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EFFECTS OF COPPER SULFATE CONTAMINATION ON THE GEOTECHNICAL BEHAVIOR OF CLAYEY SOILS

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ABSTRACT

In this research, the effects of contaminant copper sulfate ($CuSO_4$•$5H_2O$) on the chemical and engineering properties of cohesive soil are investigated. Intact soil samples are obtained from the site of the Al-Ahdab oil field in Iraq. The soil samples are contaminated artificially with three quantities of copper sulfate (100, 200, and 400 g). Each quantity of copper sulfate is dissolved in 10 liters of distilled water and added to the surface of disturbed intact soil samples and left soaked for 30 days. A set of laboratory tests is conducted on both intact and contaminated soil samples to determine the impacts of copper sulfate on the chemical and engineering properties of clayey soil samples. The copper sulfate leads to a decrease in the percentage of fines, Atterberg's limits, permeability, and optimum water content but leads to an increase in specific gravity and maximum dry density. As the concentration of copper sulfate in soil samples increases, the copper sulfate contamination leads to a decrease in the shear strength parameters, cohesion (c), and angle of internal friction (φ) but leads to an increase in the initial void ratio and the compression and recompression indexes.

Key words: Copper sulfate, soil contamination, clayey soil, geotechnical properties.

1. INTRODUCTION

Soil contamination due to heavy metals (HMs) is one of the main problems faced by the environment. Agricultural, industrial, and military activities are the main sources for the contamination due to HMs. There are two types of HMs. The first type of MHs is useful for the human metabolic system, but high concentrations of these HMs lead to negative effects on human health. The second type of HMs is not useful for the human metabolic system and may cause negative impacts even at low concentrations. Also, HMs have various effects on soil properties depending on factors such as the mobility and chemical activity of contaminants in the soil (Karkush *et al.* 2013; Uddin 2017). Cohesive soils are electrochemically active and can be influenced when the environment is contaminated by wastes. Adsorption characteristics, geotechnical properties, and chemical composition of soil are the main factors affecting the behavior of contaminant in the soil or groundwater (Karkush and Abdul Kareem 2017). In the literature, there was research investigating the impacts of different types of contaminants on the engineering characteristics of a soil. For instance, Ali (1999) and Khamehchiyan *et al.* (2007) investigated the impacts of oil contamination on the engineering properties of a soil. They concluded that contamination in soil can reduce the shear strength, hydraulic conductivity, maximum dry unit weight, optimum moisture content, and liquid and plastic limits. Karkush *et al.* (2013) investigated the impacts of different percentages of kerosene, NH_4OH, $Pb(NO_3)_2$, and $CuSO_4 \cdot 5H_2O$ on the engineering and chemical properties of a clayey soil. The results demonstrated that soil contamination can have diverse impacts on the engineering and chemical properties of a clayey soil.

Defo *et al.* (2016) investigated the relationship between the geochemical properties and the ability of soil to retain HMs (e.g., Pb and Cd). The retention ability for different soils ranges from 10% to 100% and depends on the soil properties and the HM type. Also, the organic matter content plays an important role in the retention ability, whereas the clay content, the value of pH, and the amount of cation exchangeable ions play minor roles. Chinade *et al.* (2017) investigated the effects of the infiltration of HM contamination in municipal solid waste on the soil shear strength. Unconfined compression tests were conducted on soil samples exposed to infiltration for various periods ranging from 7 to 120 days. The results demonstrated that the soil shear strength decreases with an increasing period of infiltration. Karkush and Altaher (2017) studied the impacts of total petroleum hydrocarbons (TPH) and demonstrated that TPH has significant effects on the engineering properties of a clayey soil. Karkush and Abdul Kareem (2017) investigated the impacts of different concentrations (10% and 20%) of medium fuel oil (MFO) on the engineering properties of a clayey soil. The results demonstrated that MFO has significant effects on the engineering properties of a clayey soil as well but has only slight effects on its chemical and physical properties.

