Determination of Saline Soils Specific Gravity

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ABSTRACT

The existence of salts as part of the solid phase of the soil or dissolved within the pore fluid may cause significant errors in the values of specific gravity of such soils by using conventional determination methods. Errors may arise from effects of wrong measurements of weights or volumes that take place due to dissolution of the salt during testing, precipitation during drying or dehydration of the crystals of certain salts such as gypsum.

To overcome this confusion, the standard procedure for specific gravity determination is reconsidered and the calculation methods are reanalyzed. Suggestions for a more adequate procedure for gypseous or other types of saline soils are presented and corrections required for computations are derived.

KEYWORDS: Specific gravity, Saline soils, Gypseous soils, Soil testing.

INTRODUCTION

In many regions of the world, especially in arid and semiarid zones, large areas are covered with soils containing water-soluble salts. These saline soil conditions tend to prevail in many regions of the Middle East countries (Al-Amoudi and Abduljauwad, 1995; Al-Amoudi, 2001; Bilsel, 2003, 2004). Construction on these soils is quite problematic especially in regions of dry and hot climates due to the severe effect of salt corrosion on structural elements (Rongzhen et al., 2006) and due to its high collapse potential and low-bearing strength (Al-Amoudi, 1995; 2001).

Eexperience with gypseous and marine soils showed that many errors have risen when using conventional routine tests in soil engineering. Consequently, these errors have led to erroneous estimates in basic soil properties such as the void ratio, water content, degree of saturation and parameters such as the compression index as well as soil phase relations (Noory, 1984). These errors are mainly due to the changes in soil solids volume or weight which have to remain constant and unchanged in most classical theories of soil engineering. Changes in the weight or the volume of soil solids are well expected as gypseous and marine soils may undergo dissolution, precipitation or dehydration during testing which usually involves water percolation in a way or another. No evidence is required to prove that the problem includes other saline soils. In fact, some test results for cases with salts other than gypsum may be more erroneous. The effects of such errors on design parameters and assessment of soil behavior would sometimes be very significant.

As there are no specifications or standard procedures

for engineering tests on saline soils, these errors have been passed over without major attention. In this paper, the attention is drawn to the errors in determination of specific gravity of saline soils, and the ways to overcome this problem are presented.

The specific gravity of a soil is usually determined through the knowledge of the weight of soil solid constituents and their volume. The test is carried out according to a standard testing procedure published in several codes such as the ASTM Standard Method of Test for Specific Gravity of Soils (D854-02), the BS1377-1990, Test6 and the Determination of the Specific Gravity of Soil Particles in addition to other standards. All the standards agree on the use of the weight of the displaced water to determine the volume of the solids. Such approach is well discussed in many well known references such as (Lambe, 1951) or other text books.

In short, the conventional specific gravity test consists of weighing an empty standard pycnometer or a volumetric flask, filling it with a standard fluid (used to be distilled de-aired water) up to a mark placed at the top part of the flask and re-weighing it. This enables computing the volume of the flask exactly.

In the second step, an oven-dried soil sample is weighed and added to the empty flask (alternatively, the weight may be taken after drying at the end of the test). The oven drying is usually done at 105-110° C. The flask containing the soil is filled with water up to the standard volume mark. Then the volume of the soil solids may be determined as being the volume of the water displaced. Then the specific gravity of the soil will be the calculated density of the solids divided by the density of distilled water at 4 ° C.

Effects of Salts on the Specific Gravity Test Results

Through an examination of the steps of the conventional test usually carried out to determine the specific gravity of a soil, it may be observed that there are four sources of potential errors in the result:

A portion of the salt will be dissolved in the distilled water when added to the flask containing the soil.

The calculated specific gravity does not express the actual situation of a water saturated soil, where the pore water is saline and this dissolved salt will start precipitating during the preparation of the soil sample. Subsequently, the weight and volume of the precipitated soil will be added to that of the original soil solids.

Some salts undergo dehydration and lose part or all of their crystallization water molecules when subject to heating at 105-110 °C.

In nature, gypsum is the principal salt that is affected by dehydration. Gypsum loses three quarters of its crystallization water at about 70 °C to form bassanite and all of the crystallization water at about 100 °C to form anhydrite that definitely has a different specific gravity (Weast, 1974).

If the original soil contains bassanite or anhydrite, adding water causes re-hydration and the volume of these compounds is increased. Therefore, the obtained specific gravity would not represent the correct value.

In order to overcome the problem of dissolution, some engineers use kerosene or white spirit instead of water to insure that the salts would not be dissolved. This will not prevent the second problem stated above. In addition, the specific gravity of kerosene or white spirit cannot be insured to stay constant with long periods of storage or with high temperature changes which is the situation in most laboratories in the Middle East countries.

In order to prevent dehydration of gypsum, most of soil laboratories prefer drying of soil samples at oven temperatures of less than 100°C. This is achieved by following the British Standards by using a temperature of 80°C or by following the ASTM with a temperature of 60°C.

Due to the fact that gypsum starts to dehydrate at a lower temperature, it is advised that drying of soil samples should be carried out at a safe temperature of 45°C (Al-Mufty and Nashat, 2000). The latter temperature has been adopted in many laboratories in the Middle East countries (i.e., Iraq) during the past five years.

Correction of the Conventional Specific Gravity Test

Through a conventional test, the specific gravity of a

soil is usually found according to the following equation:

$$G = \frac{M_s G_T}{M_{fw} - M_{fws} + M_s} \tag{1}$$

It may be noticed that the mass of the flask, M_f, is not show in this equation because its terms have opposite signs and eventually they are canceled out (Lambe, 1951). In order to correct this equation for the case of a saline soil that has a salt content χ, which is defined as the weight of the salt divided by the total weight of soil solids, several steps are required. First, the concentration of the salt, C, defined as the weight of the dissolved salt in a unit volume of the solution, should be known. This concentration should not exceed the solubility of salt (i.e., $C \le s$). Accordingly, the corrected equation to compute the specific gravity should be derived as follows:

$$G * \rho_{w_{4°C}} = \frac{M_s}{V_s} = \frac{M_s}{V_f - V'_w(1 - \dfrac{C}{\rho_{salt}})} \tag{2}$$

with the fact that

$$V'_w = \frac{M_w}{\rho'_{w_T}} = \frac{M'_{fws} - M_f - (M_s - CV'_w)}{\rho'_{w_T}} =$$

$$\frac{M'_{fws} - M_f - M_s}{\rho'_{w_T}(1 - \dfrac{C}{\rho'_{w_T}})} \tag{3}$$

and by substituting equation (3) in equation (2) with V_f is replaced by the corresponding mass of water, that is:

$$V_f = \frac{M'_{fw} - M_f}{\rho'_{w_T}} \tag{4}$$

thus, the following equation is obtained:

$$G * \rho_{w_{4°C}} = \frac{M_s}{\dfrac{M'_{fw} - M_f}{\rho'_{w_T}} - \dfrac{M'_{fws} - M_f - M_s}{\rho'_{w_T}(1 - \dfrac{C}{\rho'_{w_T}})}(1 - \dfrac{C}{\rho_{salt}})} \tag{5}$$

this equation can be written, after proper rearrangement for these terms, as:

$$G = \frac{M_s \; \rho'_{w_T} / \rho_{w_{4°C}}}{M'_{fw} - M_f - (M'_{fws} - M_f - M_s)\dfrac{(\rho_{salt} - C)\rho'_{w_T}}{(\rho'_{w_T} - C)\rho_{salt}}} \tag{6}$$

It may be noticed that if $C = 0$ then equation (6) turns back to its original form as given in equation (1). In all cases, the knowledge of the value of C is essential, which can be estimated by drying a fixed amount of the solution at oven temperature of 45°C. Value of the concentration C will be the mass of the precipitated salt (i.e., the salt phase that is stable at this temperature) divided by the volume of the solution. Concentration of the salt may be also measured through the weight ratio, m, which is defined as:

$$m = \frac{M_{salt}}{M_{water}} = \frac{M_{salt}}{M_{solution} - M_{salt}} \tag{7}$$

thus, the concentration in terms of C will be:

$$C = \frac{m}{1 + m} \rho'_{w_T} \tag{8}$$

and if the volume of the solution is assumed equal to the volume of the water, the concentration C may be well approximated by $C \approx m\rho_{w_T}$ which is fair to be used for anhydrous salt solutions.

