Bull Eng Geol Environ
DOI 10.1007/s10064-017-1076-6

ORIGINAL ARTICLE

Changes in chemical composition and engineering properties of gypseous soils through leaching: an example from Mashhad, Iran

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Received: 13 May 2016 / Accepted: 17 May 2017

Abstract Gypseous soils are considered problematic when used as the foundation in civil engineering structures such as roads, buildings and dams, due to their solubility. These soils are resistant and have good engineering properties in their dry state. However, when saturated by rainwater or a rising groundwater table, the soluble minerals are washed out, resulting in the subsidence of the structures built on them. In the recent decades, buildings constructed in the Southern Mashhad Metropolitan Area, Iran, have been widely faced with this problem. Since the changes in chemical composition and engineering properties of these soils are based on the amount of dissolved gypsum, the focus of this study is to characterize the soluble soils of this area and their changes throughout the leaching process. Thirty-eight samples were taken from different locations in the area. Chemical tests were conducted on the samples and the gypsum and sulfate concentration maps were produced based on these results, combined with the previously available data from 511 boreholes drilled in the area. Seven soil samples with different gypsum concentrations were selected for further analysis in four major groups of tests, including hydraulic tests (permeability and solubility), chemical tests (chemical analysis of soils samples and total dissolved solids, calcium hardness and chlorine of the leachate samples), physical tests (grain size analysis, Atterberg limits and specific gravity) and mechanical tests (consolidation and direct shear). Changes in the mentioned parameters were investigated through a 5-day leaching process. The results indicate that extensive dissolution of gypsum and removal of gypsum bonding between soil particles change soil chemical composition and decrease the soil compressibility and strength parameters. Therefore, the structures built in this area are in high risk of subsidence and foundation failure; proper measures should be taken to improve the soil quality before construction.

Keywords Gypseous soils · Engineering properties · Solubility · Leaching · Permeability coefficient

Introduction

Soils in the south of Mashhad are considered problematic due to the large quantities of gypsum deposits they contain. Cracks in the facades of buildings, uplift of walls and destruction of landscapes are some of their indicators in the area. The main problem is hollowness in gypseous soils and their subsidence due to the solution and removal of gypsum from the soil structure (Fig. 1).

Gypseous soils are typically resistant in dry conditions due to the cementing effect of gypsum. However, in cases of partial or complete soil saturation, soluble substances dissolve, resulting in a substantial loss of resistance. This problem becomes more severe when the water flow in the soil results in soil mass loss by leaching of gypsum. Leaching is a process in which the natural or artificial flow

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Published online: 29 May 2017

Fig. 1 Hollowness of gypseous soils in the area (Babaie, 2009)

of fluids in soil results in solution and removal of soluble components. This is essential to study, as the safety and behavior of the foundations of structures such as embankments and dams are highly dependent on the changes in the mechanical and chemical properties of these soils (Ahmad et al. 2012).

Gypseous soils are classified as collapsible soils. Gypsum provides an apparent cementation when dry but the intrusion of water causes dissolution and softening of the soil that may lead to partial or complete collapse of structures (Ismael 1993). Some natural factors such as temperature, quantity of water in contact with gypsum substrates, applied pressure, velocity of water and grain size can control the gypsum dissolution (Petrukhin and Boldyrev 1978).

In one of the first studies on gypseous soils, Keren and O'Connor (1982) indicated that the increase of gypsum particles smaller than 44 μm results in a significant decrease of hydraulic conductivity in soil, while particles with 0.25 to 1 mm had no such effect. Herrero and Porta (2000) found that gypseous soils could grow large void spaces after dissolution, which reduces the substrate strength substantially. Azam (2000) found out that the collapse potential is doubled when gypseous soils are soaked in brine, compared to distilled water.

Razouki and Kuttah (2004) showed that both the California Bearing Ratio (CBR) and Resilient Modulus (MR) decreased due to prolonged soaking and drop in gypsum content. They also considered dissolution as a controlling factor in changing the geotechnical properties of gypseous soil, which leads to a series of outcomes such as increase in permeability, change of the original particle size distribution of gypseous soil strata and loss of very fine non-gypsum particles like clay.

According to Razouki et al. (2008) dissolution over the long term is considered an important controlling factor in changing the geotechnical properties of gypseous soils. Their result also indicated that the loss of very fine non-gypsum particles like clay can occur, which leads to changes in the overall particle size distribution in the soil.

Johnson's (2008) study established that karstic gypsums present in dam abutment or reservoir-impoundment areas may cause a number of problems, such as loss of reservoir water or catastrophic loss of the dam itself.

Fattah et al. (2008) confirmed that gypseous soils are problematic from both agricultural and engineering points of view. Slow and continuous dissolution of gypsum by water seeping through gypsum-rich soil may result in soil failure, increasing leakage of water through the soil, soil softening and serious damage to concrete by sulfates.

Based on the Al-Farouk et al. (2009) study, some physical properties such as porosity have significant effects on gypseous soil behaviors during gypsum dissolution. They used a finite element method to analyze and calculate the changes in pore water pressure and concentration due to the dissolution of gypsum from soil, and demonstrated the relationship between fluid velocity and the dispersion coefficient. They also indicated that gypsum dissolution is decreased in brine compared to distilled water, which is contradictory to the report of Azam (2000).

Namiq and Nashat (2011) studied the effects of leaching on volume changes of gypseous soils in an area in northern Iraq using uniaxial compression tests in Row cells (Rowe and Barden 1966). They showed that consolidation tests and traditional interpretation methods are not practical for gypseous soils and derived a new form of stress-strain relationships for these soils.