In Iraq, there are several sites contaminated by HMs, so it is important to study the effects of these contaminants on the geotechnical properties of soils (UNEP 2005). The availability of intact soil samples is reduced due to the rapid urban expansion and industrial development. Although it is possible to utilize the contaminated soil samples in building foundations and road embankments, this requires the knowledge of their geotechnical properties (Shehzad *et al.* 2015). In the present study, the impacts of different concentrations of copper sulfate contaminant on the geotechnical properties of a clayey soil are investigated by conducting an intensive set of tests on the intact soil samples retrieved from the site of the Al-Ahadab oil field located in the southeast of Iraq.

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2. SOIL SAMPLES AND COPPER SULFATE

The intact soil samples, disturbed and undisturbed, are retrieved from the site of the Al-Ahadab oil field located in the southeast of Iraq. The GPS coordinates of the location of soil samples are (E = 569974, N = 359254). The soil samples are obtained from an open pit excavated to a depth of 3 m below the existing ground level (EGL). The intact soil is classified as silty clay with high plasticity (CH) according to the unified soil classification system (USCS). This type of clayey soil is sensitive to environmental changes, and its chemical reaction to contaminants is relatively high. Also, the clayey soil has a large specific surface area and a dynamic crystalline structure (Shehzad *et al.* 2015; Chandrasekaran and Ravisankar 2015). The impacts of different concentrations of copper sulfate on the chemical and engineering properties of this clayey soil are studied. The copper sulfate used in the current study has the following properties: the chemical formula is $CuSO_4 \cdot 5H_2O$, the solubility in water is 230.5 g/L, the density is 2.29 g/cm^3, and the molar weight is 249.68 g/mol.

3. PREPARATION OF CONTAMINATED SOILS

Three disturbed soil samples are placed in three plastic containers with tight covers, infiltrated by the copper sulfate solutions, and left for 30 days to allow full infiltration. The soil in each container weighs 15 kg, and the copper sulfate solution consists of copper sulfate and distilled water. The concentrations of copper sulfate in the soil samples are listed in Table 1. These concentrations are determined based on the ranges found in the literature as well as the observations obtained from our experiments. The first concentration of copper sulfate is 6666.67 ppm, which has slight effects on the geotechnical properties of the clayey soil. Therefore, two other concentrations higher than 6666.67 ppm are used in the next experiments. It is important to recognize between the impacts of contaminants on the environment and the impacts on the geotechnical properties of soil. Low concentrations of contaminants may affect the environment significantly but may not affect the geotechnical properties of soil. The soil specimens used in this work are designated with symbols given in Table 1. The distilled water is necessary to dissolve the copper sulfate. Sufficient water is necessary to submerge the soil sample and to provide an adequate water level above the soil surface (about 3 cm above) in order to allow contaminant to infiltrate into the deeper soil (Zhou 2004; Karkush *et al.* 2013). Figure 1 shows the sampling and preparation of the contaminated soil samples.

Table 1 Designation of soil samples and concentrations of copper sulfate

Symbol	Definition	Mass of copper sulfate (g)	Volume of distilled water (L)	Concentration (ppm)
H0	Undisturbed intact soil sample	0	0	0
H0R	Remolded intact soil sample	0	0	0
H1	Remolded contaminated soil sample	100	10	6666.66
H2	Remolded contaminated soil sample	200	10	13333.33
H3	Remolded contaminated soil sample	400	10	26666.67

Excavation in the field　　Preparing contaminant

Contamination of soil sample　　Processing of soil contamination for 30 days

Fig. 1 Sampling and preparation of contaminated soil samples

4. RESULTS AND DISCUSSION

The results of tests conducted on the soil samples are divided into three main parts: results of chemical tests, results of physical tests, and results of mechanical tests.

4.1 Chemical Properties of Soil Samples

The results of chemical tests are given in Table 2. The trioxide sulfate (SO_3), chloride (Cl^{-1}), organic matter (OMC), total soluble salts (TSS), and gypsum contents are higher in contaminated soil samples, while the pH value of soil is affected slightly by the contamination. The contaminant contains sulfate in its chemical composition, therefore, the percentage of SO_3 and gypsum content will increase in the contaminated soil samples. Also, the increase in chloride content may be attributed to the chemical reaction between the compounds of contaminant and the mineral compounds of the soil samples which leads to the generation of Cl^{-1}. X-ray diffraction tests are carried out on two soil samples H0 (intact) and H2 (contains approximately the average concentration of copper sulfate) to study the impacts of copper sulfate on the mineral composition of soil samples. The results of x-ray diffraction tests are given in Table 3. The copper sulfate causes the decrease of $CaCO_3$ (CaO) and the increase of quartz and clay minerals percentages. The geochemical behavior of soil affected the absorption of contaminants, so it is important to know the chemical composition of the intact soil. The main geochemical parameters are organic matter content, cation exchange capacity (CEC), pH value, and type of clay minerals (Defo *et al.* 2016).