The specific gravity of a soil is usually based on the density of distilled water taken at 4 °C. If it is required to base the specific gravity on a different temperature, the obtained specific gravity value, from equation (6), should be divided by the density of water at that temperature. The density of water samples that are usually encountered in most soil laboratories, at various degrees of temperatures, are listed in Table 1.

To determine M'_{fw}, a solution should be prepared similar to that obtained when water is added to the pycnometer and the soil. For instance, a solution that is formed when water is added to a soil sample of 100 g in a 250 cm³ pycnometer, may be proportioned by adding water to a 200 g sample placed in a 500 cm³ flask. The solution is then filtered to the 250 cm³ flask, empty and clean, and weighed. The same solution may be used to determine the concentration C.

The other problem encountered is how to determine the density of the solution ρ'_{w_T}. This may be done by weighing the flask, filled with distilled water, at the same temperature T. That is:

$$\rho'_{w_T} = \frac{M'_{fw} - M_f}{M_{fw} - M_f} \rho_{w_T} \tag{9}$$

In practice, controlling the temperature is rather difficult. Thus, plotting calibration curves is preferable. The weight of the volumetric flask is recorded at different temperatures, then it is initially filled with water and next it is filled with the solution. These two curves are used to determine M_{fw} and M'_{fw} at the same temperature T at which M'_{fws} is taken, then it is converted into mass values. An approximate value for the density of the solution, assuming that the volume is unchanged, may be calculated as:

$$\rho'_{w_T} = \rho_{w_T} + \alpha C_a \tag{10}$$

where α is a factor that depends on the valence of the cation and anion of the salt. If the salt is composed of only monovalent ions, such as NaCl, α may be equal to 0.68. For salts with a monovalent ion united with a divalent ion, such as $CaCl_2$ or $NaSO_4$, α may be equal to 0.85. If both ions are divalent, such as $MgSO_4$, α may be taken as 1.0. These figures are chosen according to the experience of the lab technician.

However, it is worth remembering that various types of salts might be present within the soil, but the most frequent and significantly soluble types are listed in Table 2. These salts have high solubility relative to the carbonates. Carbonate minerals are very rare, except those of calcium such as calcite, aragonite and dolomite but these have very low solubility and their effect on the test results is negligible. On the other hand, gypsum is the most widely spread sulfate in the soil. Although it is less soluble than the other salts listed in the table, its effect on soil behavior is significant, much more than the calcite. The low solubility of gypsum prevents it from being washed out of the soil, and the pore water is usually saturated with calcium sulfate in gypseous soils. During

the specific gravity test, it is expected that the water used in the test will be saturated by gypsum even for soils of low gypsum content; while other soluble salts cannot fully saturate the solution unless the salt content is high enough compared to the amount of water available.

The density of saturated gypsum solution at different temperatures is given in Table 3. The density of solution of the other salts should be known for the existing concentration. Table 4 presents the solution densities corresponding to a wide range of concentration for these salts but only at 20 °C. For other temperatures, the value may be corrected by multiplying it with the ratio $\rho_{w_T} / \rho_{w_{20°C}}$ as a good approximation. Values for other salts may be found in Weast (1974). It should be noted that the concentration in Table (4) is referred to as the percentage of the anhydrous phase of the salt in solution, denoted by A. The concentration C of the hydrous phase is calculated from:

$$C = C_a * \frac{M}{M - 18.01\varepsilon} \tag{11}$$

where $C_a = A * \rho_{sol}$ is the concentration of the anhydrous phase of the salt as the weight dissolved in a unit volume of the solution. So, to use the table properly, an additional column should be prepared for each salt to tabulate down the concentration values in the required style. Example (1) explains the application of the correction steps by use of equations only. Example (2) depicts the use of the additional laboratory measurements suggested above. The error in specific gravity values obtained in conventional procedure may reach 5% or even more depending on the soil water ratio, salt content and salt type.

In the case of gypseous soils with negligible content of other salts, the concentration will approach the solubility. The error will increase as the ratio of soil weight to the volume of the flask decreases. For a soil sample of 50 g and a volumetric flask of 500 cm³, the error will be about 1.5% to 2%, see example (3). The error may decrease to about 0.5% if the soil mass used is taken as 100 g and the flask volume is chosen as 250 cm³.

The existence of other salts may increase or decrease

the solubility of gypsum. Such effect should be taken into consideration when assuming the concentration.

According to equation (6), the density of the salt is required. If only a single salt exists, the salt density may be taken from Table 2. When a combination of salts exists, a harmonic mean should be calculated for ρ_{salt} as follows:

$$\rho_{salt} = \frac{\Sigma C_i}{\Sigma \dfrac{C_i}{\rho_i}} \tag{12}$$

where $\rho_i = \rho_1, \rho_2, \rho_3, ...$ are the densities of the salts and $C_i = C_1, C_2, C_3,...$ are the concentrations of these salts in the solution, respectively.

The Use of Kerosene

It is clear that the correction required for the specific gravity for saline soils is rather difficult, especially when different salts exist together. Some prefer the use of kerosene or white spirit instead of water. This requires the pre-knowledge of the specific gravity of the fluid used and its variation with temperature. In fact, a proposed alternative in ASTM D854-72 is to use kerosene. This may face two problems. The first is that the compounds of the fluid may alter during heating, vacuum or prolonged storage. The second is that the variation of the specific gravity of the alternative fluid may not be precise or usually not available. That is why it is preferred to measure and record the weights at the standard temperature at which the specific gravity of the alternative fluid is exactly supplied. It is somewhat difficult to keep the temperature constant during the test at a specific value. Anyhow, if this is done, the specific gravity may be calculated from the following equation:

$$G = \frac{M_s \ \rho_{k_{T°C}} / \rho_{w_{4°C}}}{\left(M_{bk} - M_{bks}\right)_{T°C} + M_s} \tag{13}$$

When the salt is hydrous and may lose the hydration water or part of it at 45 °C during the preparation of the sample, the use of kerosene is not suitable to overcome this problem. Further correction is needed as will be shown later.

Effect of Salinity of Pore Water

The problem of determination of a correct value for the specific gravity of a saline soil could not be fully overcome by the correction of the procedure or replacing water by another non-solvent fluid. There arises another source of error that is usually ignored in usual soil testing although it may be significant in all soils with saline pore water. Some soils do not contain salts themselves but the ground water may be salty. This may lead to significant errors in the determination of water content and void ratio in addition, of course, to the specific gravity. In a previous work (Al-Mufty, 1997) the author presented a method to correct the water content and the void ratio of soils containing saline pore water. The suggested correction for the water content is briefly explained here.