Tran et al. (2012) showed that an increase in gypsum content leads to a decreased angle of internal friction, as well as lower expansion indices and cohesion. They further indicated that compressibility decreases with decreasing salt content and increases by addition of sand to gypsum.

In their study, Albusoda and Hussein (2013) attempted to improve the bearing capacity of collapsible soils upon wetting by partially replacing the soil by dune sand. Geogrids and geotextiles were proved effective in improving the bearing capacity, and reducing settlement values.

Despite the vast neighborhood development and construction in the study area in recent decades, no study so far has attempted to map these soils to evaluate the amount, spread and concentration gypsum zones. This information is essential in order to adopt special construction methodologies to prevent potential catastrophic events in the future. Furthermore, in spite of the fact that leaching-based changes in chemical composition and engineering properties of these soils have resulted in subsidence in the area, no study so far has addressed this issue.

The aim of this research is to identify areas with the highest concentrations and spreads of gypsum in the area by providing sulfate and gypsum zonation maps in the southern Mashhad.

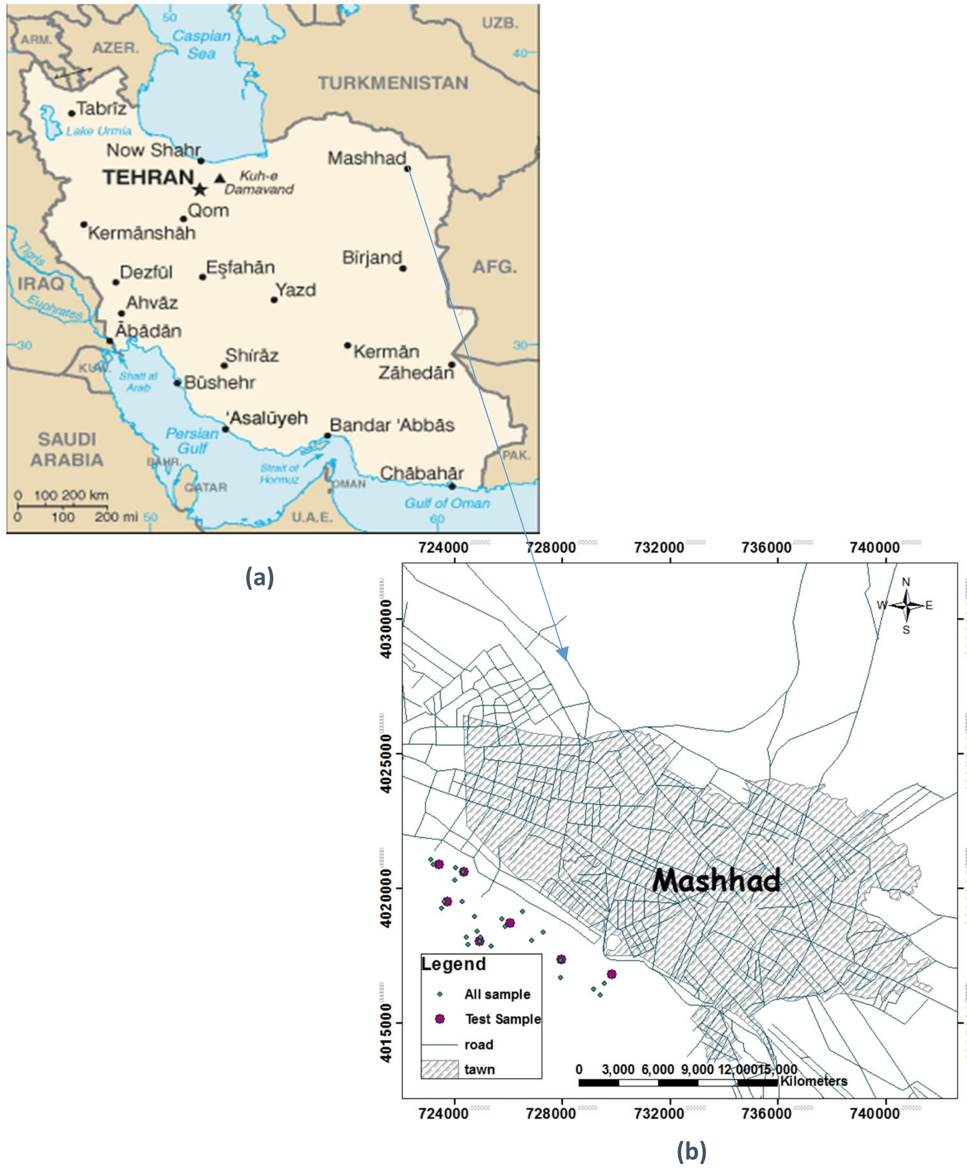

Fig. 2 Map of Iran (**a**) and map of Mashhad city with sample locations (**b**)

The effects of leaching on the changes in chemical composition and engineering properties of these soils is investigated as well.

Materials and methods

The study area is located in the Southern part of the Mashhad Metropolitan Area, in the northeast of Iran, between E 59° 26′ to 59° 36′ and N 36° 13′ to 36° 20′, with an average elevation of 1140 m. Figures 2a and b show a map of Iran and a map of Mashhad with sample locations, respectively.

The study was conducted in two major stages:

A) Thirty-eight samples were taken from different locations in the area and chemical experiments were carried out. Using these results and the available data from 511 existing cores, gypsum and sulfate zonation maps were produced for the area.

