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RETENTION OF TOXIC HEAVY METALS IN CEMENT STABILIZED SOIL CONTAINING HUMIC ACIDS

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ในงานวิจัยนี้ได้ทำสกัด และศึกษาสมบัติทางเคมีของกรดฮิวมิกจากดินปนเปื้อนโลหะหนัก 6 ชนิดได้แก่ แคดเมียม ทองแดง โครเมียม นิกเกิล ตะกั่วและสังกะสี และศึกษาการดูดซับของโลหะดังกล่าวบนดิน พบว่าการดูดซับของโลหะทุกชนิดลดลงเมื่อมีกรดฮิวมิก ศึกษาการคงตัวของโลหะหนักในดินที่มีกรดฮิวมิกโดยผ่านการปรับเสถียรและทำให้เป็นก้อนแข็งด้วยปูนซีเมนต์พอร์ตแลนด์ ปริมาณกรดฮิวมิกและโลหะในดินมีผลทำให้ความทนต่อแรงอัดของก้อนคอนกรีตลดลง ทำการทดสอบคอนกรีตตามวิธีของ TCLP พบว่ากรดฮิวมิกสามารถ ลดการชะละลายของแคดเมียมและนิกเกิลลงอย่างมีนัยสำคัญ

ศึกษาพฤติกรรมของการชะละลายของโลหะภายใต้ตัวแปรต่างๆ ได้แก่ พีเอช ชนิดของน้ำชะคือ น้ำปราศจากไอออน สารละลายโพแทสเซียมไนเตรต กรดอะซีติก และกรดฮิวมิกที่ความเข้มข้นต่างๆ อัตราส่วนระหว่างน้ำชะต่อคอนกรีต ระยะเวลาสัมผัส พบว่าพีเอชมีผลต่อการชะละลายของโลหะคือในภาวะที่เป็นกรดและเบสสูง การชะละลายจะสูงกว่าช่วงพีเอชที่เป็นกลาง ชนิดของน้ำชะมีผลต่อการชะละลายซึ่งจะแตกต่างกันสำหรับโลหะแต่ละชนิด โดยทั่วไปน้ำปราศจากไอออนและสารละลายโพแทสเซียมนเตรตให้ผลการชะที่ไม่แตกต่างกัน กรดอะซีติกจะชะโลหะได้ดีที่ความเข้มข้นมากส่วนกรดฮิวมิกที่ความเข้มข้นมากมีความสามารถชะโลหะได้ลดลง โลหะจะละลายได้มากขึ้นเมื่ออัตราส่วนระหว่างน้ำชะต่อคอนกรีตเพิ่มขึ้น เมื่อเปรียบเทียบคอนกรีตที่เติมและไม่เติมกรดฮิวมิกพบว่า การชะละลายมีความแตกต่างอย่างชัดเจนในกรณีของนิกเกิลและตะกั่ว ผลการศึกษาการชะละลายของก้อนคอนกรีตที่เวลาต่างๆ พบว่าเมื่อเวลาเพิ่มขึ้นโลหะละลายได้มากขึ้น แต่ฟลักซ์การชะละลายลดลง สามารถแยกพฤติกรรมการชะละลายในระยะยาวของไอออนต่างๆได้ 3 ประเภท คือ (1) ไอออนที่การชะละลายขึ้นกับความเข้มข้นของสารละลายในรูพรุนของคอนกรีตเพียงอย่างเดียว ได้แก่ ไอออนของโซเดียมและคลอไรด์ (2) ไอออนที่ปริมาณกรดอะซีติกและกรดฮิวมิกในน้ำชะมีผลต่อการชะละลาย ได้แก่ไอออนของแคลเซียม ทองแดงและแคดเมียม และ (3) ไอออนที่ปริมาณกรดอะซีติกมีผลต่อการชะ แต่ปริมาณกรดฮิวมิกในน้ำชะไม่มีผลต่อการชะละลาย ได้แก่ไอออนของโครเมียม นิกเกิล ตะกั่วและสังกะสี

