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Physical Characterization / *Caractérisation physique*

RELATIONSHIP BETWEEN MINERAL TYPE AND SORPTION CHARACTERISTICS OF SOIL LINER OF HAMEDAN LANDFILL

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ABSTRACT

The sorption characteristics of soils are a function of several paprameters. In the process of soil-contaminant interaction, the quantity and type of each mineral presents in soil, could behave as an important factor. In this paper a case study, a waste disposal site located in the west part of Iran, is introduced. Samples taken from this site are characterized from geotechnical and geoenvironmental point of view. By performing a set of XRD analysis the quantity and type of different minerals is determined. Having the geotechnical and geo-environmental characteristics of clay samples of this site and making a comparison among the achieved results for soil samples of this site and the results for two marly samples and one pure kaolinite sample used in this study, an attention is taken to establish a relation between soil-contaminant interaction, and mineral type of soil. The results of this paper indicate that the type and quantity of mineral present in soil not only affect the sorption characteristics of soils but also control the geotechnical and the geoenvironmental behaviour of soils that could be an appropriate criterion for waste disposal site selection.

RÉSUMÉ

Les caractéristiques de l'adsorption des sols sont fonction de plusieurs paramètres. Dans le problème de l'interaction sol - contamination la quantité et le type de chaque minéral existant dans le sol doivent comporter comme un facteur important. Pour étudier ce problème nous avons choisi une site dans une partie de l'ouest d'Iran. Après préparation des échantillons, la quantité et le type de différent minéraux ont obtenu par analyse de XRD.une comparaison entre les résultants obtenus de cet étude et les résultants existants pour deux échantillons d'un sol marne, on peut mettre en évidence une relation entre l'interaction sol – contamination et le type de minéral. Ces résultants montrent que le type et la quantité de minéral existant dans le sol influencent non seulement sur les caractéristiques d'absorption mais aussi contrôlent le comportement géotechnique et géoenvironement de sol et peut être un bon critère pour la site choisie.

1. INTRODUCTION

The role of a landfill barrier system is to protect the environment from harmful substance and, especially from wastewater seepage (Ammann & Martinenghi 1993). The use of clay barrier is one of the common methods to prevent contaminant migration from the waste disposal facility to the ground water surface. Clay mineral also can be stabilized to improve such a role. As an example Pluss (Pluss 1993) shows that fly ash from Municipal solid waste-plants can be mixed with clay and compacted for using as a liner in waste disposal projects. In general, the characteristics of soils in their positions determine flow of water (Yong & Warkentin 1975, Yong 2001). In this regard the type of clay minerals makes a major role.

One of the primary problems in evaluation of the performance of marl soils, utilized in the natural state. In fact little effort is paid to characterization of the compositional features of the soil and pore water chemistry. The general definition and perception of marl as a material consisting of a mixture of clay-sized particles (and minerals) and carbonates does not place sufficient significance on the particular roles of the soil fractions. Of considerable interest and concern are palygorskite (known as attapulgite in North America) and sepiolite in marl soils (Grim 1968, Mitchell 1993, Yong and Ouhadi 1997). The role of palygorskite on soil performance has not yet been sufficiently investigated. It is sometimes derived from pyroxenes and amphiboles

(Longchambon 1935). The main factor that distinguishes palygorskite from other clay minerals is its chain-like structure. Water in its chainlike structure is called zeolitic water. Water is combined with cations and anions on the surface and in the zeolitic type channels of its crystal.

On the other hand, the composition of municipal solid waste varies as a function of social attitudes, differences in climate and economic situation. However it is shown that the most important industrial and municipal solid waste components are copper, zinc and lead. By and large, there are several mechanisms in which clay minerals prevent the migration of contaminant to the sub-surface soil. In this regard, the evaluation of soil-contaminant interaction through the evaluation of adsorption characteristics of soil is a common method to evaluate the ability of soil for prevention of contaminant migration. In fact, different clay minerals play different interaction mechanism with contaminants. Even though a lot of attention is taken to the interaction of several clay minerals such as montmorilonite, illite and kaolinite with contaminants, there is little attention to the interaction process of palygorskite clay minerals and contaminants. In this research an attention is given to the interaction of marly soil and heavy metals. Since one of the major minerals of marly soil is palygorskite mineral (Yong and Ouhadi, 1997, Ouhadi and Yong 2001), such a study may contribute to investigate on the interaction of palygorskite and heavy metal contamination. In addition, by studying the interaction of soil samples achieved from a waste disposal site, an effort is made to investigate on the relation between mineral

type and sorption characteristics of soil liner of this landfill. For this purpose a pure kaolinite sample is used to compare the achieved results.