B) To analyze the changes in chemical composition and engineering properties of gypseous soils during the leaching process, seven samples with different gypsum quantities were chosen. Each sample was first remolded and then connected to water storage with a constant head (900 mm). The drain was kept closed for 24 h to let the samples become completely saturated. Since the drain was kept closed, the gypsum content stayed unchanged during the saturation process. Then the drain tap was opened to let the water move through the sample. Permeability, Atterberg, consolidation and direct shear tests were conducted on samples before and after leaching.

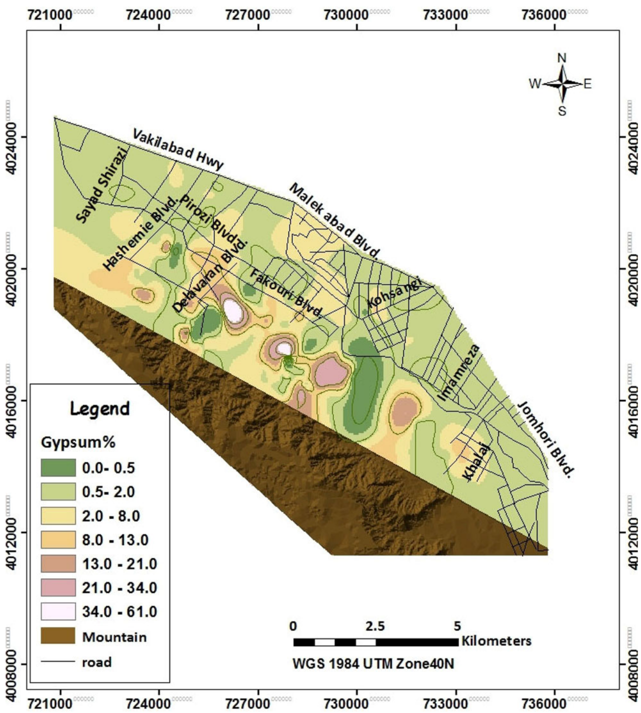

Fig. 3 Gypsum zonation map of the study area

In addition, complementary tests were carried out in four categories:

1. Chemical Tests, including chemical tests on:

    a. Natural soil samples: determination of gypsum, sulfate and chlorine, pH, total dissolved solids (TDS) and Electrical Conductivity (EC)
    b. Leachate water samples: TDS, calcium hardness (CH) and chlorine
2. Hydraulic Tests: constant head permeability test according to ASTM D2434-68
3. Physical Tests: grain size analysis according to ASTM D 422-87 and ASTM D 521-58, Atterberg limits according to ASTM D4318-87
4. Mechanical Tests: consolidation test according to ASTM D 2435-90 and direct shear test according to ASTM D 3080-90

Fig. 4 Fibrous form of gypsum in the area (a) and gypsum crystals evident in the soil (b)

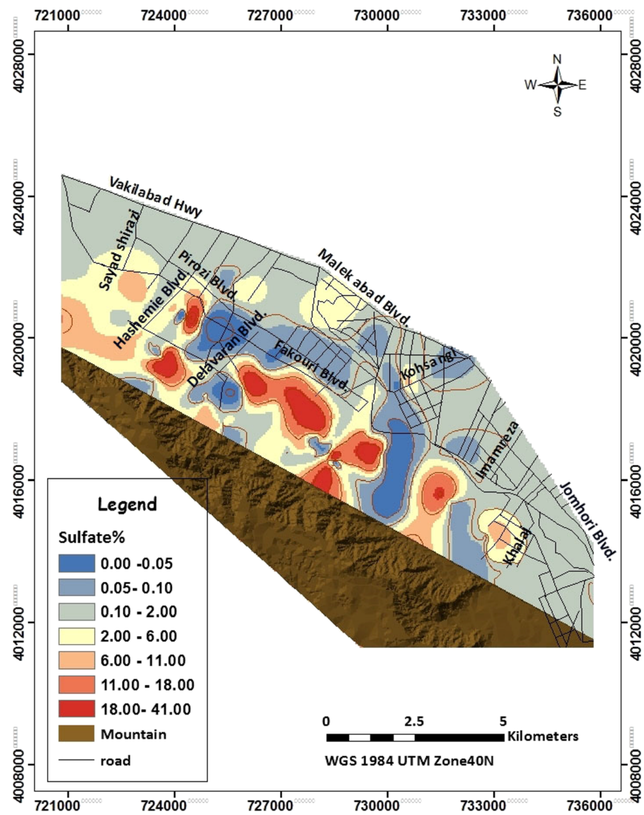

Fig. 5 Sulfate zonation map of the study area

Results and discussion

Gypsum and sulfate zonation maps of soils in southern Mashhad

As depicted in the gypsum zonation map in Fig. 3, dispersed gypsum lenses were observed from Hashemie Boulevard to Kohsangi. The highest concentration of gypsum crystals was in the west of Kohsangi. In these areas, gypsum crystals were found in large aggregates beneath the boulders of the flood plain in prismatic, acicular, fibrous and massive forms. Figures 4a and b show the fibrous form of gypsum, which is prevalent in the area. In some cases, gypsum content was more than 50% and thick gypseous soil layers of 3 to 4 m were

Table 1 Classification of sulfate concentrations in soils (Iranian Concrete Code, 2003)

So32-% (1)	Sulfate Class (2)	Samples per class (3)	Percentage in each class (4)
Less than 0.2	Soft	9	6.43
0.2 to 0.5	Medium	32	22.86
0.5 to 1	Relatively Intense	28	20.00
1 to 2	Intense	9	6.43
More than 2	Very Intense	62	44.28