ภาควิชา..............เคมี..ลายมือชื่อนิสิต...
สาขาวิชา.............เคมี.......................................ลายมือชื่ออาจารย์ที่ปรึกษา...
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The properties of extracted humic acids from heavy metals (Cd, Cu, Cr, Pb, Ni, and Zn) contaminated soil had been studied to understand of their influence on metal sorption onto soil. The results demonstrated that humic acids decreased metal sorption onto soils. The retention of six metals in cement based -stabilized soil containing humic acids had been studied. The compressive strength of concrete mortar decreased as the amount of metals and humic acids in soil increased. The TCLP test was performed on the stabilized soils, the results elucidated that humic acids in soils decreased significantly the leached amounts of cadmium and nickel.

The leaching behaviors under the factors affecting metal releasing were investigated. These factors were pH, type of leaching medium (deionized water, potassium nitrate, acetic and humic acid solutions), liquid to solid ratio and contact time of leaching. The metals could be highly released at low and high pH, while their releases were moderate at neutral pH. The amounts of released metal depend on the type of leaching media. The leaching by de-ionized water and potassium nitrate solutions were not different. The metals were well released when high concentration of acetic acid was used. The metal solubilizations from stabilized soil with and without humic acids were distinguished different especially in the case of nickel and lead species. The increase of contact time of leaching enhanced the cumulative amount of leached metals; however, the leaching flux reduced. The ion species in the stabilized soil could be categorized into three groups by their different leaching behaviors. (1) Ions whose leachability only depend on the concentration of mobile ions in pore water (Na, and chloride ions); (2) Ions whose leachabilities significantly depend on the concentration of both acetic acid and humic acids in leachants (Cu and Cd); (3) Ions whose solubilities were not affected by humic acids, but influenced by acetic acid in leachants (Cr, Ni, Pb, and Zn).

Department: Chemistry.. Student's signature……................................

Field of study: Chemistry...Advisor's signature……...…………......……..

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ABBREVIATIONS

%w/v	-Percent weight by volume
%w/w	-Percent weight by weight
°C	-Degree Celsius
°F	-Degree Fahrenheit
ΔH	-Enthalpy change
µm	-Micrometers
[M]	-Metal concentration
µg	-Microgram
AAS	-Atomic Absorption Spectrometry
AcOH	-Acetic acid
ANC	-Acid neutralization capacity
AHA	-Aldrich humic acid
ASTM	-American Standard for testing of Materials
CEC	-Cation Exchange Capacity
cm	-Centimeter
cm/s	-Centimeter per second
cm^{-1}	-Per centimeter
CS	-Compressive strength
d	-Day
D_4/D_6	-The logarithm of absorption ratio at 456 nm per 660 nm
dia.	-Diameter
DSC	-Differential Scanning Calorimetry
E_4/E_6	-The ratio of the logarithm of absorption at 400 nm to 600 nm
g	-Gram

g/cc	-Gram per cubic centimeter
h	-Hour
HA	-Humic acid
H_f	-Heat of fusion
HS	-Humic added soil
ICP-AES	-Inductively Coupled Plasma –Atomic Emission Spectrometry
IHSS	-International Humic Standard Society
K_d	-Diffusion coefficient
kg	-Kilogram
KNO_3	-Potassium nitrate
L/S ratio	-Liquid to solid ratio
LOI	-Loss of ignition
m	-Month
M	-Morality
M.W.	-Molecular weight
me	-Milliequivalents
mg kg^{-1}	-Milligram per kilogram
MHS	-Metal added to humic soil
ML	-Monolithic leaching
min	-Minute
MMF	-Maximum mobile fraction
mL	-Milliliter
mm^2	-Square Millimeter
mmol kg^{-1}	-Millimole per kilogram
mol L^{-1}	-Mole per liter
MPa	-Megapascal
MS	-Metal spiked soil