2. MATERIALS AND METHODS

Four types of soil samples are used in this study. The first type includes 10 samples from waste disposal site of Hamedan, the center of Hamedan province located at the west part of Iran, and the other types include a marly sample from Northwest part of Iran known as Tabriz marl, a marly sample from south part of Iran known as south Marl and a pure kaolinite sample. The physico-chemical properties of the first three samples are presented in the Tables 1, 2 and 3.

Table 1. Characteristics of marly soil of Tabriz.

Characteristic	Quantity Measured
Liquid Limit, %	68.2
P.I. %	40.8
TDS (Cmol/Kg)	5.02
CEC (meq/100g)	14.8
EC (dS/m) 1:10, soil-water ratio	0.66
pH (1:10, soil-water ratio)	8.9
Soil Classification	CH
Gs	2.59
Clay fraction	58%

Table 2. Characteristics of south marl.

Characteristic	Quantity Measured
Liquid Limit, %	45.8
P.I., %	24.4
Surface Area (m^2/kg)	74
CEC, (meq/100 g)	42
Carbonate content	25.7%
pH (1:10, soil-water ratio)	8.7
Soil Classification	CL/CH
Optimum water content	14%
Maximum dry density (Mg/m^3)	1.97

Table 3. Characteristics of soil sample of waste disposal site (Hamedan #8).

Characteristic	Quantity Measured
Liquid Limit, %	22.4
P.I., %	3.9
Cohesion (KN/m^2)	47
Friction Angle (degree)	21
Carbonate content	23.3%
Soil Classification	CL/ML
Optimum water content	12.5%
Maximum dry density (Mg/m^3)	1.97

For the south marl sample, XRD analyses show the presence of palygorskite, calcite, quartz, chlorite, kaolinite, dolomite, illite, feldspar, montmorilonite, gypsum, arcanite, and thendernite in decreasing order of abundance. In addition, the main clay fraction of sample taken from waste disposal site was kaolinite with traces of montmorilonite. The quantity of carbonate and quartz is noticeable in this sample as will be addressed.

Furthermore, three different solutions as heavy metal contaminant used in this study. These solutions include, $Pb(NO_3)_2$, $Cu(NO_3)_2$, and $Zn(NO_3)_2$. Solutions of these chemicals prepared within the concentration range of 0 to 5000 ppm. Batch equilibrium testing performed with making 1:10 (Soil: electrolyte) samples. Prepared samples mixed for 24 hours on the end-to end shaker. Following this process, soil-solutions mixtures kept for 96 hours to assure the achievement of complete equilibrium. After that, samples centrifuged for 10 minutes under 5000 rpm condition. The concentration of heavy metals measured at the supernatant by application of an Atomic Adsorption Spectrophotometer (AAS-GBC 932, AB Plus).

On the other hand, to investigate on the effect of pH variation of electrolyte on the adsorption characteristics of soil, with the use of acid (HNO_3), several solutions having acid concentration within 0 to 200 mmol/kg prepared. Following that, electrolytes of $Pb(NO_3)_2$ within the concentration of 0 to 500 ppm prepared with adding specific concentration of acid to them to have pH from 1 to 9. Dry soil samples added to theses solutions to provide soil-electrolyte solutions with the ratio of 1:10. In fact, each electrolyte had a specific concentration of acid and lead as a heavy metal. Following equilibrium process as addressed before, samples centrifuged, and the variation of Pb ion concentration at the liquid phase measured by an atomic adsorption spectrophotometer device. It should be emphasized that due to the low concentration of acid, the acid concentration is reported with the mmol/ kg unit. All of the physical experiments performed based on ASTM standard (ASTM 1992). In addition, all chemical analysis was done using the methods suggested by different authors (Clesceri 1989, Yong et al. 1992, Yong 2001). It should be added that the cation exchange capacity of kaolinite sample was 50 cmol/Kg and its plasticity index was 55.7 with a liquid limit of 85.8.

3. RESULTS AND DISCUSSION

3.1 Soil Classification of Waste Disposal Site

A part of this study is to evaluate the ability of clay liner of waste disposal site of Hamedan, the capital of Hamedan province located in the west part of Iran. Hamedan has a population around 400,000. The waste disposal site of this city is located in the north part of city in the area around 13 kilometers far from the city. Every day between 390-420 ton wastes dispose in this waste disposal site.