Table 2 Chemical tests results on soil samples

Sample	Gypsum $CaSO_4.2H_2O$) (Mg/ml)	SO_3 (mg/ml)	Cl (mg/ml)	pH	TDS (mg/ml)	EC
G1	28.5	67.80	0.03	8.03	26	2.07
G2	573.1	330.80	0.02	8.12	36	2.01
G3	38.7	203.20	0.30	8.27	40	2.56
G4	37.7	223.30	0.02	8.17	41	2.60
G5	29.1	30.29	0.09	8.08	21	1.88
G6	427.5	395.50	0.05	8.02	27	1.80
G7	46.0	91.50	0.03	8.01	30	1.75

Fig. 6 The cell used for soil leaching (left) and sample G2 after leaching (right)

present. The sulfate zonation map was also produced based on existing data. (Fig. 5). The map shows that the amount of sulfate in soils increases from central parts to the southern hillsides and reaches its maximum of 40% in the west of Kohsangi. The active tectonics and extreme weathering of the metamorphic and ultrabasic rocks in southern Mashhad heights have resulted in the accumulation of this ion in the area. Based on the sulfate maps and according to the Iranian Concrete Code (2003) sulfate classification, the area is classified as "very intensely sulfated" (Table 1).

Complementary tests

1. Chemical tests:

   a. Soil samples:

To determine the chemical composition of soil samples and the potential effects of its components on the amount of gypsum solution, soil samples were chemically analyzed to obtain the amount of gypsum, sulfate ion, pH, TDS and EC. The results of these tests are summarized in Table 2.

   b. Leachate water samples:

For leaching, each sample was first remolded to a perforated cell of 10.12 cm in diameter and 12.17 cm long and then connected to water storage with a constant head of 900 mm. In order to prevent leakage, filter papers were applied to the top and bottom of the cell and the drain was kept closed for 24 h to let the samples become saturated. The tap was then opened to let the water (TDS = 1.45 mg/ml, CH = 0.085 mg/ml, mean Cl = 0.2×10^{-4} mg/ml, temperature = 21.8 °C) move through the samples. Figure 6 shows the cell used for soil leaching and sample G2 after leaching. For each sample, every 150 ml of the leachate was gathered and used to determine TDS, chlorine, CH and pH. Between each water collection stage, the

Table 3 Chemical analysis results on leachate samples

Sample	TDS Max (mg/ml)	TDS Min	TDS Mean	Cl Max (mg/ml)	Cl Max	Cl Mean	CH Max (mg/ml)	CH Min	CH Mean	pH Max	pH Min	pH Mean
G1	1500	1310	1400	0.00736	0.00439	0.00574	0.272	0.157	0.214	6.00	7.30	6.65
G2	3000	1200	2100	0.01795	0.00604	0.01199	0.395	0.239	0.317	7.30	8.40	7.85
G3	1340	1260	1300	0.00931	0.00378	0.00654	0.399	0.099	0.249	7.17	8.20	7.68
G4	1390	1200	1290	0.00680	0.00450	0.00565	0.194	0.070	0.132	7.30	7.80	7.55
G5	1310	1190	1250	0.00888	0.00468	0.00678	0.220	0.159	0.189	6.64	7.90	7.27
G6	2330	1320	1820	0.00980	0.00348	0.0664	0.224	0.107	0.165	7.00	7.80	7.40
G7	1270	1180	1220	0.00899	0.00438	0.00668	0.260	0.130	1.950	7.10	8.00	7.55

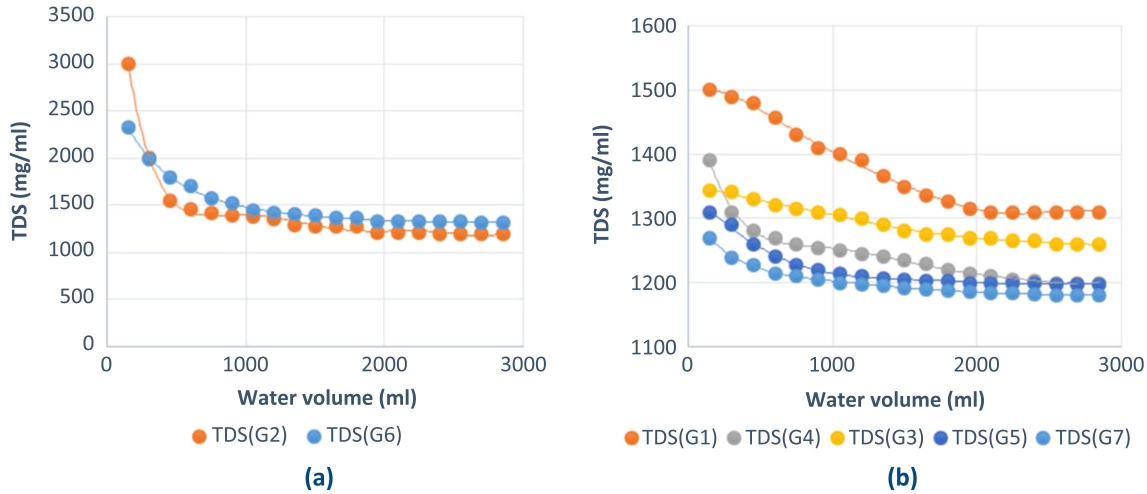

Fig. 7 The changes in TDS for G2 and G6 (a) all samples (b)

drain tap was kept closed for 1 to 2 h to let the salts concentration balance (Ismael and Mollah 1998). Leaching was then continued until the TDS, chlorine, and CH of the leachate reached a constant value. The degree of saturation for each sample was estimated after leaching by measuring the pore-pressure coefficient B (Skempton 1954). The pore water composition had a significant effect on the porosity.