N	-Normality
N	-Newton
NH_4OAc	-Ammonium acetate
nm	-Nanometer
OM	-Organic matter
OS	-Original soil
PAS	-Photoaqoustic Spectrometry
PE	-Polyethylene
PET	-Polyethylene tetraphatalate
pm	-Picometer
ppm	-Parts per million
PW	-Pore water
rpm	-Round per minute
RWC	-Residue water content
s	-Second
S/L ratio	-Solid to liquid ratio
S/S	-Stabilized/ Solidified
SHA	-Soil humic acid
TCLP	-Toxicity Characteristic of Leaching Procedure
T_f	-Fusion temperature
TGA	-Thermal gravimetric analysis
US EPA	-The United State Environmental Protection Agency
USDA	-The United State Department of Agriculture
w	-Week
y	-Year

CHAPTER I

INTRODUCTION

1.1 State of the problem

The increasing urbanization and industrialization as well as the increase of world population have resulted in the pollution of the environment. The land disposal of industrial wastes is one of the becoming serious problems. Heavy metals are concerned because of their increasing abundance in the environment which are released into soils from a wide range of natural and anthropogenic sources, as well as, their relatively high toxicity even at low concentration [1-3]. Once released into the soil matrix, heavy metals can impact environmental quality and human health via ground water and surface water [4-6]. Accordingly, complex treatment processes or immobilization technologies to prevent and control the pollution have been established.

Most common treatment options for metal-contaminated sites are stabilization and solidification (S/S) technology that can be employed both ex situ and in situ. However, there are some factors limiting the applicability [7-8], and effectiveness of the in situ S/S in long term including:

(1) Future usage of the site may "weather" the materials and affect ability to maintain immobilization of contaminants

(2) Certain wastes are incompatible with variations of this process. Treatability studies are generally required.

1.2 State of art in humic substances and S/S technologies

As the development of humic chemistry is interesting nowadays, a number of scientists who study about this subject and their publications are more increasing than the early centuries. The research activity has been focused continuously in various branches and applications, e.g. process of formation (humification), statistical modeling of humification, complexing ability of humic acids [9], characterization of humic matter in difference origin source [10], molecular structure [11], kinetics and adsorption isotherm of humic – metal ion binding [12-15] etc. Furthermore, considered suitability procedures for extraction, and fractionation both of terrestrial and aquatic humic matter have been challenged by a number of scientists until now. In agrology, with the increased knowledge in humic acid chemistry, humic acid is now realized as an important component in soils, which play a role in plant growth. The effect on soil physical and chemical properties, the soil redox system and soil biological properties are currently in topic of researches. In environmental science, humic matter plays a significant role in the preservation of soil organic matter, mobilization/immobilization of elements, biological detoxification, and degradation of the soil ecosystem. Moreover, some reports considered humate (salt of humic acid) as an innovative approach for the removal of heavy metals in water and soils [9]. Humate materials sometime have potentials in soil and wastewater remediation. They can be very effective in removing excess of pesticide from sandy soils containing very low organic matter. They incorporate high ion exchange capacity and ability to adsorb and detoxify metals [16]. The catalytic effect of humic substances on the degradation of organic chemicals in water and soil environments is particularly strong in photooxidation and biooxidation of large molecules such as phathalates, fatty acids, and polyaromatic hydrocarbons (PAHs). These properties make humic substance an attractive material for bioremediation. Humate was used to treat waste brine at US Army Facility, removing As, Hg, and Pb to meet EPA TCLP requirements. Treatability tests were also conducted using humate for the removal of radionuclide contaminants.

The researches on solidification/stabilization of solid wastes are interesting; including methodology [20] and leaching model [18, 21-22], as much as the study of the humic matter in environment. However, knowledge of the long-term fate of contaminants in landfill and its relation to waste processes is, as yet, insufficient and needed for additional research [19] especially the information such as leaching rate of heavy metals contaminated soils in humic phase in the field of the cement-based management. Consequently, it has been necessary to study towards better knowledge in those situations both of short and of long - term perspectives [17, 19].

1.3 Rationale

The importance of humic acids originates from their ability to interact with heavy metals and other chemical pollutants, and thus affect their mobility in the environment [23-26]. The most important functional groups in the humic molecules are carboxyl and phenolic – OH groups, defined as the total acidity. The interaction comprises adsorption, cation exchange, and complexation. These reactions play an important role in soil ecosystem. Results of studies on chelation and complexation indicate that metal chelation by humic acids appears to be more effective than that by fulvic acids, although humic acids are expected to be smaller in negative charges when they are protonated.

