# WATER DESORPTION CHARACTERISTIC OF RED GYPSUM

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# ABSTRACT

Red gypsum (RG) is a waste that generated during the process of titanium dioxide production from ilmenite. It is a soil with reddish colour due to the present of iron. This reddish waste being highly produced every year in Malaysia, which is 341000 tonnes and they are mostly disposed to landfill. In this study, the water desorption characteristic of Red Gypsum are tested as well as physical and chemical properties. The physical and chemical properties of Red Gypsum were determined. Other than that, a suction-water content soil-water characteristic curve (SWCC) is formed. The techniques used with the aim of obtaining the data for drying SWCC are vapour equilibrium and osmotic technique. In osmotic technique, the suction ranged from 0.23 to 3.28 MPa, while in vapour equilibrium technique, suctions used were between 3.6 to 111.77 MPa. The result of SWCC able to give an important information about Red Gypsum. As a result, Red Gypsum has a soil suction around 22.5 MPa and gravimetric water content around 50 % at air entry value (AEV), while at residual condition, the gravimetric water content is 26% and soil suction is around 38 MPa. In conclusion, RG has the drying suction-water content soil-water characteristic curve which almost the same as yellow bentonite. So, it can have the applications as yellow bentonite.

# ABSTRAK

Gipsum merah (RG) ialah sisa yang dihasilkan semasa proses penghasilan titanium dioksida daripada ilmenit. Ia adalah tanah yang berwarna merah kerana kewujudannya besi dalam gypsum merah. Sisa yang berwarna merah ini dihasilkan dengan jumlah yang besar di Malaysia tiap- tiap tahun, iaitu 341000 tan dan kebanyakannya dilupuskan dalam tapak pelupusan. Ciri penyaherapan air, sifat- sifat fizikal dan kimia giysum merah diuji dalam kajian ini. Selain itu, lengkung ciri tanah-air dengan kandungan sedutan- air dibentukkan. Teknik yang digunakan untuk mandapat data yang berkaitan ialah teknik keseimbangan wap dan teknik osmosis. Dengan menggunakan teknik osmosis, sedutan yang digunakan adalah di antara 0.23-3.28 MPa, manakala untuk teknik keseimbangan, sedutan digunakan adalah di antara 3.6-111.77 MPa. Keputusan lengkung ciri tanah-air dapat memberikan informasi yang penting tentang gipsum merah. Ia juga memainkan peranan yang penting dalam membuat anggaran kekuatan ricih dan kebolehtelapan sisa ini sebab kekuatan ricih dan kebolehtelapan tanah amat sukar untuk diketahui dengan menjalankan ujian makmal. Akibatnya, gypsum merah mempunayai sedutan tanah lebih kurang 22.5 MPa dan kandungan air gravimetric kira-kira 50 % semasa sampainya nilai kemasukan udara, manakala dalam keadaan residual, kanduangan air gravimetric adalah lebih kurang 26 % dan sedutan tanah kira-kira 38 MPa. Kesimpulannya, gypsum merah ini mempunyai lengkung ciri tanah-air yang hampir sama dengan bentonit kuning. Oleh itu, ia mempunyai aplikasi yang seperti bentonit kuning.

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| | |
|---|---|
| $C_c$ | Swell Index |
| $C_s$ | Compression Index |
| $C_u$ | Undrained Shear Strength |
| $C_v$ | Coefficient of Secondary Compression |
| $C_\alpha$ | Coefficient of Consolidation |
| Ca | Calcium |
| $CH_3COOK$ | Potassium Acetate |
| $h_m$ | Matric suction |
| $h_t$ | Total suction |
| $h_\pi$ | Osmotic suction |
| g | Gravity acceleration |
| Fe | Iron |
| $Fe(OH)_2$ | Iron (II) Hydroxide |
| K | Potassium |
| $K_2CO_3$ | Potassium Carbonate |
| $K_2SO_4$ | Potassium Sulphate |
| KCl | Potassium Chloride |
| Kl | Potassium Iodide |
| KNO | Potassium Nitrate |
| $LiCl{\cdot}H_2O$ | Lithium Chloride Monohydrate |
| M | Molar mass of water |
| $M_A$ | Mass of crucible and soil sample after ignition |
| $M_C$ | Mass of crucible |