Table 2 Chemical properties of tested soil samples

Soil sample	SO_3 (%)	Cl^{-1} (%)	SiO_2 (%)	CaO (%)	OMC (%)	Gypsum (%)	TSS (%)	pH (value)
	ASTM D516	ASTM D512 A	ASTM D859	ASTM D4373	ASTM D2974	ASTM D518	ASTM D5907	ASTM D4972
H0	0.036	0.5442	32.37	18.31	0.620	0.040	3.60	7.6
H1	0.620	0.836	32.58	17.93	0.610	0.043	3.53	7.5
H2	0.326	0.758	32.49	17.67	1.103	2.400	4.11	7.4
H3	0.293	1.187	31.64	18.11	0.656	3.560	6.92	7.3

Table 3 Results of x-ray diffraction tests

Soil sample	Non-clay minerals (%)					Clay minerals (%)
	$CaCO_3$	Quartz	Halite	Dolomite	Dialuminium	
H0	46.0	25.9	0.0	11.7	12.0	4.4
H2	37.1	45.9	6.0	5.4	0.0	5.6

4.2 Physical Properties of Soil Samples

The physical properties of tested soil samples are given in Table 4 and Fig. 2. The oxygen atoms of contaminant will create covalent bonds with the negatively charged clay minerals. The results demonstrated that the presence of copper sulfate in the soil samples tended to increase the percentage of particles for those with size larger than 0.005 mm (Karkush *et al.* 2013). $CaCO_3$ and OMC are the main compounds in providing the cementation of soil particles and are responsible for the sticking of the soil particles and stabilizing of the soil aggregate (Craig 2004). The electro negativity is the main factor controlling the metal adsorption capability of soil. Copper has a greater tendency to be adsorbed

Table 4 Physical properties of tested soil samples

Soil sample	Sand (%)	Silt (%)	Clay (%)	LL (%)	PL (%)	PI (%)	G_s	$\rho_{d,\,max}$ (g/cm^3)	ω_{opt} (%)	k ($\times 10^{-8}$) (cm/sec)
	ASTM D422			ASTM D4318			ASTM D854	ASTM D 698		ASTM D2434
H0	0.02	25.98	74	55	27	28	2.74	1.678	21.6	3.22
H1	0.10	34.90	65	50	27	23	2.77	1.692	21.4	1.63
H2	0.20	36.80	63	48	27	21	2.79	1.766	15.0	1.16
H3	0.57	47.43	52	46	23	23	2.82	1.800	14.5	1.06

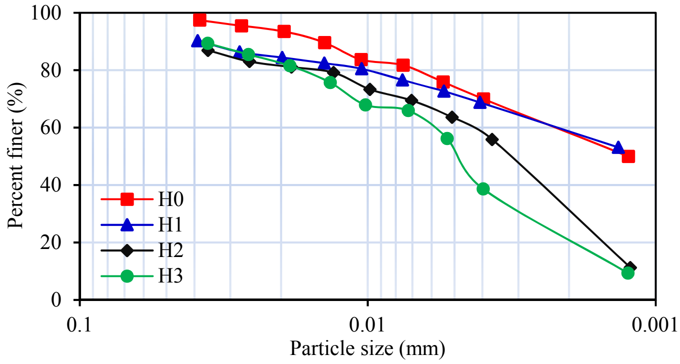

Fig. 2 Particle-size distribution curves of tested soil samples

on the surfaces of clay particles than other types of heavy metals, leading to stronger cation connections among the particles of clayey soil. As a result, the structure of the soil aggregate is more stable.