Similar to previous research, the void ratio of the samples that were leached with saline water was about twice that of those leached with distilled water (Azam et al. 1998). This was mainly due to the effect of high concentration of Na^{+} and Cl^{-} ions on the solubility of calcium sulfate. As time passed, the amount and rate of calcium sulfate solubility and consequently the concentration of Na^{+} and Cl^{-} ions in pore water increased. Due to the presence of chlorine in tap water, leaching was significantly higher with more calcium sulfate solubility compared to leaching with distilled water.

At the end of leaching, there were still some salts in the samples that were not readily soluble in freshwater and needed specific chemical additives to be dissolved. Since the objective of this research was to simulate a natural leaching situation, no effort was made to dissolve the remaining salts. The penetration of fluids and leaching of SO^{2-} and Ca^{2+} ions broke the crystal bonds of gypsum in the first stages of the test. This prevented the calcium sulfate from showing its complete volume change. The concentration of Ca^{2+} ions was always higher than that of SO^{2-} and, as a result, several large void spaces remained in the soil (Azam et al. 1998).

Chemical analysis results for all water samples, including minimum, average and maximum TDS, Cl, CH and pH are summarized in Table 3. The changes in TDS, CH and Cl in time are also plotted in Figs. 7, 8 and 9 (since the amount of gypsum in samples G2 and G6 was over tenfold that of other samples, the changes in the mentioned parameters were more significant in these two samples; the purpose of

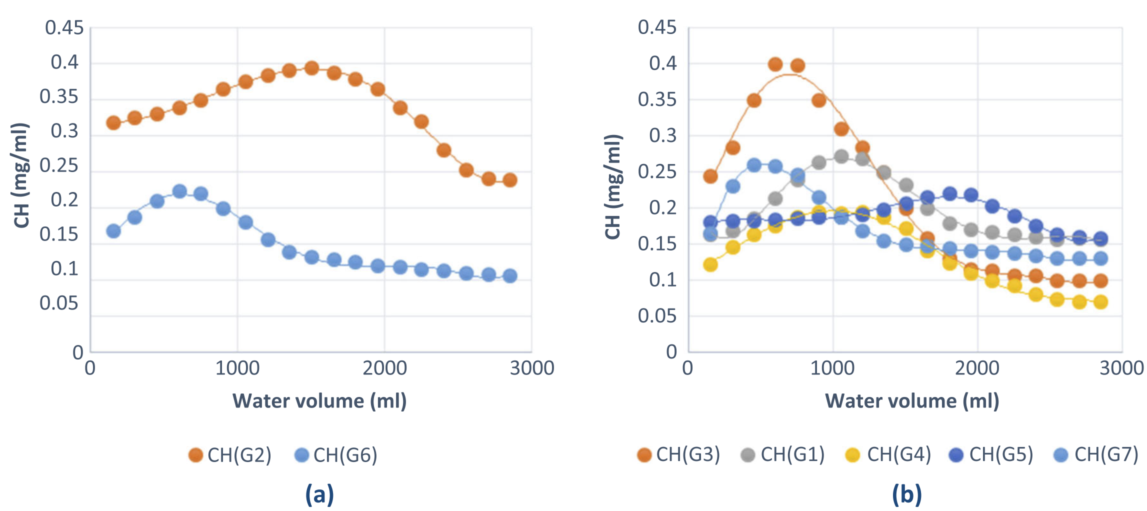

Fig. 8 The changes in Calcium Hardness (CH) for G2 and G6 (a) all samples (b)

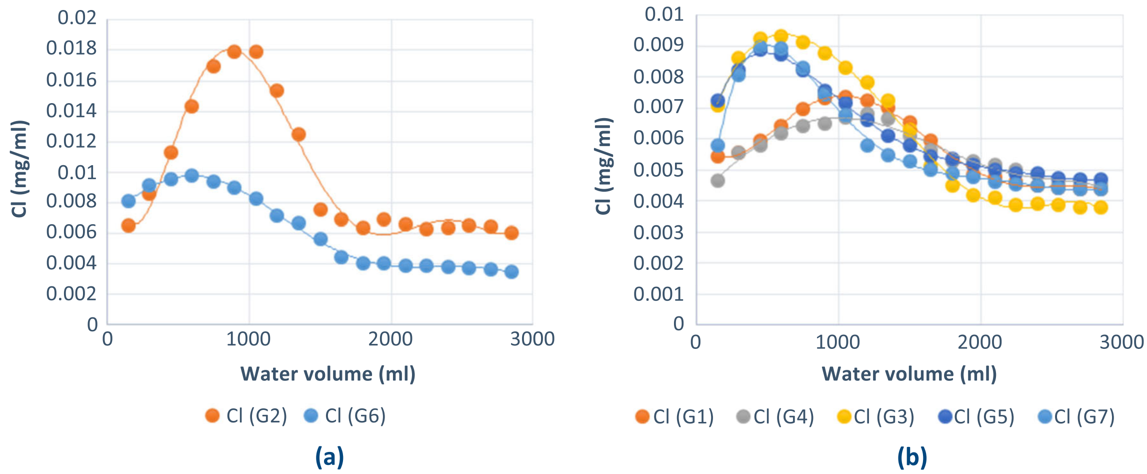

Fig. 9 The changes in chlorine (Cl) for G2 and G6 (a) all samples (b)