The water content of a soil is usually determined as:

$$w = \frac{M_{wet} - M_{dry}}{M_{dry}} \tag{14}$$

with oven temperature maintained at 105-110°C for 24 hours. Here, 45°C is adopted for drying until the weight stabilizes.

It may be noticed that if the pore water is saline, the drying causes precipitation of the salt and its weight will be added to the weight of the soil solids instead of being part of the pore fluid. This means that the measured water content will be:

$$w_{meas} = \frac{M_{water}}{M_{solids} + M_{salt}} \tag{15}$$

while the correct water content should be:

$$w_{corr} = \frac{M_{water} + M_{salt}}{M_{solids}} = \frac{M_{fluid}}{M_{solids}} \tag{16}$$

A correction for the measured water content may be obtained as follows:

$$w_{corr} = F w_{meas} \tag{17}$$

where F is a correction factor:

$$F = \frac{1 + m}{1 - m w_{meas}} \tag{18}$$

The value of F is plotted for different percentages of m in Figure 1. The void ratio is also affected. If the volume of the solution is assumed equal to the volume of the water and referring to the approximation of equation (8), a more correct void ratio is computed as:

$$e_{corr} = \frac{G_{corr} w_{corr}}{S(G_T + C/\gamma_{w_{4°C}})} \approx \frac{G_{corr} w_{corr}}{SG_T(1+m)} \qquad (19)$$

It may be noticed that if there is no salt, $m = 0$, and $T = 4°C$, the well known relation, $Gw = Se$, is obtained.

The existence of salt leads to incorrect measurement of the specific gravity as the precipitated salt from the evaporation of the saline pore water will add to the weight of the soil solids; i.e., the measured specific gravity will not be for the original soil solids as it should be. The correct specific gravity can be found starting from the definition of the incorrect (conventionally measured) one:

$$G_{meas} = \frac{M_{solids} + M_{salt}}{(V_{solids} + V_{salt})\rho_{w_{4°C}}} \qquad (20)$$

or

$$G_{meas} * \rho_{w_{4°C}} = \frac{G_{corr} * \rho_{w_{4°C}} + \dfrac{mM_{water}}{V_{solids}}}{1 + \dfrac{mM_{water}}{\rho_{salt}V_{solids}}} \qquad (21)$$

Substituting

$$\frac{mM_{water}}{\rho_{salt}V_{solids}} = \frac{mw_{meas}(M_{solids} + M_{salt})}{V_{solids}} \qquad (22)$$

and rearranging, the following is obtained:

$$G_{meas} * \rho_{w_{4°C}} = \frac{G_{corr} * \rho_{w_{4°C}} + \dfrac{G_{corr} * \rho_{w_{4°C}} mw_{meas}}{1 - mw_{meas}}}{1 + \dfrac{G_{corr} * \rho_{w_{4°C}} mw_{meas}}{\rho_{salt}(1 - mw_{meas})}} \qquad (23)$$

Simplifying and rearranging again, the correct specific gravity will be:

$$G_{corr} = \frac{G_{meas}G_{salt}(1 - mw_{meas})}{G_{salt} - G_{meas}\,mw_{meas}} \qquad (24)$$

If the specific gravity of the salt is close to that of the soil solids, the error becomes negligible. The error in the specific gravity increases as the salinity of pore water increases, the difference between the specific gravity of the salt and that of the soil solids increases or the water content increases. In soils with slightly brackish ground water, the error is very small. For example, a soil with a measured specific gravity of 2.6, a measured water content of 40%, a salt percentage $m = 0.01$ (approximately 10000 ppm) and a salt specific gravity of 2, equation (24) will yield a correct specific gravity of 2.603. The effect of increasing salinity on the result may be simply detected. The calculated correct specific gravity for the same soil becomes 2.67 for a salt percentage $m = 0.2$ which is normal in highly saline soils such as sabkha soils.

The concentration represented as m or C should be predetermined to apply the above equations properly. An amount of pore water solution should be obtained. This may be done by squeezing a soil sample of a suitable amount using a Rowe cell type consolidometer or expelling some of the pore water using the centrifuge techniques. The concentration is then found by evaporation of water or through electrical conductivity of the solution. Both m and C represent the salt phase that is expected to precipitate after oven drying whether at 45°C or 105°C.

Separation of Salt before Testing

In a previous paper (Al-Mufty, 1997), the separation of the salt from the soil solids was suggested as a solution to the problem of determination of specific gravity of a saline soil that may be subject to dissolution and leaching in the future. It is recommended to dissolve all the salt present by mixing the soil with a sufficient amount of water. The specific gravity test is then performed on the soil free of salt, following the conventional test procedure. If χ represents the salt content, M_s is the mass of soil solids including the salt obtained at 45°C and s is the solubility of the salt, then the required amount of water should be greater than $\chi M_s / s$. If the specific gravity of the salt is known, the average specific gravity of the soil may be calculated as:

$$G = \frac{G_{soil}G_{salt}}{G_{salt} + (G_{soil} - G_{salt})\chi} \qquad (25)$$

When more than one salt exists, the salt content will be the summation of individual salt contents, $\chi = \chi_1 + \chi_2 + \chi_3 + ...$ and the average specific gravity of the salts will be $G_{salt} = \chi /(\chi_1 / G_1 + \chi_2 / G_2 + \chi_3 / G_3 + ...)$. In soils containing low percentages of highly soluble salts, pore water may be enough to dissolve all the salt. In such cases, the separation is very effective.

This method is very important in gypseous soils, because these soils may undergo leaching and the percentage of gypsum is altered with time. This means that the specific gravity of a gypseous soil may vary during water percolation and the engineering properties will vary accordingly. The application of equation (25) allows the calculation of the specific gravity any time during leaching as long as the gypsum content is determined.

The relation given in equation (25) is plotted in Figure 2 for gypseous soils. Several specific gravity values for soil solids are chosen and the average specific gravity calculated is plotted against the gypsum content. The graphs may also be used to evaluate the accuracy of the specific gravity test result. For instance, an obtained value of 2.7 for specific gravity for a gypseous soil having 30% gypsum content could not be accepted as the point would fall outside the range of the curves. The small plot shown on the right side of the figure presents the specific gravity values for 33 different gypseous soils (data collected by authors). Only 6 of the 33 tests (i.e., 18%) were unreliable and they should be re-evaluated and the soil components reanalyzed.

Corrections Required for Dehydration Phases of Gypsum

Salts may be hydrous or anhydrous. Crystallization water is usually detached from the salt at certain temperature depending on the salt type, the pressure and the relative humidity. The existence of different phases of a salt may lead to erroneous values of specific gravity of a soil if only conventional test calculations are followed.

As the most widely encountered salts in the soil are highly soluble to percolation of ground water which causes leaching of these salts from the soil, their effect of hydration-dehydration is comparatively low due to their low percentages. Also, such soils are usually wet and the dominant phase of the salt will be the completely hydrated phase, hence no corrections are required. The only salt that represents a major problem in this case is calcium sulfate. This salt has three main phases according to the hydration level; anhydrite $CaSO_4$, bassanite $CaSO_4.0.5H_2O$ and gypsum $CaSO_4.2H_2O$. All of these phases are stable below 45 °C and the gypseous soils are usually dry, and a combination of these phases may occur in the soil simultaneously.