Table 4 indicated that the contamination of soil with copper sulfate causes reduction of Atterberg's limits of soil samples. There are several factors affecting the liquid and plastic limits. Reduction of clay content in the contaminated soil samples leads to the reduction of Atterberg's limits. And the coating of fine particles with copper sulfate will increase the surface area required for permeating. Also, the dissolution of salts may reduce the thickness of diffused double layer and flocculation ability of the clay particles (Sasikumar 2016). The specific gravity (G_s) increases with the increase of copper sulfate concentration in the soil samples because the density of copper sulfate is higher than the density of the soil (Karkush *et al.* 2013). According to the results of falling head tests, the permeability of contaminated soil samples is smaller than that of intact soil. The permeability of soil sample H1 decreased by 49% and it drops more with the increase of copper sulfate content in soil. The contamination of soil with copper sulfate causes dissolution and precipitation of soluble salts in the voids between the particles which leads to a reduction of the connected voids responsible for the permeability of soil (Khan *et al.* 2016).

The compaction curves of tested soil samples are shown in Fig. 3. Increasing the content of copper sulfate in soil causes obvious shifting of the compaction curves and the increase of maximum dry density. The optimum moisture content (ω_{opt}) also decreases as a result. The decrease in optimum moisture content may be resulted from the reduction of surface area required for permeating, which in turn causes an increase in the maximum dry density. Also, the contact points between the clay particles are covered by copper sulfate, so the engineering performance of soil has changed and the tendency of clay particles to dissociate with water molecules is decreased. From the observation, the copper sulfate

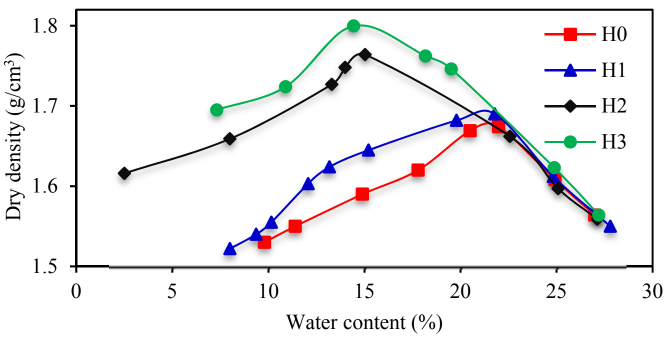

Fig. 3 Compaction curves of tested soil samples

contaminated clayey soil will need more time or compaction effort to reach the desired maximum dry density (Ota 2013).

4.3 Mechanical Properties of Soil Samples

The impacts of copper sulfate on the compressibility and shear strength of soil are investigated by a series of 1-D consolidation test and shear strength tests.

4.3.1 Compressibility Properties

Consolidation is a well known phenomenon that the pore water is slowly squeezed out of soil aggregate under an applied pressure (Head 1994). The main parameters from an oedometer test (ASTM D2435) are the initial void ratio (e_o), recompression index (C_r), compression index (C_c), preconsolidation pressure (P_c), and coefficient of consolidation (C_v). These parameters are listed in Table 5 and the test results are shown in Fig. 4. The results of 1-D consolidation tests showed a significant decrease in the coefficient of consolidation with an increasing content of copper sulfate in the tested samples. This decrease of C_v may be attributed to the decrease in permeability of copper sulfate contaminated soil samples. Also, the results showed that as the initial void ratio increased, the compression and recompression indexes also increased. The increase in C_c and C_r may be resulted from the presence of copper sulfate in the soil pores which leads to the sliding of soil particles. Changes in the molecule charge and the nature of the pore fluid may also impact the cation adsorption ability on the particles surface (Grim 1953; Karkush and Altaher 2017).

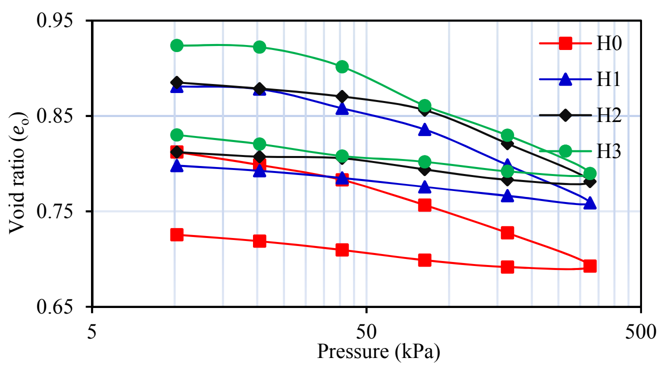

Fig. 4 Variation of void ratio versus pressure of tested soil samples (1-D consolidation test results)