| | |
|---|---|
| $M_V$ | Coefficient of Volume Change |
| $M_S$ | Mass of crucible and oven dried soil sample |
| Mg | Magnesium |
| $MgCl_2 \cdot 6H_2O$ | Magnesiumchlorid Hexahydrat |
| Mn | Manganese |
| NaBr | Sodium Bromide |
| NaCl | Sodium Chloride |
| P | Phosphorus |
| $P_1$ | Partial water vapour pressure |
| $P_0$ | Saturated water vapour pressure |
| R | Constant of perfect gases |
| Si | Silicon |
| $TiO_2$ | Titanium Dioxide |
| $u_a$ | Air pressure |
| $u_w$ | Water pressure |
| V | Volume of wet soil pat |
| $V_0$ | Volume of dry soil |
| $V_1$ | Soil volume after swelling |
| $V_S$ | Volume of dry soil pat |
| W | Moisture content of wet soil pat |
| $W_S$ | Weight of oven dry soil pat |
| $\theta_r$ | Residual water content |
| $\theta_s$ | Saturated water content |
| $\Psi_a$ | Air entry value |
| $\Psi_w$ | Water entry value |

## LIST OF ABBREVIATIONS

| | |
|---|---|
| AEV | Air Entry Value |
| ASTM | American Society for Testing and Materials |
| BS | British Standard |
| CEC | Cation-Exchange Capacity |
| EGME | Ethylene glycol mono-ethyl ether |
| FS | Free swell |
| GGBS | Ground Granulated Blast furnace Slag |
| MWCO | Molecular Weight Cut Off |
| PEG | Polyethylene Glycol |
| RH | Relative Humidity |
| RG | Red Gypsum |
| SSA | Specific Surface Area |
| SWCC | Soil-Water Characteristic Curve |

# CHAPTER 1

# INTRODUCTION

## 1.1 BACKGROUND OF STUDY

During the industrial process of titanium dioxide ($TiO_2$) production, a waste product Fe $(OH)_2$ is produced (Gazque *et al.*, 2009). The red colour from iron caused this waste product to be named as 'Red' Gypsum (RG) (Fauziah *et al.*, 1996). In Malaysia, RG produced is around 341000 tonnes per year, which is quite a large amount of volume (Pau, 2013). Almost all of the waste product, RG, will be disposed to the landfill. (Singh *et al.*, 2004). Recently, many researches have been done on RG and the researchers found that RG is a very useful waste in geotechnical field. By using RG in an effective way, landfill problem can be reduced as well as make benefit on RG. Hence, firstly, properties of RG were investigated. The properties of RG can be similar to that of clay, thus may be considered as a substitute material for geotechnical applications.

Soil suction characteristic curve (SWCC) is a fundamental property in soil physics and soil mechanics (Heshmati and Motahari, 2012). It defines the relationship between moisture content and soil suction. In fact, SWCC contains a lot of importance information as shear strength and permeability of soil are related to this curve. Hence, it also function as a tool to estimate the unsaturated soil properties such as diffusivity and shear strength of soil (Fredlund *et al.*, 2011). In this study, the desorption characteristic of RG was investigated and the drying suction-water content SWCC was established.

## 1.2 PROBLEM STATEMENT

In Malaysia, the annual production of titanium dioxide is around 61000 tonnes, while the RG produced is 341000 tonnes per year and this waste product will be disposed to a landfill with the area of approximately 11084 acres. It means that the production of the waste is more than 5 times of the titanium dioxide produced. This indicates that the waste problem is quite serious and cannot be neglected. Although the landfill tax in Malaysia is free, but the improper disposal of Red Gypsum will give an impacts to our environment. In fact, there are some heavy metals found in RG which may cause pollution. The iron compounds in RG may irritating to the respiratory tract and eyes, vomiting, diarrhoea, pink urine, liver damage and kidney damage. Other than that, the negative effect of landfill include hydrological effects which will affect the marine life. The iron compounds may have their effect to the wildlife that comes into contact with them. Therefore, it will cause the landfill problems in the future very soon not only due to its amount yet the pollution problems. In this case, red gypsum should be investigated in order to find out more applications of it to this world other than just dispose it at landfill. Other than that, the drying characteristic of Red Gypsum has not yet been explored by the researchers. So, this investigation about Red Gypsum is needed.