Table 4 Summary of the results as maximum, minimum and mean hydraulic conductivity (K)

Sample	Max $K*10^{-5}$ (cm/s)	Min $K*10^{-5}$ (cm/s)	Mean $K*10^{-5}$ (cm/s)
G1	3.34	2.89	3.11
G2	0.20	0.10	0.15
G3	8.76	7.53	8.14
G4	0.10	9.34	9.98
G5	4.48	4.32	4.40
G6	0.47	0.19	0.33
G7	5.26	4.71	4.99

separating G2 and G6 samples was to emphasize on this importance). As the table and graphs depict, in the initial stages of leaching, samples had large quantities of gypsum, TDS was maximum, and Cl and CH were increasing. As the leaching continued, all three of these parameters decreased and tended to a constant value.

Hydraulic tests

A permeability test was conducted on the samples at the same time as the leaching test according to ASTM D2434-68 (Reapproved 2000), and hydraulic conductivity (K) was measured at the end of each time step in the leaching process. The summary of the results is presented in Table 4 as maximum, minimum and mean K. The K changes in time were plotted for all samples in Fig. 10. As depicted in Fig. 10a, in samples with the highest amount of gypsum (G2 and G6), hydraulic conductivity was initially high and then decreased rapidly.

Several reasons were proposed for this rapid decrease in leachate volume. For instance, in the beginning of saturation, this decrease was due to the changes in soil-water transferred ions ratio and dispersion of the particles and then due to the

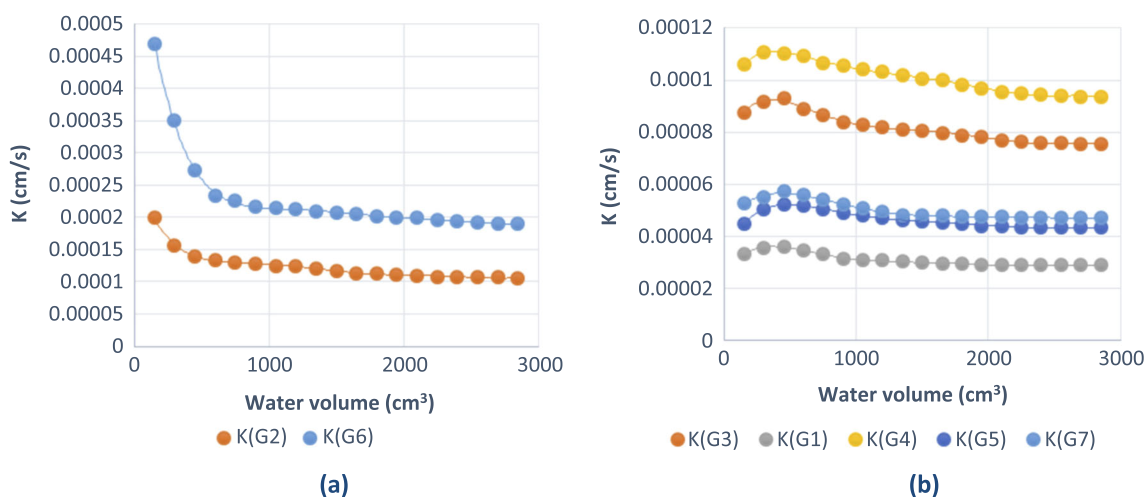

Fig. 10 Changes in K for G2 and G6 samples (a) and all samples (b)

weakening bonds of the gypsum cement, collapse of the soil particles and subsidence under static load. Furthermore, in samples with lower permeability coefficients, the decrease was lower and the equilibrium state was reached faster (Fig. 10b). In samples with higher permeability coefficients (G2 and G6), on the other hand, reaching the equilibrium state took longer (Fig. 10a).

As depicted in Fig. 10b, in samples with lower gypsum content (G1, G3, G4, G5, G7), permeability coefficients tended to a constant value after a small initial increase. Previous research showed that the permeation capacity of gypseous soils increases in the initial stages of leaching and then decreases and tends to a constant value (Jackson 1974). This small initial increase in the permeability coefficient might have been due to the increase in the saturation level of samples. The increase of permeability in the unleached samples was related to continuous expansion and formation of new micro joints (Jackson 1974).

Physical tests:

Physical tests were conducted on samples before and after leaching. ASTM D 422-87 and ASTM D 521-58 were followed for grain size analysis, ASTM D4318-87 for Atterberg limits and ASTM D 698-78 for dry density. In order to prevent the effect of high temperature on interparticle water in gypseous soil, an oven temperature of 35^o was adopted for drying samples. Summary of the results is presented in Table 5.

As depicted in Table 5 and in Fig. 11, the liquid limit (LL) was affected by calcium sulfate, as the LL increased after leaching. We also observed the highest increases of LL after leaching in sample G2, with 11.2%, and sample G6, with a 9.9% increase. Since the amount of gypsum decreased after leaching, the soil softened and its plasticity index (Pl) increased. Therefore, a significant change in plasticity was observed in the two samples, with the largest increase in gypsum content after leaching (G2 with 9.5% and G6 with 5.5% increase in PI).