Table 5 Results of 1-D consolidation tests

Soil samples	e_o	C_c	C_r	P_c (kPa)	m_v (m²/kN)	C_v (cm²/sec)
H0	0.816	0.100	0.033	69.0	0.00020	0.00054
H1	0.881	0.123	0.033	45.0	0.00027	0.00018
H2	0.895	0.143	0.047	69.0	0.00050	0.00013
H3	0.893	0.125	0.034	33.0	0.00046	0.00010

4.3.2 Shear Strength of Soil

The shear strength parameters of soil are important in evaluating the bearing capacity of soil and stability of slope.

• Direct Shear Test (DST)

Direct shear tests were conducted to obtain two shear strength parameters, which are the cohesion (c) and angle of internal friction (ϕ). The results listed in Table 6 indicated a significant reduction in c and ϕ of the contaminated soils, which is perhaps resulted from the decreasing in friction and bonding between the particles of the contaminated soil mass. The copper sulfate contaminant infiltrates the particles of soil and forms a thin layer coating around the soil particles. This mechanism retards the cohesive forces between the molecules that are responsible for the bondage of the cohesive soil particles (Oyegbile and Ayininuola 2013). Karkush *et al.* (2013) showed that the cohesion of copper sulfate contaminated soil samples decreased by 16.9% ~ 58.5%. While in the present study, the decrease in cohesion ranged from 50.9% to 92.6%. This difference may be attributed to the variation of organic matter content and content of fine particles.

Table 6 Results of shear strength tests

Soil sample	DST ASTM D3080		UCT ASTM D2166			UUT ASTM D2895-95
	c (kPa)	ϕ (°)	ε_a (%)	q_u (kPa)	c_u (kPa)	c_u (kPa)
H0	108	13.4	11.05	161	81	125
H0R	–	–	15.70	143	72	105
H1	53	5.0	9.276	131	66	95
H2	18	7.8	18.75	58	29	26
H3	8	3.4	17.039	38	19	24

• Unconfined Compression Test (UCT)

The UCTs were carried out on two types of intact soil (undisturbed and remolded) to investigate the effect of sampling disturbance on the shear strength of soil. In addition, the contaminated soil samples were remolded according to the field density and natural water content to investigate the influences of copper sulfate on the cohesion between the particles of soil. The stress-strain relationships of the tested soil samples are given in Fig. 5 and a summary of the UCT results are given in Table 6. The sensitivity of soil (St) can be calculated using Eq. (1). The sensitivity of soil is about 1.125 and the soil sample can be classified as slightly or low sensitive clays (Skempton and Northey 1952; Rosenqvist 1953). The copper sulfate contaminant causes reduction of the soil cohesion. This reduction may be attributed to the coating on the surface of soil particles with copper sulfate that causes a reduction in bonding and further sliding between the particles.