When some free moisture is available, gypsum will be found dominant and no phase correction is needed. In soils subject to desiccation and evaporation and where no free water is left, gypsum may turn to bassanite and anhydrite. If the water-pycnometer method is used, then the specific gravity obtained should be further corrected according to the following. To determine the phase existing and its content in the soil, that is $\chi_{CaSO_4.\varepsilon H_2O}$ and the amount of crystallization water through the number of water molecules ε, Al-Mufty and Nashat (2000) have shown that the content of gypsum or other phases could be found from the determination of hydration water ratio. This is performed through three steps. First, a sample is put in a 45 °C oven in its natural state and left in the oven until the weight is stabilized. The sample is then immerged with distilled water and put in the oven again. The third step is to move the sample to a 105 °C oven and it is left there for 24 hours. The calcium sulfate content and ε may be calculated from the following two equations:

$$\chi_{CaSO_4.\varepsilon H_2O} = \frac{M'_s - M_{dry}}{M_s} \times \frac{136.14 + 18.01\varepsilon}{36.02} \times 100 \qquad (26)$$

$$\varepsilon = \frac{2(M_s - M_{dry})}{M'_s - M_{dry}} \qquad (27)$$

where M_s is the mass of the sample in its natural state after oven drying at 45 °C and M'_s is the mass of the

sample after flooding and re-drying at 45 °C while M_{dry} represents the sample mass after drying at 105-110 °C. If the soil is wet in its natural state, there is no need for the second step and $\varepsilon = 2$.

Next, the specific gravity test is performed with needed corrections and $\chi_{CaSO_4.2H_2O}$ is found as the existing phase after the test. The specific gravity of the soil solids other than gypsum will be:

$$G_{soil} = \frac{2.32G(1 - \chi_{CaSO_4.2H_2O})}{2.32 - G\chi_{CaSO_4.2H_2O}} \qquad (28)$$

This equation is a rearranged form of equation (25). The same equation is then used to compute the correct specific gravity of the natural soil with the real phase of calcium sulfate:

$$G_{corr} = \frac{G_{soil}G_{CaSO_4.\varepsilon H_2O}}{G_{CaSO_4.\varepsilon H_2O} + (G_{soil} - G_{CaSO_4.\varepsilon H_2O})\chi_{CaSO_4.\varepsilon H_2O}} \qquad (29)$$

The curve shown in Figure 3 is suggested to specify a value for $G_{CaSO_4.\varepsilon H_2O}$ knowing that the exact values of specific gravity of the main three phases of calcium sulfate are 2.32, 2.74 and 2.96 for gypsum, bassanite and anhydrite, respectively.

Effect of Hydration Water on the Specific Gravity of Saturated Soils

For other salts, such as some of those listed in Table 1, which have different phases, one may notice that applying oven drying at 45°C causes alteration to the anhydrous phase in several cases. This eliminates the significance of the specific gravity obtained in a conventional test even if the result was corrected for test procedure or salinity of pore water at this temperature. This will cause an error when the salt percentage is relatively high. The transition temperatures from the hydrous to the anhydrous phase for different salts are given in Table 5.

For a saturated saline soil, the salinity of the pore water extract is measured at the required temperature. The state at this temperature will be denoted by the subscript b. It is also better to measure the density of the solution.

After that the water content is measured and the weight of the dry soil is recorded using oven drying at 45°C or any other specified temperature. Then a conventional specific gravity test may be performed and needed corrections are made. The specific gravity obtained represents that of the dry soil with the salt phase corresponding to the drying temperature. Hereafter, the latter state is denoted by the subscript, a.

The salt percentage at stage a should be known. If not, the salt content is found through leaching and re-weighing or through the use of electric conductivity measurement. If the anhydrous (or whatever phase obtained) salt content is known, the specific gravity of the soil solids other than the salt may be found using a rearranged form of equation (25):

$$G_{soil} = \frac{G_{salt,a}G_a(1 - \chi_a)}{G_{salt,a} - G_a\chi_a} \qquad (30)$$

where the specific gravity of the salt phase at the higher temperature, $G_{salt,a}$, should be known.

The weight of soil solids at the lower temperature will be greater than the weight of the soil solids at the higher temperature. The difference is the additional hydration water gained which may be determined through, $\Delta\varepsilon$, the difference in the number of attached water molecules in the two cases, ε_b-ε_a, and the weight of the dry soil at the higher temperature. If the ratio r is defined as the weight of the additional hydration water gained divided by the molecular weight of the salt phase at the higher temperature; i.e., $r = 18.01\Delta\varepsilon / M_a$, then, $M_{salt,b} = M_{salt,a}(1+r)$ and $M_{s,b} = M_{s,a} + rM_{salt,a}$. The salt content at the lower temperature; i.e, in the more hydrated phase, may be found as follows:

$$\chi_b = \frac{1+r}{1+r\chi_a}\chi_a \qquad (31)$$

Thus, the specific gravity of the soil with the hydrated salt (considered as dry soil) is found using equation (25). If correction for the salinity effect of the pore water considering the natural state at the temperature specified is needed, the water content at this temperature should be measured to make use of equation (24). Of course, water content test at low temperatures could not be performed.

So, the required water content may be easily related to the measured water content at the higher temperature. Considering that the difference is due to the subtraction of the weight of the hydration water gained from the weight of the free water and the addition of the same weight to the soil solids:

$$w_b = \frac{w_a - r\chi_a}{1 + r\chi_a} . \tag{32}$$

After the water content is found (note that this is not the correct water content but measured in a conventional procedure), the correct specific gravity of the solids may be determined exactly as the situation in the natural state using equation (24). An application for this correction procedure is presented in example 4.

Examples for Correction

Example 1

In a conventional specific gravity test carried out for a soil containing a highly soluble salt, the measurements and data were as follows:

Weight of the dry soil = 52.2 g.

Weight of the empty volumetric flask of 500 cm³ nominal volume = 176.37 g.

Weight of the flask filled with distilled water= 673.67 g at 30 °C.

Weight of the flask+water+soil = 706.53 g at 30 °C.

An X-ray diffraction test has shown that the dominant salt was epsomite, $MgSO_4.7H_2O$, and the salt content was found to be χ=10%.

Using these values, the specific gravity calculated according to equation (1) substituting 0.9957 for the specific gravity of water at 30 °C will be:

G = (0.9957*52.2)/(673.67-706.53+52.2) = 2.69.

What did truly take place, and how much is the error in this result?

First, the concentration of the dissolved salt should be known. This should be found experimentally, but here, and for better explanation of the concepts, it will be assessed by calculations. Since the salt is highly soluble, *s* is more than 250 g/l, all the salt will be assumed

dissolved and the weight of the remaining soil after dissolution will be 0.9*52.2 = 46.98 g. The volume of the solution covering the soil and filling the flask will be approximately 500 - 46.98/2.69 = 482.53 cm³, say 482 cm³. This volume is enough to dissolve about 250*482/1000 = 120.5 g of the salt which exceeds the available salt amount in the soil which is 5.22 g. The latter result confirms the assumption that all the salt would be dissolved and the concentration may be taken as C = 5.22/482 = 0.0108 g/cm³. The concentration of the anhydrous phase may be found using equation (11), M = 246.48 g/mol, from Table 2, ε = 7, hence C_a = (246.48-18.01*7)*0.0108/246.48 = 0.0053 g/cm³.