Owing to the complex solubility effects to transport of metals in soil environment, the complexes can migrate in long distance and may pollute the ground water or reappear at other locations. Fortunately, the heavy metals Cu, Zn, Mn, Co, Hg, and Cd, originating from sewage sludge; are deactivated due to chelation by humic acids. The effect of complexation formation on sorption is dependent on the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH, ionic strength, and redox potential.

By reason of the stabilization and solidification (S/S) refers to treatment processes to improve the physical characteristics of the waste and/or reduce the contaminant solubility prior to land filling, the literature or laboratory data that include the presence of humic acids are needed. If we ignore their existence, it may lead to significant overestimation or underestimation of metal mobility in stabilized products.

1.4 Objectives

In order to assess the long -term effectiveness of S/S technologies, the influence on the metal mobility/immobility should be taken into investigation especially in the contaminated soil containing humic substances or during in the humic phase. The change of leaching behavior may affect to retain or release metals. For example, changing pH during the humic phase may lead to a substantial degradation of the stabilized concrete and thus increase the solubility of metals.

It is crucial that there is a need to systematize, understand, and quantify the long - term process and to evaluate the flux of metal leaching. The overall objectives of this research are:

(1) Study of the influence of humic acids to cement – based stabilized heavy metals contaminated – soil.

(2) Study of leaching behavior of heavy metals containing cement – waste mortar carried out with a solution containing humic acids as leachant.

CHAPTER II

THEORY and LITERATURE REVIEW

2.1 Solidification and Stabilization Technologies [7-8, 27-30]

There is a very wide range of remediation methods available to tackle contamination although three broad approaches can be distinguished:

1. Engineering approaches- there are primarily the traditional methods of excavation and disposal to landfill, or the use of appropriate containment systems
2. Biological, chemical, and thermal approaches
3. Natural attenuation

Solidification involves the formation of a solidified matrix that encapsulate hazardous waste into a solid material of high structural integrity. Encapsulation involves either fine waste particles (microencapsulation) or a large block or container of wastes (macroencapsulation). Stabilization, also referred to as fixation; usually utilizes a chemical reaction to convert the hazardous wastes to a less soluble, mobile, or toxic form; thus minimizing their potential migration offsite. Solidification/Stabilization (S/S) processes utilize one or both techniques. The S/S can be operated in various ways, in which recipe development and control of a stable and durable -product is a main objective.

S/S technologies can immobilize many heavy metals, certain radionuclides, and selected organic compounds while decreasing waste surface area and permeability for many types of sludge, contaminated soils, and solid wastes. Common S/S agents include Type I Portland cement or cement kiln dust; lime, quick lime, or lime stone; fly ash; various mixtures of these materials; and various organic binder (e.g. asphalt). The mixing of wastes and S/S agents can occur outside of the ground (ex situ). During in situ operations, S/S agents are injected into and mixed with the waste and soil up to depths of 30 to 100 feet using augers.

2.1.1 Technology drawback

Although S/S technology is currently being used to treat a variety of wastes contaminants and as metals, there are some factors that may limit the applicability and effectiveness of the in situ S/S. **Table 2.1** summarizes the advantages and disadvantages of the stabilization and solidification.

Table 2.1 Advantages and disadvantages of stabilization and solidification

Advantages	Disadvantages
- Applicable to inorganic and organic contaminants, although organics are less proven - Applicable to soils, sludge and liquids - Improved handing and geotechnical properties - Rapid treatment possible - Ex situ methods relatively easy to apply	- Contaminants contained rather destroyed or detoxified - Increase in volume of material following treatment - Some process produce heat which can cause gaseous emissions that required capture and subsequent treatment - Quality assurance measures needed, especially for in situ methods - Uncertainty over long term performance, especially with organic contaminants thus special proprietary binding agents will be necessary - Long term monitoring required