To study the soil-contaminant interaction of clay barrier of this site, the area divided to the 10 sections. With taking 10

different samples from this area, several experiments performed to provide a go-environmental-geotechnical soil classification of clay liner of this waste disposal site. With application of several extensive experimental studies (Ouhadi 2003), a soil sample called "Hamedan #8" chosen for the rest of research work. Some of the physico-chemical characteristics of this sample are presented in Table 3. In fact, one of the main objectives of this study was to evaluate the ability of soil sample of this area for contributing of the prevention of contaminant migration to the ground water. In other words, with comparing the soil-contaminant interaction of this site and three other soil samples used in this study, the evaluation of soil behaviour of this site from geo-environmental point of view is provided.

3.2 Evaluation of Soil Samples -Contaminant Interaction

For evaluation of soil contaminant interaction, several batch equilibrium testing performed using the four mentioned soil samples, and three types of artificial contaminant as addressed before. These include the interaction of soil samples and, copper, lead and zinc cations as an artificial contaminant. These will be discussed in the following.

3.3 Soil- Copper Interaction

Figure 1 shows the evaluation of soil and copper ions interaction. The concentration of copper ions is varied within the range of 50 to 5000 ppm. To make sure about the experimental procedure, for each chosen concentration, a blank sample is prepared and its concentration is measured and controlled with calculation. Five different concentrations are provided including, 50, 100, 500, 1000, and 5000 ppm. With preparing several batch test experiments the interaction of artificial contaminants with soil samples are monitored according to the experimental procedure addressed before. Figure 1 shows the results of these batch equilibrium experiments for those four samples of Tabriz marl, south Marl, kaolinite sample and soil sample #8 from waste disposal site. In the Figure 1, the horizontal axis shows the equilibrium concentration of copper ion (Cu) at the end of batch equilibrium testing measured at the pore fluid. These measurements performed after 24 hours keeping soil-solution on the shaker and centrifuging for separation supernatant from solid fraction. At this Figure, the vertical axis indicates the variation of copper ions adsorbed in soil samples. As can be seen in this Figure, the south Marl has the highest adsorption characteristic in comparison to the other three samples. Tabriz marl, sample from waste disposal site and Kaolinite has less adsorption characteristics, respectively.

To provide more cleared comparison between the adsorption characteristics of these samples, the variation of retained copper in soils samples is presented in the Figure 2. The horizontal axis of Figure 2 shows the variation of concentration of Cu cations in solution at the beginning of batch test and before processing the batch test. The vertical axis presents the variation of percentage of retained copper cation as a contaminant in the soil fraction. As can be seen in this Figure, the difference between the behaviour of kaolinite and other soil samples used in this study observes

both in low and high concentration of contaminants. In this regard, at the low concentration of contaminant up to 500 ppm, all soil samples except kaolinite, adsorbed and retained the whole added contaminant. With increasing the concentration of copper, south marl adsorbs most part of added artificial contaminant. While at the 5000-ppm concentration of Cu, the kaolinite sample only adsorbs 20% of added copper ions.
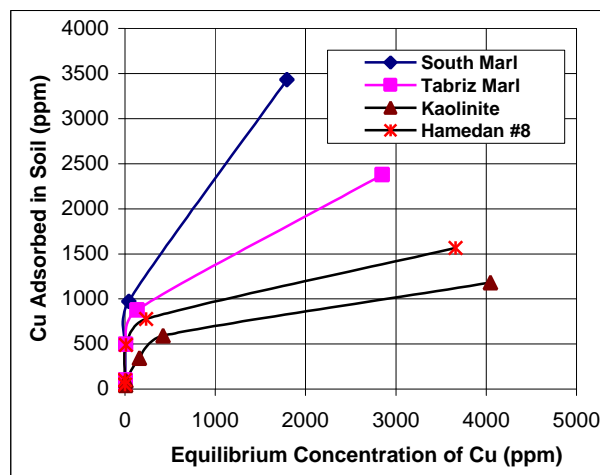