Next, ρ'_w, the density of solution is determined. From Table 4, for epsomite, the density of solution varies from ρ_{sol} = 1.0033 for C_a = 0.005*1.0033 = 0.0050 to ρ_{sol} = 1.0084 for C_a = 0.01*1.0084 = 0.0101. Using interpolation, for C_a = 0.0053, ρ_{sol} = 1.0036 g/cm³. This value is for 20 °C and should be corrected for 30°C. The density at 30 °C, ρ'_w, is approximated to 1.0036*0.9975= 1.0011 g/cm³, as the ratio $\rho'_{w\,at\,30°C} / \rho'_{w\,at\,20°C} = 0.9975$. This may be compared with equation (10), $\rho'_w = \rho_w + \alpha C_a$ = 0.9957+1*0.0053 = 1.001 g/cm³.

Then the value of M'_{fw} can be determined (in the laboratory it is better to measure M'_{fw} and ρ'_w experimentally). As $V_f = (M_{fw}-M_f)/\rho_w = (673.67-176.37)/0.9957 = 499.45$ cm³ then $M'_{fw\,at\,30°C}$= 499.45*1.0011+176.37 = 676.37 g. The value of M'_{fws} is the same as for M_{fws} which is measured in the laboratory during the conventional procedure; i.e., 706.53 g. Now, the correct specific gravity may be found using equation (6):

$$G = \frac{52.2*1.0011}{676.37 - 176.37 - (706.53 - 176.37 - 52.2)\frac{(1.68 - 0.0108)*1.0011}{(1.0011 - 0.0108)*1.68}} = 2.62$$

and the error in the specific gravity in the conventional calculations is (2.69-2.62)/2.62*100 = 2.7%.

Example 2:

In a similar conventional specific gravity test carried out for a soil containing a highly soluble monovalent-monovalent salt, the measurements and data were as

follows:

Weight of the dry soil = 52.2 g.

Weight of the empty volumetric flask = 176.37 g.

Weight of the flask filled with distilled water= 673.67 g at 30 °C.

Weight of the flask+water+soil = 706.34 g at 30 °C.

Additional measurements were recorded to consider the effect of salt:

Weight of the flask filled with a solution prepared from a proportional soil water mix = 677.47 g at 30 °C.

Concentration of the salt measured was 0.0108 g/cm^3 with no hydrous phase expected in the soil.

Average specific gravity of salt = 2.16.

Using these values, the incorrect specific gravity calculated according to equation (1) substituting 0.9957 for the specific gravity of water at 30°C will be:

G = (0.9957*52.2)/(673.67-706.34+52.2) = 2.66.

The density of solution may be calculated from equation (9):

$$\rho'_{w_{30°C}} = \frac{677.47 - 176.37}{673.67 - 176.37} * 0.9957 = 1.0033$$

or may be approximated using equation (10):

$\rho'_w = \rho_w + \alpha C_a = 0.9957 + 0.68*0.0108 = 1.0030$ g/cm^3.

Now, the correct specific gravity may be found using equation (6):

$$G = \frac{52.2 * 1.0033}{677.47 - 176.37 - (706.34 - 176.37 - 52.2)\frac{(2.16 - 0.0108)*1.0033}{(1.0033 - 0.0108)*2.16}} = 2.55$$

and the error in the specific gravity in the conventional calculations is:

(2.66-2.55)/2.55*100= 4.31%.

Example 3:

Let a soil sample of 52.2 g consist of 10% gypsum. In a conventional test to determine the specific gravity of the soil, the following was recorded:

Weight of the dry soil = 52.2 g.

Weight of the empty volumetric flask = 176.37 g.

Weight of the flask filled with distilled water = 673.67 g at 30 °C.

Weight of the flask+water+soil = 706.95 g at 30 °C.

Using these values, the specific gravity calculated according to equation (1) substituting 0.9957 for the specific gravity of water at 30 °C will be:

G = (0.9957*52.2)/(673.67-706.95+52.2) = 2.75

In the available volume of solution not all the gypsum will be dissolved; i.e., the amount of water is not enough to dissolve 5.22 g of gypsum. Hence, the concentration will saturate the solution $C = s = 2.09*1.2646 = 2.64$ g/l and the density of the solution may be taken from Table 3 as 0.9979 at 30°C. Compare this with the density calculated from equation (10), that is:

$\rho'_w = \rho_w + \alpha C_a = 0.9957 + 1.0*0.00209 = 0.9978$ g/cm^3.

The volume of the flask is the same as in example (1); i.e., 499.45 cm^3, then:

$M'_{fw\ \text{at 30°C}} = 499.45*0.9979 + 176.37 = 674.77$ g.

Now, the value of the correct specific gravity may be found from equation (6):

$$G = \frac{52.2 * 0.9979}{674.77 - 176.37 - (706.95 - 176.37 - 52.2)\frac{(2.32 - 0.00264)*0.9979}{(0.9979 - 0.00264)*2.32}} = 2.70 \quad .$$

The error in the conventionally obtained specific gravity value = (2.75-2.70)/2.70*100 = 1.85%.

Example 4:

For a soil sample containing sodium sulfate, the following data were obtained:

The concentration of the anhydrous phase of the salt, C_a, in the pore water at 20°C was 0.146 g/cm^3. The density of the solution was 1.1223 g/ cm^3. After oven drying at 45 °C, the measured water content was 40% and the weight of the dry soil was 71.43 g. The total soluble salt content at this stage was 0.16. The specific gravity was obtained through a corrected test and found to be 2.78. It is required to determine the real specific gravity value of the soil solids in its natural saturated state at 20°C.

As the soil cannot be dried at 20 °C, the specific gravity at this degree should be calculated using the information given for the soil at 45 °C. First, let us find the specific gravity of soil solids other than the salt, using equation (30):

$$G_{soil} = \frac{G_{salt}G(1-\chi)}{G_{salt}-G\chi} = \frac{2.67*2.78(1-0.16)}{2.67-2.78*0.16} = 2.80 .$$

Second, the water content at 20°C, as it would be measured if full evaporation is maintained, is calculated from the measured water content at 45°C, which is of course not the correct fluid content (not corrected for salinity effects of pore water). At the hydrated phase, mirabilite, is stable at 20°C, $r = 18.01*10/142.04 = 1.268$ for $M_a = 142.04$ g/mol, see Table 2. Using equation (32) the required water content will be:

$$w_{meas,20°C} = \frac{w_{meas,45°C} - r\chi_a}{1 + r\chi_a} = \frac{0.4 - 1.268*0.16}{1 + 1.268*0.16} = 0.164.$$

In a similar manner, the salt content at 20°C is calculated using equation (31):

$$\chi_b = \frac{1+r}{1+r\chi_a}\chi_a = \frac{1+1.268}{1+1.268*0.16}*0.16 = 0.302.$$

Now, a value for the specific gravity of the soil solids including the hydrated salt at 20°C in the imaginary dry state may be found using equation (25),

$$G = \frac{G_{soil}G_{salt}}{G_{salt} + (G_{soil} - G_{salt})\chi} = \frac{2.8*1.46}{1.46 + (2.8-1.46)*0.302} = 2.19,$$

which is significantly different from the value obtained for the dry soil at 45°C.