Factors that may interfere with S/S processes involve physical mechanisms, chemical mechanisms, and environmental conditions that can affect the concrete matrix structure. Physical mechanisms that can interfere with the S/S process include incomplete mixing due to the presence of high moisture or organic chemical content resulting in only partial wetting or coating of the waste particles with the binding agents and the aggregation of untreated waste into lumps. Wastes with high clay content may clump and interrupt the polymerization chemistry of the S/S agents. Wastes with a high hydrophilic organic content may interfere with solidification by disrupting the gel structure of the curing cement or pozzolonic mixture. The potential for under mixing is greatest for dry or pasty wastes and least for freely flowing slurries. All in situ systems must provide for the introduction and mixing of the S/S agents with the waste in the proper proportions in the surface or subsurface waste site environment. Quality control is inherently more difficult with in situ products than with ex situ products.

Chemical mechanisms that can interfere with S/S of cement - based systems include chemical adsorption, complexation, precipitation, and nucleation. Known inorganic chemical interferants in cement-based S/S processes include copper, lead, and zinc, and sodium salts of arsenate, borate, phosphate, iodate and sulfide. Sulfate interference can be migrated by using a cement material with low tricalcium aluminate content (e.g., Type V Portland cement). Problematic organic interferants include oil and grease, phenols, surfactants, chelating agents, and ethylene glycol. For thermoplastic micro- and macroencapsulation, stabilization of a waste containing strong oxidizing agents reactive toward rubber or asphalt must also be avoided. Pretreating the wastes to extract chemically potential interferants should minimize these problems, but the cost effective must also be lost, depending on the characteristics and volume of the waste and the type and degree of pretreatment required. Organic polymer additives in various stages of development and field testing may significantly improve the performance of the cementitious and pozzolanic S/S agents with respect to immobilization of organic substances, even without the addition of sorbents.

Volume increases associated with the addition of S/S agents to the waste may prevent returning the waste to the land whereas landfill volume is limited. Where post-closer earthmoving and landscaping are required, the treated wastes must be able to support the weight of heavy equipment. The EPA recommends a minimum compressive strength of 50 to 200 psi; however, this should be a site – specific determination.

Before implementation of S/S technology, environmental conditions must be considered. For example, extremes of heat, cold, and precipitation can adversely affect S/S applications. In cement - based S/S processes the engineering properties of the concrete mass produced for the treatment of the waste are highly dependent on the water/waste ratio and the degree of hydration of the cement. High water/cement ratios yield large pore sizes and thus higher permeability. These factors may not be readily controlled in environment applications of S/S, pretreatment of the waste may be required.

Scale up for S/S processes from bench - scale to full-scale operation involves inherent uncertainties. Variable such as ingredient, flow rate control, materials mass balance, mixing, materials handling, and storage along with the weather compared to the more controlled environment of the laboratory, all may affect the success of a field operation. These potential engineering difficulties emphasize the need for a demonstration prior to full-scale implementation.

2.1.2 Cement - based technology [7, 27, 30-31]

Cement- based binders and stabilizers are common materials used for implementation of S/S technologies. Cement-based stabilization is suitable for inorganic wastes, especially those containing heavy metals. The most common cement is Portland cement, hydraulic cement which is made by firing a mixture of limestone and clay (or other silicate) in a kiln at high temperatures. The kiln produces a clinker, which is ground to a powder that is a mixture of calciumsilicate, aluminates, aluminoferrites and sulfates. The main constituents are tri-and dicalcium silicate. Cement chemically reacts with water to form a solid cementitious matrix which improves the handling and physical characteristics of the waste. The pH of the water raises, this can help precipitating and immobilizing some heavy metal contaminants. The metals are retained in the form of insoluble hydroxide or carbonate salts within the hardened structure.

Waste materials are mixed with cement followed by addition of water for hydration forming a crystalline structure. Reactions occur during the hydration of Portland cement as shown in **Fig. 2.1**.