## 1.3 RESEARCH OBJECTIVES

The aim of this research is to investigate the water desorption ability of red gypsum.

1.3.1 To establish the drying suction-water content soil- water characteristic curve.

## 1.4 SCOPE OF STUDY

In this study, Red Gypsum from Tioxide (Malaysia) Sdn. Bhd. in Kemaman, Terengganu was considered. Samples were taken from the site and transported back to the laboratory in seal plastic containers. Several tests were carried out in Soil and Geotechnical Laboratory in University Malaysia Pahang. The variables involved in this study were gravimetric water content and soil suction. The soil-water characteristic curve that being drawn is only the drying curve and there are only 2 techniques were used in order to obtain the relevant data, which included vapour equilibrium technique and osmotic technique. For these 2 techniques, the initial water content of the soil samples is 1.2 times of its liquid limit. The suctions applied ranged from 0.23 to 111.77 MPa.

## 1.5 SIGNIFICANCE OF PROPOSED RESEARCH

This study enables people to understand RG much deeper hence it bring benefits to research purpose. Some estimations (for example, compressibility, permeability, shear strength and volume change behaviour of red gypsum) can be done from the drying SWCC and the result of this study can be used for future researches to give the researchers a clearer information about Red Gypsum.

Other than that, based on this research, its usages was predicted when it comes to applications. From the SWCC, since it is a fundamental geotechnical properties of soil, so this research might be a great exploration of Red Gypsum.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 INTRODUCTION

In this chapter, Red Gypsum and its applications were discussed. Other than that, soil suction, soil suction measurement techniques and soil suction controlling techniques were presented. Lastly, the review on SWCC is done.

## 2.2 RED GYPSUM (RG)

The process of extraction from ilmenite by using sulphuric acid leads to the production of titanium dioxide ($TiO_2$). In Malaysia, 61000 tonnes of titanium dioxide is produced annually (Pau, 2013). This titanium dioxide is in used with many products for instance plastics and cosmetics. However, a waste, iron sulphate, is produced during the extraction process. Lime or limestone is used to neutralize this produced weak acid in the final stage of titanium dioxide manufacturing. The process of neutralization leads to the generation of a by-product, Red Gypsum (Azdarpour et al, 2014). This by-product is being produced about 341000 tonnes per year in Malaysia. It mostly contains of Ca, Fe, Si, Mn, Mg, K, and P (Fauziah, Zauyah, and Jamal, 1996). Table 2.1 shows the components of Red Gypsum.

**Table 2.1:** Components of Red Gypsum (after Adiano *et al.*, 1980)

| **Parameter** | **Red Gypsum** |
|---|---|
| **Major element (%)** | |
| Calcium | 18.87 |
| Iron | 8.55 |
| Silicon | 0.9 |
| Manganese | 0.32 |
| Magnesium | 0.15 |
| Potassium | 0.03 |
| Phosphorus | 0.01 |
| **Parameter** | **Red Gypsum** |
| **Minor element (mg/kg)** | |
| Zinc | 188 |
| Copper | 18 |
| Lead | 7 |
| Cadmium | 5 |
| Arsenic | 5 |
| Chromium | 125 |
| Nickel | 6 |
| Boron | 18 |

The present of high amount of iron is the main factor that Red Gypsum has a reddish colour. For the normal gypsum, it is white in colour which is definitely look different from Red Gypsum physically. In terms of the properties of Red Gypsum, the researchers, August, Noble and Tooze (2004), had compare Red Gypsum with White Gypsum. The comparisons of these two gypsums are shown in Table 2.2.