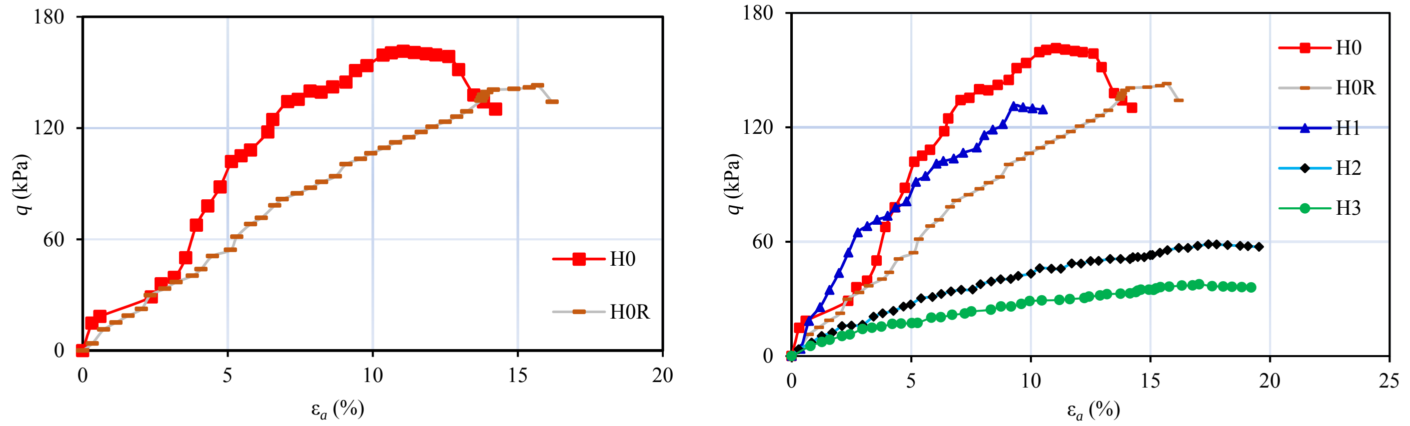

Fig. 5 Stress-strain relationship of unconfined compression tests

$$St = \frac{\text{Undrained shear strength of undisturbed soil sample}}{\text{Undrained shear strength of remolded soil sample}} \quad (1)$$

• Unconsolidated Undrained Triaxial Test (UUT)

A unconsolidated undrained triaxial test consists of several stages. In the first stage, saturation of the soil sample must be completed. In the second stage, the cell pressure (σ_3) is applied and in the third stage, an incremental deviator stress is applied until the failure of soil sample. Cohesion between particles of soil is highly influenced when the contaminant enters the soil matrix and breaks the bonds between soil particles. The variation of deviator stress versus axial strain obtained from tested soil samples are shown in Fig. 6. Mohr circles for the tested soil samples are given in Fig. 7. In this study, the effects of copper sulfate on the shear strength of silty clay are similar to that obtained by Karkush *et al.* (2013). Both studies found this contaminant leads to the decrease of the soil cohesion.

5. CONCLUSIONS

The copper sulfate contaminant has significant impacts on the characteristics of tested soil samples (chemical, physical, and mechanical). The level of impact depends on the concentration and type of the contaminant as well as the type of soil. The geotechnical properties of soil are negatively influenced when the concentration of contaminant increases. As the content of copper sulfate in soil increased, the percentage of particles with particle size less than 0.005 mm, optimum moisture content and permeability all decreased. However, the copper sulfate contaminant causes the increase in specific gravity and maximum dry density of soil. The coefficient of consolidation decreased in contaminated soil samples, while the initial void ratio, compression and recompression indexes, and coefficient of volume change all increased. The impacts of copper sulfate on C_c, C_r, and m_v in soil sample H3 subsided, but the values of these parameters remained higher than the corresponding values of the intact soil. The shear strength parameters are significantly decreased in contaminated soil samples and continue to decrease with the increase of copper sulfate concentration in the soil samples.