In order to correct this value for the effect of the dissolution of some of the salts in the pore water, equation (24) may be used. The concentration of the hydrous phase as m is computed using equation (8) which requires the knowledge of C and the density of the solution. Hence,

$$C = C_a * \frac{M}{M - 18.01\varepsilon} = 0.146 * \frac{322.14}{142.04} = 0.331\,\text{g/cm}^3,$$

see equation (11).

$$m = \frac{C}{\gamma'_{w_T} - C} = \frac{0.331}{1.1223 - 0.331} = 0.418,\text{ a rearranged}$$

form of equation (8),

$$G_{corr} = \frac{G_{meas}G_{salt}(1 - mw_{meas})}{G_{salt} - G_{meas}mw_{meas}} = \frac{2.19*1.46*(1-0.418*0.164)}{1.46 - 2.19*0.418*0.164} = 2.274.$$

This value may not be compared to that found for the soil dried at 45°C, because the latter was not corrected for salinity effects of pore water. Correcting the value 2.78, determined for the soil dried at 45°C, requires the knowledge of the salinity of pore water as it would be for a saturated soil at this temperature. Thenardite, the anhydrous phase of sodium sulfate, is soluble at 45 °C to about $m = 0.19$ (Seidell 1958). Using equation (24) yields a corrected specific gravity of:

$$G_{corr} = \frac{G_{meas}G_{salt}(1 - mw_{meas})}{G_{salt} - G_{meas}mw_{meas}} = \frac{2.78*2.67*(1-0.19*0.4)}{2.67 - 2.78*0.19*0.4} = 2.79.$$

The difference is small as the specific gravity of the salt in its anhydrous phase is closer to that of the soil. The void ratio at both temperatures may be found after correcting the measured water contents. For m values of 0.19 and 0.418 and corresponding measured water contents of 40% and 16.4%, the correction factor F may be found using equation (18) or (Figure 1) as 1.28 and 1.52 for the cases of 45°C and 20°C, respectively. The corresponding corrected water contents will be 51.2% and 24.9%.

The void ratio of the saturated soil at 20°C is computed from equation (19):

$$e_{corr} = \frac{G_{corr}w_{corr}}{S(G_T + C/\gamma_{w_{4°C}})} = \frac{2.27*0.249}{1.0*(0.9982 + 0.331/1.00)} = 0.425.$$

The void ratio of the saturated soil at 45°C may be computed by the approximate form of equation (19) as the salt phase in this case is the anhydrous one (if the exact form is to be used, the density of solution should be determined to be able to compute C),

$$e_{corr} \approx \frac{G_{corr}w_{corr}}{SG_T(1+m)} = \frac{2.79*0.512}{1.0*0.9903(1+0.19)} = 1.212.$$

It is really surprising to find that the void ratio of a soil may decrease to 35% of its value due to a temperature decrease from 45 °C to 20 °C. This means that a saline soil may alter from the normally consolidated state to the over-consolidated state without any changes in stress. The latter phenomenon should be further investigated in future research.

CONCLUSION

For saline soils, the values of specific gravity obtained through conventional testing may require corrections due to the dissolution of the salts. The error in the conventionally calculated values of specific gravity for such soils increases as the ratio of water to soil in the testing volumetric flask increases.

The existence of other phases of gypsum may lead to a false value of specific gravity of a gypseous soil due to the effect of rehydration or dehydration during the test. Correction for this error is presented in the paper.

All the drying should be at 45 °C to overcome the loss of crystallization water above this temperature. If the specific gravity is required at lower temperatures, the effect of hydration of the salt should be considered and special corrections are needed.

The use of kerosene or white spirit for specific gravity determination of saline soils is recommended when the variation of the specific gravity of the fluid with temperature is well established. In this case, only corrections for the effect of salinity of the ground water and for the effect of hydration water at low temperature are required.

Notation

α	concentration factor
ε	number of water molecules in a hydrous salt molecule
χ	the salt content, wt. of salt/ wt. of solids
$\rho_{4°C}$	density of water at 4 °C
$\rho_{kT°C}$	density of kerosene at temperature, T
ρ_{salt}	density of the salt contributing to the density of the soil solids
ρ_{sol}	density of the solution
ρ_{wT}	density of distilled water at temperaure T
ρ'_{wT}	density of solution containing a concentration C at temperaure T
A	percentage of weight of anhydrous salt dissolved to the weight of solution
C	concentration of salt in solution, wt. of dissolved salt over the volume of solution, the phase of salt that is expected to precipitate
C_a	concentration of anhydrous phase of the salt in solution, wt. of dissolved anhydrous salt over the volume of solution
e	void ratio
e_{corr}	corrected void ratio
F	a correction factor for water content
G	average specific gravity of soil
G_{corr}	corrected specific gravity of soil solids in case of saline pore water
G_{meas}	measured specific gravity of soil solids in case of saline pore water
G_{salt}	specific gravity of salt
G_{soil}	specific gravity of soil solids other than the salt
G_T	specific gravity of water at temperature T and the density of water in g/cm^3
M	molecular weight of the salt, g/mol
R	the ratio of hydration water to the molecular weight of the salt
S	degree of saturation, vol. of pore fluid over the volume of voids
s	solubility of a salt, wt. of dissolved salt in a volume of a saturated solution
V_f	volume of the flask

V_s	volume of soil solids including the salt
V_{salt}	volume of salt precipitated within the soil solids
V_{solids}	volume of soil solids including the salt content of the pore fluid
V'_s	volume of soil solids after dissolution of some of the salt or all of it
V'_w	volume of water added over the saline soil to the flask (volume of the solution)
M_f	mass of the flask
M_{fk}	mass of the flask filled with kerosene
M_{fks}	mass of the flask filled with kerosene and the soil
M_{fw}	mass of the flask filled with distilled water
M'_{fw}	mass of the flask filled with the solution containing C of dissolved salt
M_{fws}	mass of the flask filled with water and the soil
M'_{fws}	mass of the flask filled with the solution and the undissolved soil
M_{dry}	mass of dry soil, obtained at 45 °C unless otherwise specified
M_{fluid}	mass of solution or fluid in the pores
M_s	mass of soil solids including the salt, obtained at 45 °C
M'_s	weight of the soil after flooding with water and drying at 45 °C
M_{salt}	mass of salt in the pore fluid
M_{solids}	mass of the soil solids other than the salt content of pore fluid
$M_{solution}$	mass of the solution
M_w	mass of water
M_{water}	mass of water in the solution of pore fluid
M_{wet}	weight of wet soil
W	water content of the soil
w_{corr}	corrected water content of the soil
w_{meas}	measured water content of the soil

Table (1): Density of distilled water at different temperatures, *ASTM, Designation: D 854 -02*.

T (°C)	γ_{w_T} (g/cm^3)	T (°C)	γ_{w_T} (g/cm^3)	T (°C)	γ_{w_T} (g/cm^3)
0	0.99987	20	0.99821	27	0.99652
4	1.00000	21	0.99799	28	0.99624
5	0.99999	22	0.99777	29	0.99595
10	0.99973	23	0.99754	30	0.99565
15	0.99910	24	0.99730	35	0.99406
18	0.99860	25	0.99705	40	0.99224
19	0.99841	26	0.99679	45	0.99025

Table (2): Salts encountered in soils with their densities and solubility, (Weast 1974).