**Table 2.2:** Comparison of properties between Red Gypsum and White Gypsum (after August *et al.*, 2004)

| Properties | White Gypsum | Red Gypsum |
|---|---|---|
| pH | 7.4 | 7.4 |
| Free moisture (%) | 10-17 | 10-50 |
| Particle density ($mg/m^3$) | 3.05 | 2.71 |
| Dry density ($mg/m^3$) | 1.21 | 1.21 |
| Erosion (Dispersion) | Non-dispersive, 2 | Dispersive, 4 |
| Liquid limit (%) | 58 | 105 |
| Plastic limit (%) | Non- plastic | Non- plastic |
| Californian bearing ratio (CBR%) | Not obtainable | 23.05 |
| Optimum moisture content | 39 | 41 |
| Consolidation testing (50- 400 $kN/m^2$) | - | - |
| Coefficient of volume change ($M_v$ $m^2/MN$) | 3.643-0.32 | 0.907-0.179 |
| Coefficient of consolidation ($C_v$ $m^2$/year) | 1.19-0.102 | 0.855-0.232 |
| Coeffiecient of secondary Compression ($C_\alpha$ $m^2$/year) | 0.05-0.02 | 0.004-0.002 |
| Compression index, $C_c$ | 0.218 | 0.242 |
| Swell index, $C_s$ | 0.08 | 0.131 |
| Permeability (kv x $10^{-9}$ m/s) | 1.043-6.92 | 3.314-6.92 |
| Undrained shear strength ($C_u$ $kN/m^2$) | 95-104 | 194-355 |
| Strain to failure (%) | 5 | 10 |

From the Table 2.2, it shows that White Gypsum has a higher value in particle density, coefficient of volume change, coefficient of consolidation, and coefficient of secondary compression. On the other hand, the free moisture content, liquid limit, optimum moisture content, undrained shear strength, compression index, swell index, permeability, and strain to failure of Red Gypsum gives a higher value if compared to White Gypsum.

### 2.2.1 Application of Red Gypsum

Red Gypsum is considered as a useful waste in civil engineering field (August *et al.*, 2004). It can replace natural gypsum in the production of cement since it has calcium sulphate as its main component, it can perform the same as natural gypsum and it can even save the usage of clinker in cement up to 4-5% without giving a decrease of the quality (Gazque *et al.*, 2013). Furthermore, RG has been used for improving the soil properties (August *et al.*, 2004). It can be an effective binding agent in silty sands when mixed with Ground Granulated Blast furnace Slag (GGBS) (Hughes and Glendinning, 2005). From the study of Kamarudin and Zakaria (2007), they stated that red gypsum has the potential to be used for commercial glazes preparation. They also mentioned that the Red Gypsum glazes produced can be used for glazing wall tiles and glazing table wares. Nevertheless, Hustman Tioxide was developed the uses of Red Gypsum with the help of Coventry University and Imperial College. They found that Red Gypsum can be used as the trench backfill together with oxygen slag dust. So, as to figure out more uses of RG, a study on the properties of RG is a must.

## 2.3 SOIL SUCTION

In fact, a study on soil suction may give a better understanding on geotechnical project in order to provide safer design, economy and follow up of the behaviour (Marinho, n.d.). Soil suction is the water potential in soil- water system (Blatz *et al.*, 2008). They also mentioned that only 2 components of total suction in in soil, in general, are considered for the engineering studies which are matric and osmotic components. Matric suction is generated by capillary, whereas osmotic suction is generated by pore fluid chemistry and water adsorption. Lucian (2012) proposed a relationship between total suction, osmotic suction and matric suction can be expressed as the Eq. (2.1).

$$h_t = h_m + h_\pi \tag{2.1}$$

Where $h_t$ = total suction

$h_m$ = matric suction

$h_\pi$ = osmotic suction

(Assuming gravitational and external pressure effects are negligible)

Matric suction, in general, indicates the effect of climatic environment on the ground surface (Rowe, 2001). So, it is mostly influence by the surface environment and vary with time due to the environment changes. Osmotic suction is due to the salt content in pore of soil. Shear strength, volume change and mechanical behaviour of soil may be affected by the changes in osmotic suction. Although the changes in osmotic suction is less significant than the changes in matric suction due to the chemical contaminant of soil, however, during the changes in water content, the changes in total suction is verified essentially equivalent to the changes in matric suction especially in high suction, which is greater than about 1500 kPa (Krahn and Fredlund, 1971). In this study, total suction and matric suction of Red Gypsum were measured by using 2 techniques, which included osmotic and vapour equilibrium technique.