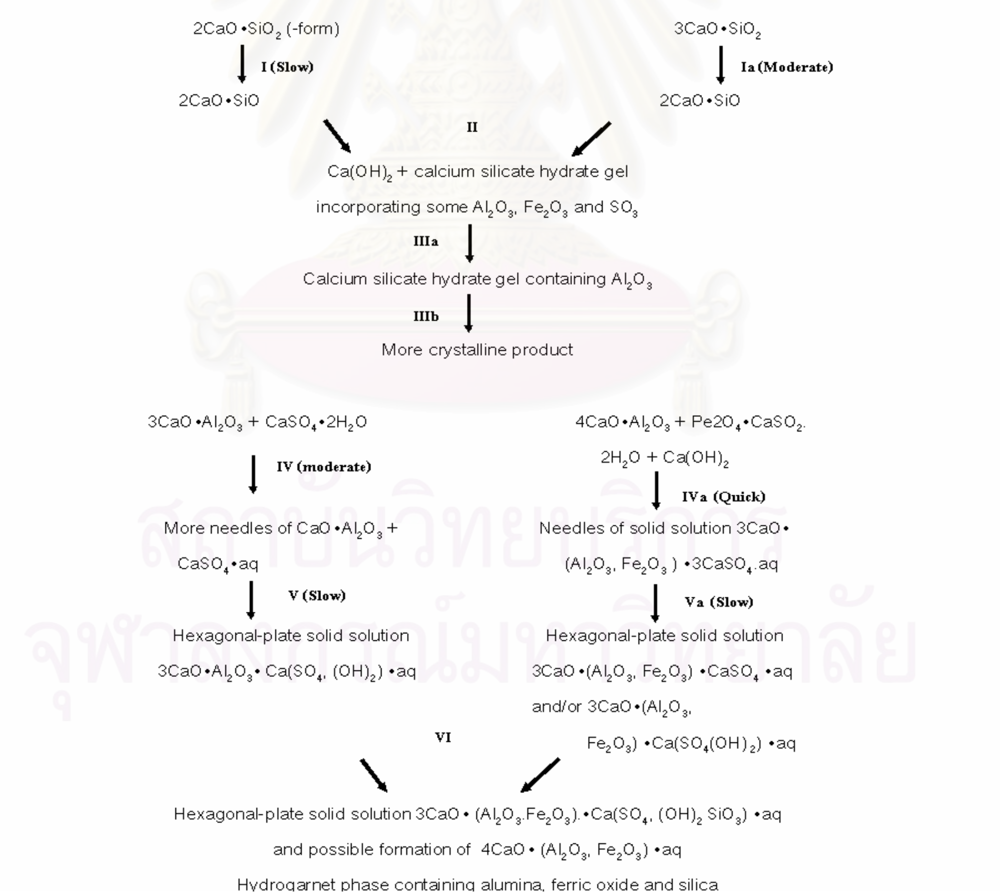


Figure 2.1 Portland cement reactions

2.1.3 Assessment of the effectiveness of stabilization

A wide range of performance tests may perform in conjunction with S/S treatability studies to evaluate short- and long-term stability of the treated materials. These include total waste analysis for organics, leachability using various methods, permeability, unconfined compressive strength (UCS), treated waste and/or leachate toxicity endpoints, and freeze/thaw and wet/dry weathering cycle tests performed according to specific procedures. The selection of appropriate testes and the interpretation of the tests depend on the objectives and/or goals of the stabilization program. These tests are classified into three approaches.

1.) Extraction and Leaching Tests

Leaching tests are listed in **Table 2.2**. The reasons to conduct a leaching are: as a regulatory test run to provide the basis for a consistent and uniform decision- making process, as a predictive test run to generate data that can be used to model real – world contaminant migration, and as an investigatory test run to study the basis binding mechanism, interference factors, and the underlying principles of stabilization technology. The main factors affecting leachability of the stabilized materials are the alkalinity of stabilized products, the surface to volume ratio of the waste, and the tortuosity. Because leaching test types differ in goals and methods, the result of each leaching test type could not be directly compared with others. Therefore, the proper selection of leaching test should be importantly accounted for helping the assessment of the effectiveness of stabilized materials especially on purpose to apply to actual field scenario.