Salt formula	Salt name	Molecular weight, M, g/mol	Specific gravity	Solubility at 20 °C, as $A\%$	Solubility at 25 °C, as $A\%$
$CaCl_2.2H_2O$	…	147.02	0.84	42.7	52.1
$CaCl_2.6H_2O$	…	219.08	1.71	…	…
$CaSO_4$	Anhydrite	136.14	2.96	…	…
$CaSO_4.0.5H_2O$	Bassanite	145.15	2.74	…	…
$CaSO_4.2H_2O$	Gypsum	172.16	2.32	0.2014	0.2082
$MgCl_2$	…	95.22	2.32		
$MgCl_2.6H_2O$	Bischofite	203.31	1.57	35.3	35.5
$MgSO_4$	…	120.37	2.66	…	…
$MgSO_4.H_2O$	Kieserite	138.39	2.45	…	…
$MgSO_4.4H_2O$	Leonhardtite	202.45	2.01	…	…
$MgSO_4.6H_2O$	…	238.47	1.72	…	…
$MgSO_4.7H_2O$	Epsomite	246.48	1.68	25.2	26.7
KCl	Sylvite	74.55	1.99	25.5	26.4
K_2SO_4	Arcanite	174.27	2.66	10.0	10.75
$NaCl$	Halite	58.44	2.16	26.38	26.43
Na_2SO_4	Thenardite	142.04	2.67	…	…
$Na_2SO_4.10H_2O$	Mirabilite	322.14	1.46	15.97	21.88

Table (3): Solubility of gypsum and density of saturated solution at different temperatures, (Seidell 1958).

Temperature, °C	Solubility of $CaSO_4$, g per litre of solution[a]	Density of solution, g/cm^{3}
0	1.759	1.00197
10	1.928	1.00173
18	2.016	1.00059
25	2.080	0.99911
30	2.090	0.99789
35	2.096	0.99612
40	2.097	0.99439
55	2.009	0.98796
65.3	1.932	0.98256
75	1.847	0.97775

[a] to compute the concentration or the solubility for gypsum the values in the second column should be multiplied by 1.2646, where for gypsum, $M = 172.16$.

Table (4): Density of solution of different salts for various concentrations, data collected from Weast (1974). The numbers in the shaded cells are interpolated.

salt formula and name	$CaCl_2.2H_2O$	$MgCl_2.6H_2O$ Bischofite	$MgSO_4.7H_2O$ epsomite	KCl sylvite	K_2SO_4 arcanite	$NaCl$ halite	$Na_2SO_4.10H_2O$ Mirabilite
A%	density of solution at 20 °C, g/cm³						
0.1	1.0005	1.0004	1.0007	1.0003	1.0004	0.9989	1.0005
0.2	1.0010	1.0009	1.0013	1.0006	1.0009	0.9997	1.0011
0.3	1.0014	1.0013	1.0020	1.0008	1.0013	1.0004	1.0016
0.4	1.0019	1.0018	1.0026	1.0011	1.0018	1.0011	1.0022
0.5	1.0024	1.0022	1.0033	1.0014	1.0022	1.0018	1.0027
1.0	1.0065	1.0062	1.0084	1.0046	1.0062	1.0053	1.0071
1.5	1.0106	1.0103	1.0135	1.0078	1.0102	1.0089	1.0116
2.0	1.0148	1.0144	1.0186	1.0110	1.0143	1.0125	1.0161
2.5	1.0190	1.0185	1.0238	1.0142	1.0183	1.0160	1.0206
3.0	1.0232	1.0226	1.0289	1.0174	1.0224	1.0196	1.0252
3.5	1.0274	1.0268	1.0341	1.0207	1.0265	1.0232	1.0298
4.0	1.0316	1.0309	1.0392	1.0239	1.0306	1.0268	1.0343
4.5	1.0358	1.0343	1.0445	1.0271	1.0347	1.0304	1.0389
5.0	1.0401	1.0394	1.0497	1.0304	1.0388	1.0340	1.0436
5.5	1.0443	1.0447	1.0545	1.0336	1.0429	1.0377	1.0481
6.0	1.0486	1.0479	1.0602	1.0369	1.0470	1.0413	1.0526
6.5	1.0529	1.0522	1.0655	1.0402	1.0512	1.0450	1.0572
7.0	1.0572	1.0564	1.0708	1.0434	1.0553	1.0486	1.0619
7.5	1.0615	1.0608	1.0762	1.0467	1.0595	1.0523	1.0666
8.0	1.0659	1.0651	1.0816	1.0500	1.0637	1.0559	1.0713
8.5	1.0703	1.0695	1.0870	1.0533	1.0679	1.0596	1.0760
9.0	1.0747	1.0738	1.0924	1.0566	1.0721	1.0633	1.0808
9.5	1.0791	1.0782	1.0979	1.0600	1.0763	1.0670	1.0856
10.0	1.0835	1.0826	1.1034	1.0633	1.0806	1.0707	1.0905
11.0	1.0923	1.0916	1.1146	1.0700	…	1.0781	1.1002
12.0	1.1014	1.1005	1.1257	1.0768	…	1.0857	1.1101
13.0	1.1105	1.1097	1.1371	1.0836	…	1.0932	1.1201
14.0	1.1198	1.1189	1.1484	1.0905	…	1.1008	1.1301
15.0	1.1292	1.1281	1.1601	1.0974	…	1.1085	1.1402
16.0	1.1386	1.1372	1.1717	1.1043	…	1.1162	1.1503
17.0	1.1482	1.1463	1.1836	1.1114	…	1.1240	1.1604
18.0	1.1579	1.1553	1.1955	1.1185	…	1.1319	1.1705
19.0	1.1677	1.1648	1.2077	1.1256	…	1.1398	1.1806
20.0	1.1775	1.1742	1.2198	1.1328	…	1.1478	1.1907

Table (5): Transition temperatures between phases of some salts, collected from Seidell (1974).