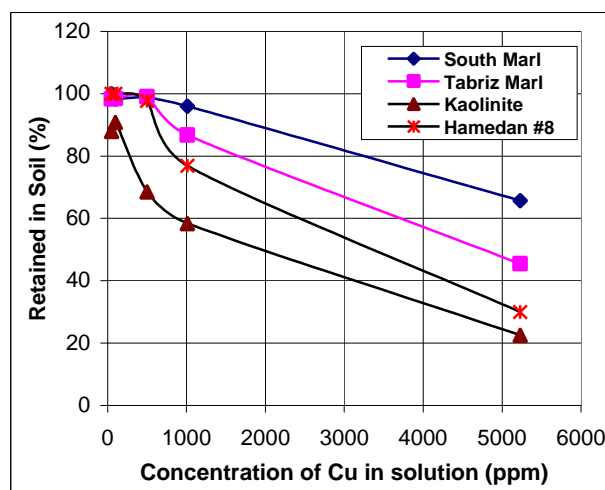Figure 1. Variation of soil-copper cations interaction

Figure 2. Retained contaminant in soil samples

This performance not only can be attributed to the low cation exchange capacity of kaolinite in comparison to that of other soil samples, but also can be attributed to the different types of mineral appears on the soil sample. As addressed before, the main mineral fraction of south marl is palygorskite with a relatively low cation exchange capacity and open structure (Ouhadi and Yong 2001). This open structure provides much more ability for soil to adsorb and retain contaminant. This open structure, not only provides

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more adsorption at high concentration of contaminant, but also makes the soil sample to adsorb higher quantity of contaminant up to 1000 ppm copper ion in pore fluid. As an example, for sample having 1000 ppm copper ion, still more than 96% of contaminant is retained by south marl. With increasing the concentration of contaminant and saturation of open structure of south marl with copper ion, the cation exchange capacity of this soil sample contributes to the adsorption of contaminant. This makes the south Marl to adsorb more than 65 % of contaminant at the concentration of 5000 ppm. It is important to note that the south marl with having relatively lower cation exchange capacity in comparison to kaolinite samples still has higher contaminant adsorption ability. In the other words, the open structure contributes to the contaminant interaction as much as the cation exchange capacity of soil.

3.4 Soil –Zinc Cation Interaction

To investigate on the process of interaction of soil samples and Zinc cations, a set of batch equilibrium experiments performed according to the sample preparation as addressed before. Figure 3 shows the variation of adsorbed
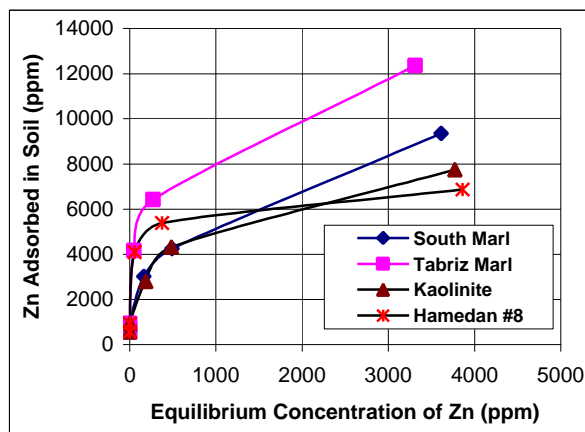

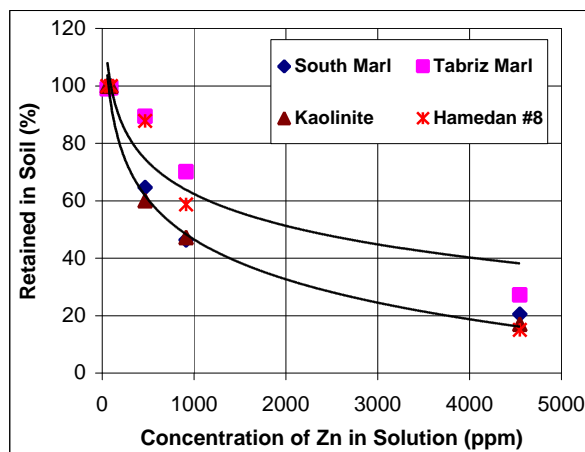Figure 3. Variation of soil-Zinc cation interaction

Figure 4. Retained contaminant in soil samples

zinc cation versus the equilibrium concentration in these series of experiments. As can be seen, according to these results, kaolinite sample adsorbed less zinc cation in comparison to other soil samples. In addition, the Tabriz marl has the highest adsorbing characteristics than that of other samples. South Marl still has relatively high adsorbing characteristics. The lower adsorbing characteristics of south marl (Figure 4) in comparison with the results presented in Figure 2 for copper ion can be attributed to the selectivity behaviour of clay soils (Ouhadi 1998, Yong 2001).