### 2.3.1 Soil Suction Control Techniques

In order to control the soil suction, there are few types of techniques, for example axis transition technique, osmotic technique, vapour equilibrium technique, and humidity control technique. (Ng and Menzies, 2007 and Delage *et al.*, 2008). Each techniques will have different suction ranges and suction components (Tarantino *et al.*, 2008). In this study, only osmotic and vapour equilibrium technique were used.

#### 2.3.1.1 Osmotic Technique

Osmotic technique is a technique of controlling suction that introduced by Kassiff and Ben Shalom in 1971 (Delage and Cui, 2008). The condition of suction applied by the osmotic technique is stated to be closer to reality than in the axis-translation method since no artificial pressure is applied to air (Delage *et al.*, 2008). Other than that, by using this technique, high level of suctions can easily apply to the sample. The highest suction that can be generated by this method is 10MPa and possibly can up to 12MPa (Blatz *et al.*, 2008). However, in the study of Murray and Sivakumar (2010), they stated that the maximum pressure that can be applied is limited by chemical breakdown of the semi-permeable membrane.

In osmotic technique, Polyethylene Gylcol (PEG) was used in order to generate suctions. PEG is a polymer that consist of large molecule which formulated as HO-[$CH_2$-$CH_2$-O]$_n$-H. The PEG that commercially available have the molecular weight of 1000 to 50000, however, in geotechnical field, PEG 6000 and 20000 are mostly used (Delage and Cui, 2008). The osmotic suction applied is depended on the solution used. The higher the concentration of the solution, the higher the osmotic suction will be produced.

The PEG used is then dissolved in distilled water and the soil sample is placed in the solution with the cover of semi- permeable membrane. In this case, the PEG molecules cannot pass through the semi- permeable membrane and only the water molecules can do so. Hence, the process of osmosis occurred between the soil samples and solution. The semi- permeable membrane that used are mostly cellulosic membranes that manufactured from nature cellulose re-formed from cotton fibres. In order to fix with the PEG solution, there are few degree of fineness of the semi- permeable membrane available which defined by molecular weight cut off (MWCO). Different PEG solutions must be used with the semi- permeable membrane with different MWCO so that the PEG molecules cannot pass through the semi permeable membrane due to the degree of fineness. The PEG molecular weight corresponding with semi- permeable membrane as shown in Table 2.3.

**Table 2.3** PEG molecular weight corresponding with semi- permeable membrane (after Delage and Cui, 2008)

| Molecular weight of PEG | Molecular weight cut off (MWCO) of semi permeable membrane |
|---|---|
| 20000 | 12000- 14000 |
| 6000 | 3500 |
| 4000 | 2000 |
| 1500 | 1000 |

### 2.3.1.2 Vapour Equilibrium Technique

Vapour equilibrium technique is used to control the suction. In this technique, the saturated salt solutions may affect the relative humidity of air in the closed container, where the soil sample placed (Sun *et al.*, 2014). The suction produced by different type of solutions are shown in Table 2.4.

**Table 2.4** Saturated salt solution and corresponding suction with temperature of 20˚C (after Sun *et al.*, 2014)

| Salt solution | RH (%) | Total suction (MPa) |
|---|---|---|
| $LiCl·H_2O$ | 12.0 | 286.70 |
| $CH_3COOK$ | 23.1 | 198.14 |
| $MgCl_2·6H_2O$ | 33.1 | 149.50 |
| $K_2CO_3$ | 43.2 | 113.50 |
| NaBr | 59.1 | 71.12 |
| Kl | 69.9 | 48.42 |
| NaCl | 75.5 | 38.00 |
| KCl | 85.1 | 21.82 |
| $K_2SO_4$ | 97.6 | 3.29 |

The water molecule is moved from the salt solution into the soil pores by vapour phase. The liquid and vapour phase net water exchange occurs in the closed container until both of these phases achieve equilibrium (Blatz *et al.*, 2008). The relationship between relative humidity and suction is shown in the Eq. (2.2).

$$u_a - u_w = R\,T/Mg \cdot \ln(P/P_0) \quad (2.2)$$

Where $u_a$ is air pressure, $u_w$ is water pressure, $R$ is constant of perfect gases, T is absolute temperature, $M$ is molar mass of water, $g$ is the gravity acceleration and $P/P_0$ is the relative humidity equal to partial water vapour pressure, $P$ divided by saturated water vapour pressure, $P_0$ (Rabozzi, 2005).