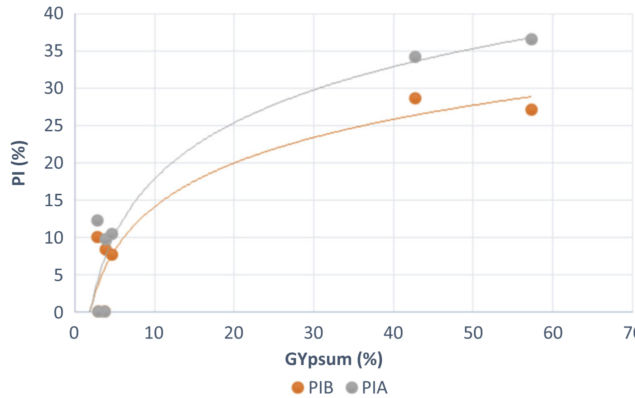

Fig. 11 Changes in Plasticity Index (PI) of all samples before (PIB) and after leaching (PIA)

Mechanical tests

a. Consolidation test

To evaluate the effects of leaching on the deformation (subsidence and swelling) of gypseous soils, a consolidation test was conducted according to ASTM D 2435-90. The unleached and leached samples were remolded with their natural specific gravity, which was calculated by the Pycnometer method, and then were placed in consolidation molds 49.70 mm in diameter and 20.60 mm in depth. The molds were then placed in a loading chamber filled with water for 24 h. After this period, one-dimensional volume changes in the samples were recorded and then the consolidation test was conducted. To determine the deformation of samples due to leaching in 24 h of saturation, no overload was placed on the samples and the only load was the upper plate (1 KPa).

Although samples G2 and G6 had the highest amount of gypsum and a large amount of swelling in the natural (unleached) state (swelling index = 0.85 and 0.68, respectively), they showed very little swelling after the leaching process, with values of 0.02 and 0.08. This showed that the swelling pressure was high in these two samples and the five-day leaching period was not enough to remove all of the gypsum from the samples (Table 6).

Table 5 Summary of the physical tests before and after leaching

No.		Before Leaching				After Leaching	
	Unified Soil classification	LL%	PL%	PI%	LL%	PL%	PI%
G1	SM	29	19	10	33	21	12
G2	SM	48	21	27	59	22	36
G3	ML	25	17	8	27	18	10
G4	SC	22	NP	NP	29	NP	NP
G5	SM	28	NP	NP	29	NP	NP
G6	ML	56	27	28	65	31	34
G7	CL-ML	27	19	7	30	20	10

Table 6 The changes in consolidation parameters before and after leaching for all samples

No.	Before Leaching					After Leaching				
	Void Ratio	Cc kPa	Cs kPa	Free Settlement %	Free Swell %	Void Ratio	Cc kPa	Cs kPa	Free Settlement %	Free Swell %
G1	0.525	24.2	27.8	2.840	-	0.595	28.6	11.8	0.120	-
G2	1.102	28.6	2.3	-	0.85	1.132	33.9	1.6	-	0.02
G3	0.558	24.3	1.8	1.38	-	0.567	26.9	1.6	0.018	-
G4	0.466	23.9	2.8	0.99	-	0.593	29.2	1.7	0.040	-
G5	1.522	19.3	5.3	1.400	-	1.524	21.9	2.4	0.510	-
G6	1.728	25.2	2.8	-	0.68	1.834	44.2	2.5	-	0.08
G7	1.232	24.3	2.3	0.360	-	1.322	31.6	2.0	0	-

Before leaching, as soon as the water was added, all samples (except for G2 and G6) showed large subsidence. This subsidence was reduced significantly after leaching, which might be due to the following reasons:

1. Since the amount of gypsum in these samples was much lower than samples G2 and G6, their subsidence process was dominant over the swelling.

2. In the 24 h of saturation, the gypsum in these samples was dissolved. Therefore, the unleached samples showed great subsidence while the leached samples, due to lower amounts of gypsum, had less subsidence.

The changes in consolidation parameters of all samples, before and after leaching, are shown in Table 6. The e-log p graph of sample G2 in both unleached and leached states is shown in Fig. 12. As depicted in the figure, all samples had large amountsof void spaces due to the presence of gypsum. These void spaces were increased by the leaching process, resulting in the increased compaction of the samples. This increase in compression can be associated to the disruption of gypsum cementing bonds due to leaching.

The pre-consolidation pressure (PC) of the G2 sample was 63.74 in the unleached and 98.06 kPa in the leached state. Based on the consolidation test, after leaching, the compression index of samples increased, whereas their swelling index decreased. For instance, after leaching, samples G2 and G6 had 5.3% and 19% increases in compression index and 31.6% and 41.4% decreases in swelling index, respectively.

b. Direct shear test

To evaluate shear strength parameters and the behavior of gypseous soils before and after leaching, a direct shear test was conducted on all samples according to ASTM D 3080–90, the results of which are summarized in Table 7. The shear parameters in sample G2 from the lowest confining pressure (σn = 150 kPa) to the highest confining pressure (σn = 550kpa) before and after leaching were measured and the results were plotted in Fig. 13.