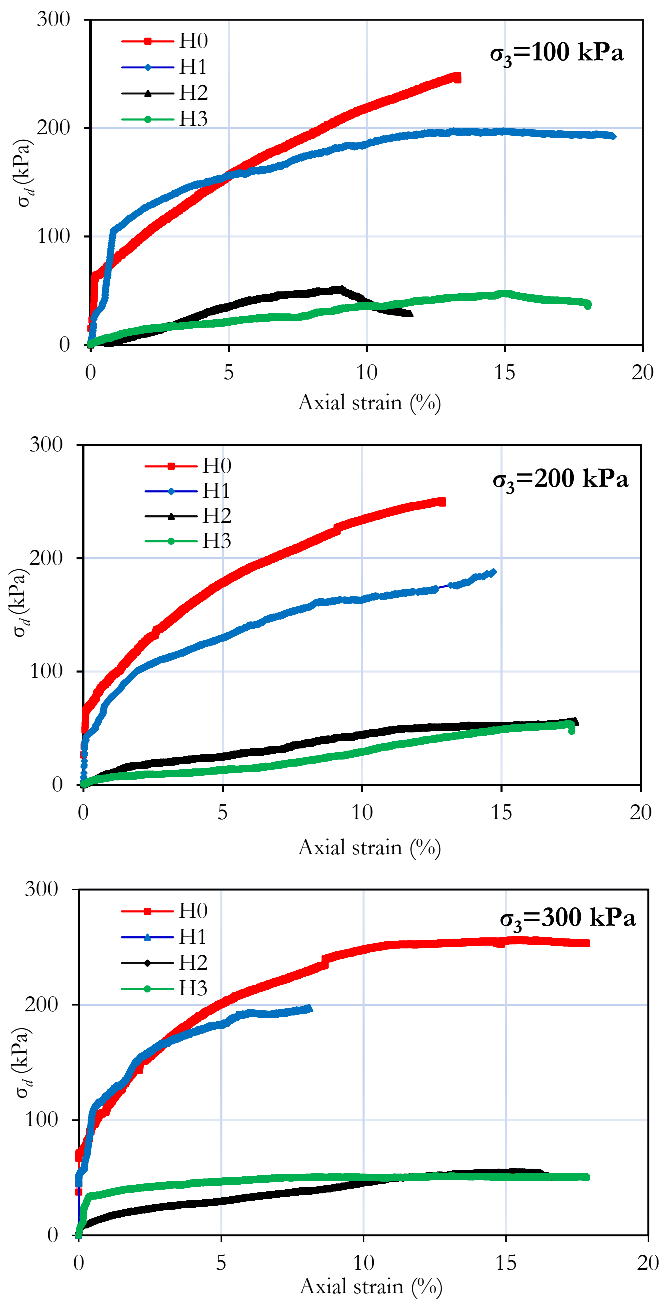

Fig. 6 Results of unconsolidated undrained triaxial tests

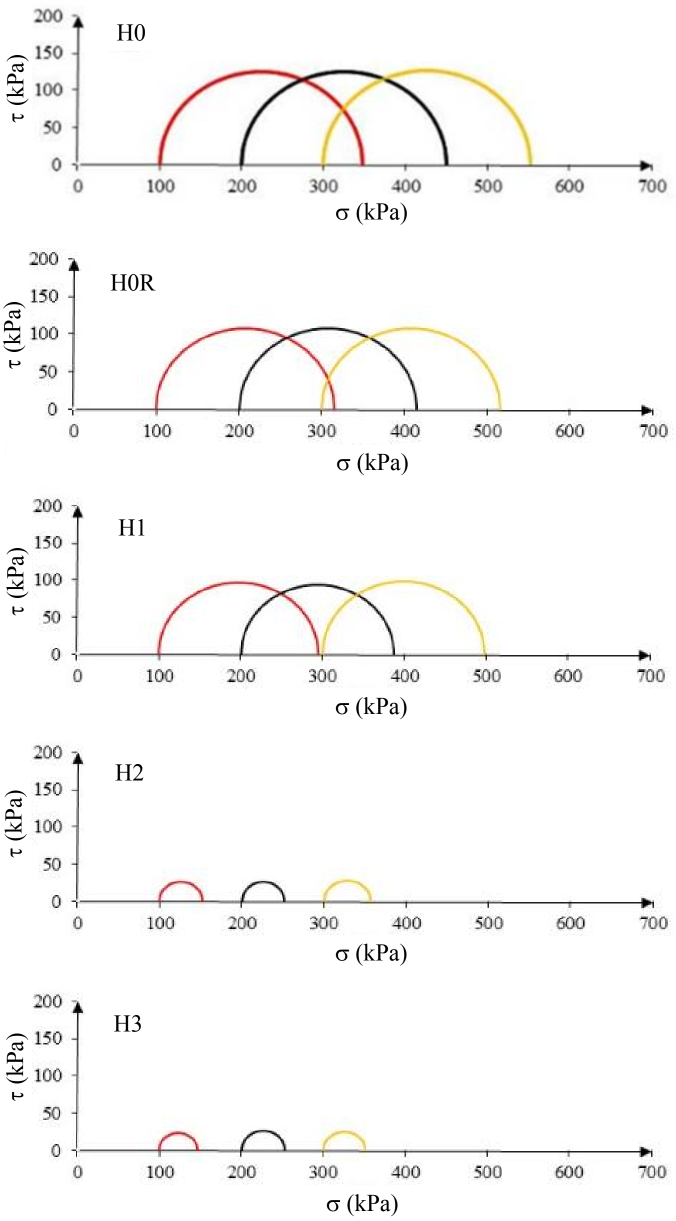

Fig. 7 Mohr circles of tested soil samples

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