This technique is much more time- consuming if compare to other techniques since the vapour transfer depends on diffusion (Delage *et al.*, 2008). It is normally take one to two months for the soil samples to reach its equilibrium (Tang and Cui, 2005).

### 2.3.2 Soil Suction Measurements

An accurate soil suction measurement and its interpretations is important to understand the soil behaviour. There are two types of soil suction measurement techniques, which are direct soil suction measurement techniques and indirect soil suction measurement techniques (Hu *et al.*, 2010). For the direct soil suction measurement technique, it measures the soil-water system equilibrium by not involving external medium, while the indirect soil suction measurement techniques is the reverse of direct soil suction measurement technique. (Murray and Sivakumar, 2010). In the research of Hu *et al.* (2010), they stated that the direct soil suction measurements included axis-transition technique, tensiometer and suction probe. The indirect soil suction measurements are further divide into 3 categories (matric suction, osmotic suction, and total suction). For matric suction, the technique used are electric conductivity sensors, thermal conductivity sensor, in- contact filter paper, and time domain reflectometry. Squeezing technique and saturation extract method are used for osmotic suction. Lastly, the total suction measurement technique included psychrometer technique, relative humidity sensor, chilled- mirror hygrometer technique and non- conduct filter paper.

## 2.4 SOIL- WATER CHARACTERISTIC CURVE

Soil- water characteristic curve (SWCC) was being investigated in this study. It is defined as the relationship between the soil suction and moisture content of soil (Roopnarine *et al.*, 2014). SWCC is obtained through wetting or drying a soil sample while controlling the changes of moisture content in soil sample. Different soils will give a different soil- water characteristic curve. The soil- water characteristic curve can be affected by many factors, such as type of soil, soil structure, mineralogy, texture, stress history, initial water content, method of compaction, and void ratio (Maaitah, 2012). However, from Maaitah's literature review, the most effective factors are initial water content and stress history of soil. Indeed, SWCC can be generated by several empirical methods, however, it is better to obtain SWCC through laboratory testing due to accuracy (Fredlund, 2007).

SWCC, in general, is representing the basic characteristic of partial saturated soil (Heshmati and Motahari, 2012). Soil- water characteristic curve is actually included drying SWCC and wetting SWCC, where wetting SWCC can be estimated from drying SWCC. The wetting SWCC differs from drying SWCC due to hysteresis and even the starting point of drying curve would be different from the end point of wetting curve as a result of air entrapment in soil.

Suction- water content soil- water characteristic curve is usually plotted as water content versus soil suction. The water content in soil means that the amount of water in soil pores. However, the variables to generate SWCC is slightly different if compare soil science to geotechnical engineering practice. In soil science, normally, volumetric water content, $\theta$, will be used, while in geotechnical engineering practice, gravimetric water content, $w$, is mostly used (Fredlund and Xing, 1994).

# CHAPTER 3

# METHODOLOGY

## 3.1 INTRODUCTION

The characteristics of Red Gypsum found out through laboratory testing. There are 2 characteristics of Red Gypsum being investigated, such as physical and chemical. Each of these characteristics were tested by different tests. For physical characteristic of Red Gypsum, the particle size distribution test, moisture content test, atterberg limit test, free swell test and Lost on Ignition test were done. Other than physical, the chemical properties of Red Gypsum was determined by carrying out X- Ray fluorescence (XRF) and cation- Exchange capacity (CEC).

Besides the physical and chemical properties of Red Gypsum, SWCC of Red Gypsum can be obtained by many techniques which included osmotic and vapour equilibrium technique. In this chapter, the way to carry out all the tests were discussed.