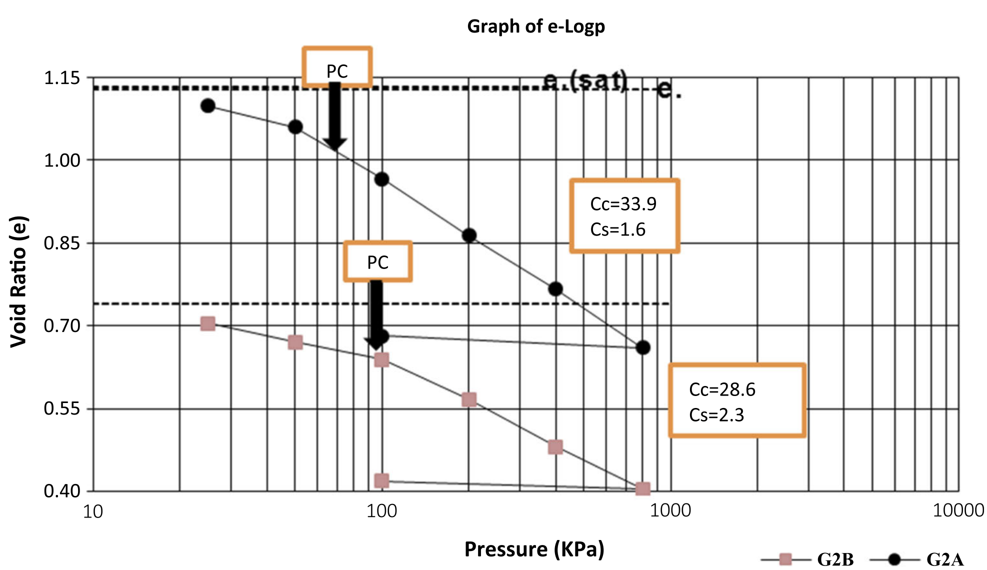

Fig. 12 The e-log p graph of sample G2 before (G2B) and after leaching (G2A)

Table 7 The shear strength parameters before and after leaching for all samples

No.	Before Leaching		After Leaching	
	C kPa	Deg.	C kPa	Deg.
G1	260	20.6	0	28.4
G2	170	41.2	50	42.8
G3	20	28.2	0	31.4
G4	210	33.2	0	40.8
G5	50	37.9	10	40.4
G6	60	26.1	40	26.4
G7	50	17.8	20	28.5

In all of the samples, cohesion (C) decreased and internal friction angle (φ) increased after leaching. The decrease in cohesion can be associated with the effect of water on the interparticle bonds and the solution of gypsum from the particle contact areas (Petrukhin and Arakelyan 1984). Furthermore, the reduction of pore spaces caused a rearrangement of soil particles and thus an increase of internal friction. IAs shear resistance is a function of vertical stress, loss of cohesion and the increase of internal friction could not be definitively attributed to the reduction of shear strength.

Conclusions

The objective of this study was to investigate the effects of high gypsum content on the chemical and geotechnical properties of soils and their changes throughout leaching. A case study in southern Mashhad, Iran, was conducted and soils were tested in the four major groups of hydraulic, physical, chemical and mechanical properties.

The five-day leaching process showed significant changes in chemical composition of these soils, especially on carbonates and TDS, which is representative of the disolved salts, including sulfates, in soils. The amount of free subsidence and swelling were measured before and after leaching, and the results indicated substantial decreases in permeability coefficients and strength parameters due to the loss of gypsum cementing bonds between soil particles. The main conclusions of this study include:

1. In the initial phase of leaching, while samples had large amounts of gypsum, TDS was at its maximum and the concentration of chlorine and calcium were increased. As the leaching progressed, all three parameters decreased and tended to a constant value.
2. The large sudden subsidence that was observed after adding water to unleached samples in the consolidation test was not due to the removal of gypsum, but rather a result of softening or disruption of gypsum bonds between soil particles.
3. In the first stages of leaching, the permeability coefficients of gypseous soils were high, then gradually decreased and tended to a constant value.
4. Saturation of gypseous soils removed the gypsum and resulted in the collapse of the soil and an increase in its compression. During leaching, the compression index (Cc) was increased, while the pre-consolidation pressure (Pc) and swelling index (Cs) were decreased.
5. During leaching, the shear strength decreased. This decrease was attributed to the loss of cohesion due to the removal of gypsum by leaching as well as to the increase of internal friction angle due to the increase in soil compression.

These results demonstrate a high susceptibility of structural failure in this and similar areas, and calls for extensive soil chemical and geotechnical tests and appropriate soil remediation and improvement processes to mitigate these risks.

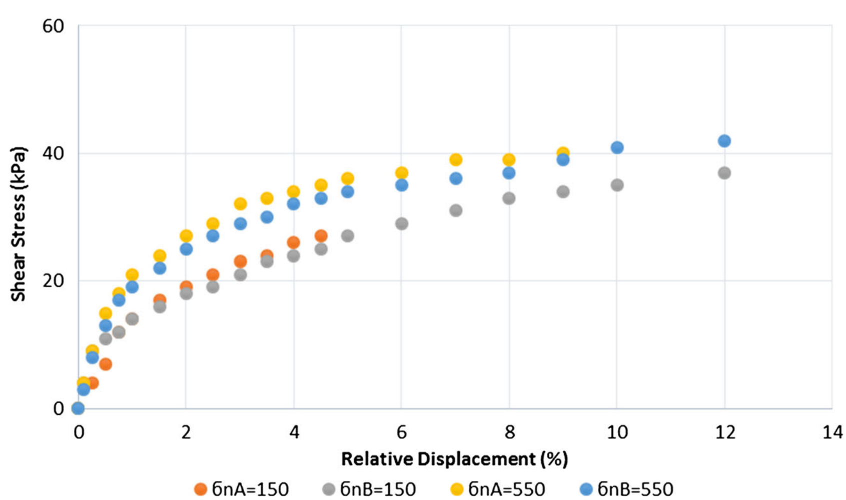

Fig. 13 Direct shear plot of sample G2 before (nB) and after leaching (nA)

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