonates to form calcium silicate. This may be explained by the dynamically unstable ions or a composite mixed crystalline carbonates is formed which is acid resistant. The treatment using Na₂SiO₃ + CaCl₂ + retarder helped the contaminated samples to gain significant strength but not to the degree of restoring the original intact strength. Therefore this method is deemed successful but sodium silicate alone is considered the most effective chemical treatment among

Table 8. Wet chemical analyses on intact, contaminated and sodium silicate treated samples

Type of sample	SiO ₂ %	Fe ₂ O ₃ %	Al ₂ O ₃ %	TiO ₂ %	CaO%	MgO%	SO ₃ %	Na ₂ O%	K ₂ O%	L.O.I%	Total
intact	11.16	0.35	2.22	0.25	33.06	10.10	1.0	0.5	1.19	39.70	99.53
	14.04	0.31	2.03	1.10	30.08	9.21	0.5	1.05	0.5	40.98	99.8
	13.8	0.16	1.9	0.25	29.8	11.70	0.8	1.02	0.6	38.98	99.01
	22.47	6.22	16.42	0.4	17.62	6.4	0.7	1.4	1.32	26.27	99.22
Mean	15.36	1.76	5.64	0.5	27.64	9.35	0.75	0.99	0.9	36.48	99.93
contaminated samples from depths between 1 and 11m	12.34	1.22	1.817	0.163	31.4	10.58	4.25	0.52	0.38	37.2	99.87
	10.82	1.03	2.266	0.138	28.04	13.2	5.8	0.44	0.64	37.59	99.96
	4.6	0.43	0.779	0.063	28.6	17.65	4.5	0.38	0.24	42.75	99.99
	11.5	1.06	2.31	0.35	26.62	10.93	6.25	0.76	0.5	39.48	99.79
	10.2	1.35	2.48	0.55	27.32	11.70	4.8	0.26	0.33	40.98	99.97
	8.86	0.4	1.09	0.3	30.54	9.85	5.5	0.65	0.58	40.70	98.47
Mean	9.72	0.91	1.79	0.26	28.75	12.31	5.18	0.50	0.44	39.78	99.67
samples treated with sodium silicate	15.38	0.73	1.345	0.1	23.55	14.01	1.5	5.3	0.35	37.67	99.93
	19.7	0.92	1.51	0.125	25.8	10.08	2.8	5.6	0.27	33.19	99.99
	21.41	0.40	1.35	0.05	23.72	10.03	0.92	9.84	0.4	30.91	99.03
	24.41	0.55	2.38	0.21	20.04	8.70	1.8	10.84	0.22	30.28	99.43
Mean	21.84	0.62	1.74	0.12	23.18	9.60	1.84	8.76	0.29	31.46	99.48

others. It is known that the injection of these materials provide a continuous gel network through stabilized soil (Karol, 1983). Bearing in mind that the network effect can not be reproduced in scale, the degree of success may be higher in the field.

The values of bulk density, porosity and specific gravity of the intact samples are given in Table 7 along with the corresponding values for the treated samples. Only the mean values are given with the standard deviation (σ_n) and the number of samples (n). Obviously the low specific gravity of the chemicals reduced the bulk density. The laboratory mixing technique increased the porosity while the field injection under pressure may reduce the porosity.

Wet chemical analyses were conducted on intact and contaminated specimens as well as on specimens treated using sodium silicate as the latter samples showed the most successful results. Fourteen samples were tested; the results are given in Table 8. All samples showed that calcium oxide (CaO), magnesium oxide (MgO), silicon dioxide (SiO₂) and loss on ignition (1000°C) are the main constituents. The high concentration of calcium oxide even in the samples highly contaminated with sulphuric acid supports the interpretation previously given according to equation 3. The significant concentration of magnesium oxide supports the previously mentioned expectation of the occurrence of dolomitization. Iron oxides (Fe₂O₃) and alumina oxides (Al₂O₃) are present in variable amounts. On bases of alumina content the presence of some clay minerals is expected. Titania (TiO₂) is present in all samples ranging from 0.05 to 1.10%.

The contaminated samples contain significant percentages of SO₃ ions while sodium oxide (Na₂O) is obviously higher in the treated samples.

The fourteen samples subjected to wet chemical analyses were also employed in the X-ray diffraction analyses. The XRD revealed that the major minerals are calcite, dolomite, and gypsum. Other admixtures present are quartz, alunite, anhydrite, melanterite, bassanite, epsomite, goethite, jarosite and anatas.

In the XRD diffractogram of contaminated samples treated with sodium silicate only peaks of major minerals were recognized due to the presence of non crystalline amorphous sodium silicate in the samples. No peaks for gypsum or other sulfate and hydrosulfate minerals were occurred after treatment with basic sodium silicate which neutralizes the acidic ions in the treated samples. Full details may be consulted in a thesis by Sagman (2004).

CONCLUSIONS

The ground of a large sulphuric acid factory, which is composed mainly of limestone, had been subjected to the percolation of sulphuric acid, in a high rate, for more than ten years.

Field investigations were subsequently conducted. The alterations in the geology of the substrata are assessed. A laboratory investigation is conducted on field samples to find out the most effective chemical grout in order to stabilize the ground by injection. The following conclusions may be drawn;

- 1) The non-steady percolation of the acid caused the isolated footings to suffer a heave-settlement pattern of movement.
- 2) The chemical reaction between the main constituent of limestone, calcium carbonate, and the acid produces

gypsum and results in a “reaction pressure” which uplifts the footings as far as the applied load is less than that reaction pressure which was found to be 430 kN/m².

- 3) In spite of the great amount of the percolated acid over years the carbonate content remains in balance with the sulphate content apparently due to the occurrence of a dynamic equilibrium and a reversible reaction.
- 4) The phenomenon of dolomitization has then taken place in the site ground. The source of magnesium ions is thought to be from the break-up of the marly clay basic structural units or from the effluents of other facilities in the Phosphate Fertilizer Complex.
- 5) Many proposed chemical grouts have been tested in the laboratory using field contaminated samples. Mechanical and chemical tests were employed to assess the treated specimens. It is found that sodium silicate is the best alternative for ground injection.
- 6) Sodium silicate may react with the present calcium ions to form calcium silicate which is hard and resistant to acids and may also deal with the excess sulphuric acid to form a silica gel.
- 7) The use of sodium silicate + calcium chloride + retarder gave also good results. It is thought that the pressure injection in the field may give even better performance.

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