3.5 Soil-Lead Cation Interaction

To investigate on the selectivity of clay minerals for contaminant adsorption, a set of batch equilibrium experiments performed using soil samples and lead nitrate. Figure 5 shows the lead-soil sample interaction in these experiments. As can be seen, with the use of lead as a contaminant in these series of experiments, almost the whole concentration of lead within the range of 50 to 5000 ppm is adsorbed by all samples. Such a performance can be attributed to the both selectivity behaviour and pH effect during soil- contaminant interaction. In other words, during the process of soil-contaminant interaction, due to the different pH of heavy metals, one will be faced with different adsorption characteristics, which is a result of variation of soil buffering capacity.
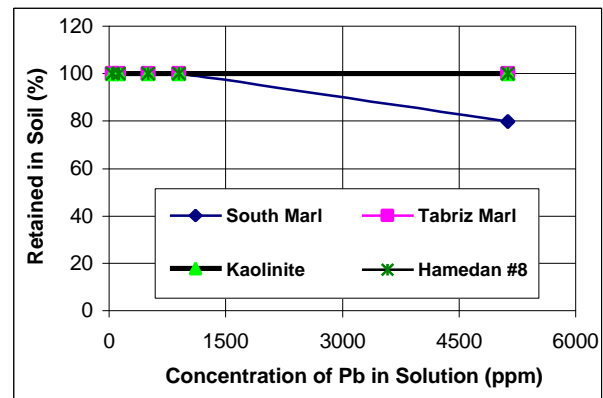

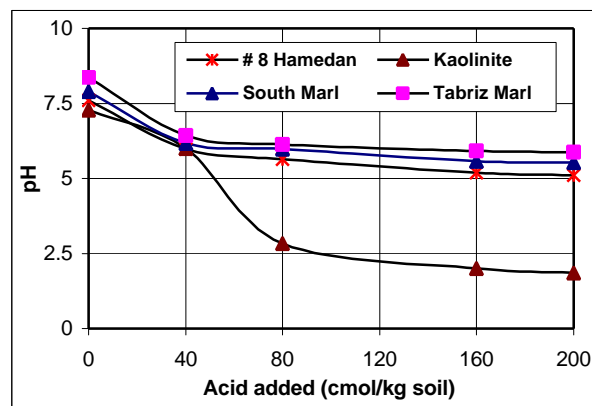Figure 5. Variation of soil-Lead cation interaction

Figure 6. Buffering capacity evaluation of soil samples

3.6 Buffering Capacity Evaluation of Soil Samples

The ability of a soil to retain contaminant (mainly heavy metals) can be achieved by determination of soil buffering capacity. This is considered both from physical and chemical point of view. The principal item of relevance is the ability of the soil system to maintain a natural pH level (within acceptable limits) in spite of input of acidic or alkaline contaminates leachate (Yong 2001). To attempt to relate the above mentioned results, the buffering capacity of soil samples evaluated by adding specific concentrations of acid to soil samples and measuring the pH of soil samples. These results are presented in Figure 6.

The horizontal axis of this Figure shows the quantity of acid added to soil samples. The vertical axis indicates the measured pH after addition of acid and equilibrium. As can be seen in this Figure, two types of behaviour can be observed. These behaviors can be classified at low and high concentration of acid. In this regard, at low concentration of acid within the range of 0-to 40-cmol/kg soils, the rate of decrease in pH is relatively higher than the variation of pH at the higher concentration of added acid. In addition, kaolinite sample has the lowest buffering capacity than other samples as already being addressed by different authors (Quigley 1984, Yong et al. 1992, Ouhadi 1998, Yong 2001). At the higher acid concentration, the pH of all soil samples except kaolinite does not significantly change. This performance can be attributed to the buffering capacity of soil samples mainly due to the presence of carbonate mineral as addressed in characterization of soil samples.

4. CONCUDING REMARKS

The results of this research provide the following conclusions;

1- Mineral type and quantity of each mineral of clay liners may have a noticeable effect on the process of soil-contaminant interaction.

2- Buffering capacity of waste disposal liner is also affected by variation of different minerals and their quantity in soil. In this regard, the open structure of palygorskite of marly soil contributes to prevention of contaminant migration by its open structure and adsorption characteristic.

3- Even though the major clay fraction of the waste disposal site is kaolinite with low buffering capacity, due to the presence of carbonate in this site, the Hamedan #8 sample shows a higher contaminant adsorption than the pure kaolinite sample.

4- One of the best criteria for selection of waste disposal site is evaluation of soil-contaminant interaction in conjunction with XRD analysis to take into consideration the long-term performance of soil. This is an important point since the soil buffering capacity varies due to the changes in pH and concentration of heavy metals.

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