Salt formula, 1st phase	2nd phase	3rd phase
$CaCl_2.6H_2O$	15-30 °C -$4H_2O$	175 °C -$5H_2O$
$CaSO_4.2H_2O$	42-45 °C -$1.5H_2O$	100-105 °C -$2H_2O$
$MgCl_2.6H_2O$	116-130 °C -$2H_2O$	
$MgSO_4.7H_2O$	48 °C -H_2O	100-150 °C -$6H_2O$
$Na_2SO_4.10H_2O$	32-35 °C -$10H_2O$	
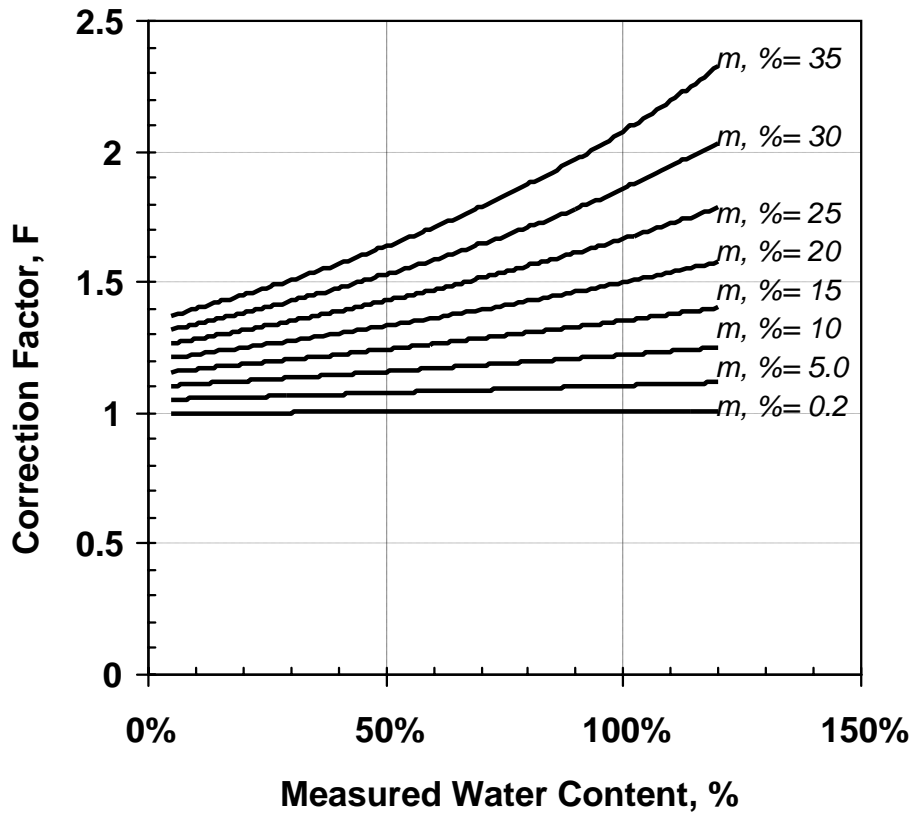
Figure (1): Correction factor for water content for soils containing saline pore water, *m* being the concentration of the solution in percent.
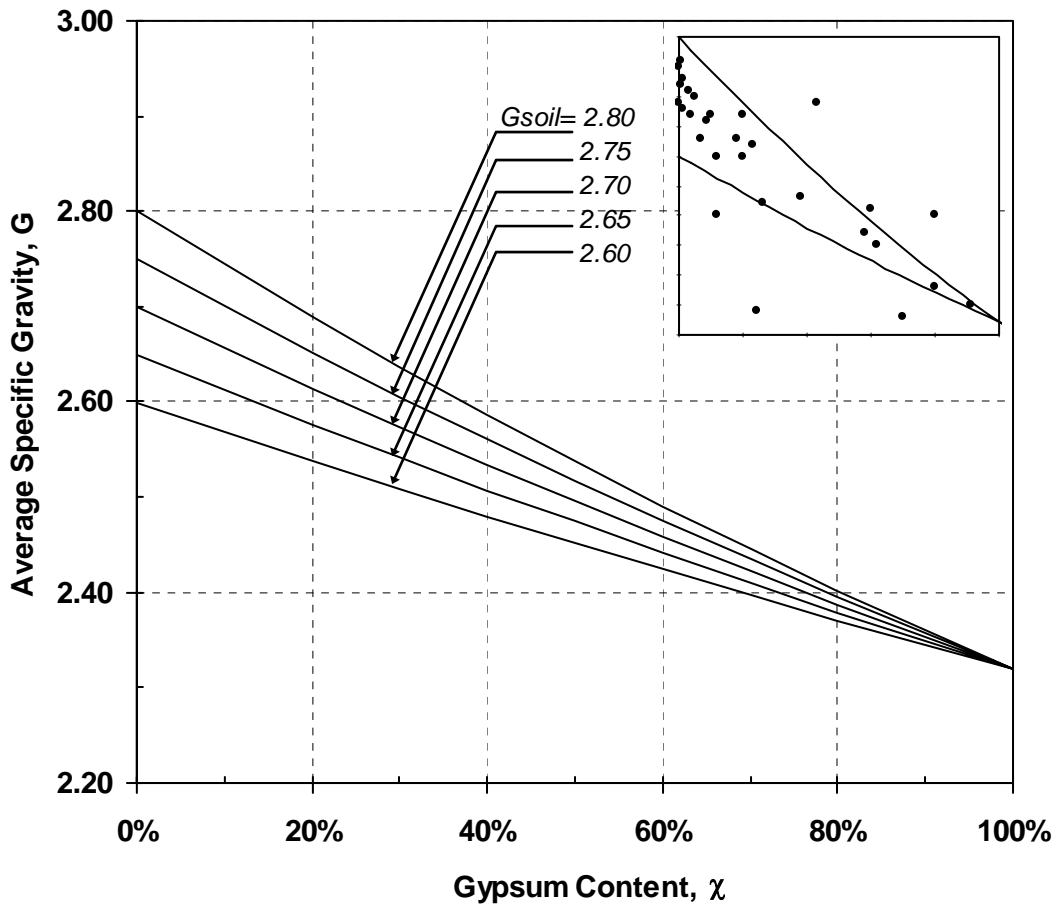
Figure (2): The variation of the specific gravity of a gypseous soil with the gypsum content. On the right, results of specific gravity tests for 33 different soils are plotted with the lower and upper bounds.
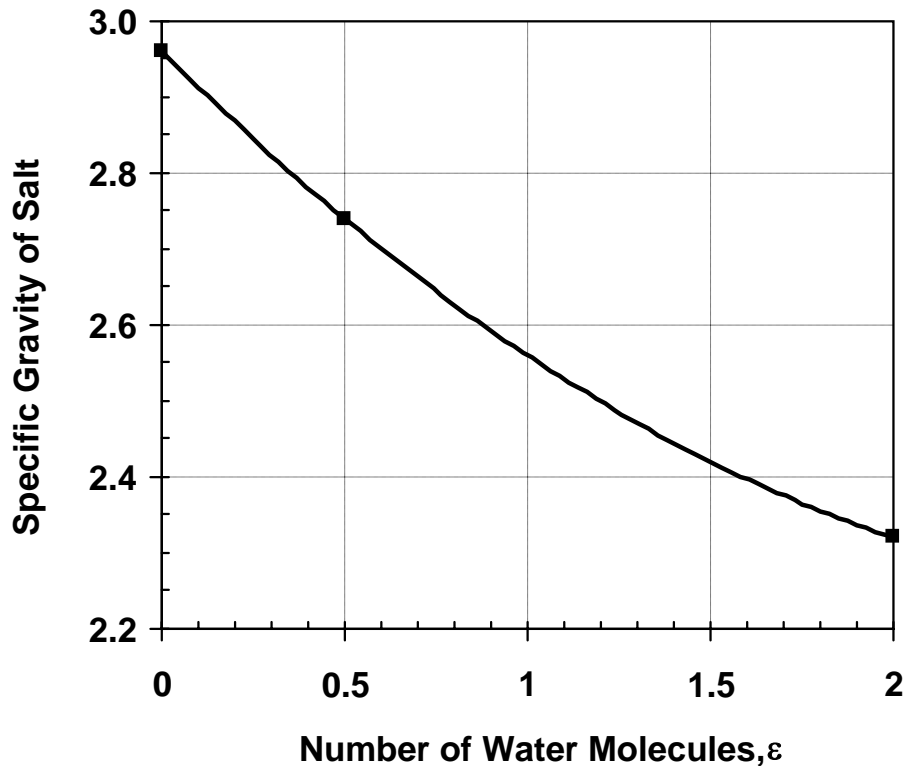
Figure (3): The average specific gravity of calcium sulfate $CaSO_4.2H_2O$ **according to the number of crystallization water molecules.**

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