Table 2.2 Leaching test methods

- Paint filter test
- Liquid release test
- Extraction procedure toxicity test (EPTox)
- Synthetic precipitation leaching procedure (SPLP)
- Sequential leach test (sequential chemical extraction)
- Equilibrium leach test
- Dynamic leach test
- Multiple extraction procedure
- Toxicity characteristic leaching procedure (TCLP)
- Modified uniform leach procedure (ANS 16.1)

The toxicity characteristic leaching procedure (TCLP) is widely used to evaluate the effectiveness of stabilization and adopted by the US EPA under the Hazardous and Solid Waste Amendments of 1984. In this method, the stabilized material is crushed into particles smaller than 905 mm. The extraction fluid is prepared with water and diluted acetic acid to obtain a pH of 2.88 ±0.05, selected to mimic conditions in the municipal landfill. The crushed material is mixed with acetic acid extraction liquid for a week, in a liquid- to- solid weight of 20:1, and agitated in a rotary extractor for a period of 18 hours at 30 rpm and 22 ° C. After 18 hours of agitation, the sample is filtered through a 0.6 to 0.8 μm glass fiber filter, and the filtrate is defined as the TCLP extract. This TCLP extract is analyzed for a wide variety of hazardous waste constituents including volatile and semivolatile organics, metals, and pesticides. The results of the extract analysis are compared to the regulatory level shown in **Table 2.3** to determine the non hazardous classification.

2.) Chemical test methods

The type of analysis and the analytical procedures are frequently specified in the leaching procedure by citing standard methods or U.S. EPA protocols. Chemical tests preformed on the leachate or soil frequently employed to evaluate the effectiveness of stabilization included total waste analysis for metals by ICP spectrometry or AAS and for organics by GC and MS, total organic carbon, loss on ignition, pH, FTIR, DSC and TGA.

Table 2.3 shows the maximum metal concentration of contaminants for the toxicity characteristics

Metal contaminant	**Regulatory level,** mg L^{-1}
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

3.) Physical, engineering, and durability property tests

Table 2.4 Physical, engineering, and durability property tests

Property	Purpose
Physical properties	
Moisture content	Phase calculations (saturation, void ratio)
Wet and dry bulk density (unit weight)	Stress and volume calculations
	Phase calculations (saturation, void ratio)
Specific gravity	Classification descriptor (e.g., distinguishes sand, silt, or clays)
Particle size distribution	
Pocket penetrometer	As- mixed strength
Microstructural examination by : X- ray diffraction, Optical microscopy, SEM (scanning electron microscopy)	Crystallization
Supernatant formation during curing	Curing time
Rate of setting	Excess liquid in mixture
Engineering properties	
Strength	Stability analysis
Compressibility (consolidation)	Settlement analysis
Hydraulic conductivity	Flow and transport calculations
Durability properties	Long - term integrity
Wet/dry, Freeze/thaw	

These tests are adapted from the civil engineering area to evaluate the physical integrity and engineering properties, listed in **Table 2.4** with their purpose.

2.2 Humic Acids

2.2.1 Chemical structure and properties

Humic substances are biological-chemical-geological decomposition products of the earthy life. They are composing the greatest part of the organic substances (biomass) on the Earth. They are yellow to dark brown polymers, contained in all soils, waters, and organic-containing sediments [32]. One of the central problems with humic substances is their heterogeneous composition [25] with ligands sites that cannot be characterized in terms of their nature and 3- dimensional structure of ligand atoms [33]. The chemical composition of humic substances can vary in space and time. Decomposition process of the earthy biomass can be divided into two phases: humification and carbonization.

The so called recent humic substances have been formed during the humification and the fossil humic substances during the carbonization process. Starting substances for forming humic acids have been the mortified vegetable parts, which have been transformed during chemical-biological oxidation-reduction processes. Humic substances are often classified based on chemical analysis, in which three fractions are found: humin; insoluble at high pH, humic acids; soluble in acid ($pH \leq 1$ and insoluble at high pH), and fulvic acids; water-soluble under all pH conditions [13, 32, 34].

Humic acids are often considered to be polydisperse [32], structured polyelectrolyte of an amphiphilic nature. Humic acids are thought to be complex aromatic molecules with amino acids, amino sugars peptides, aliphatic compound involved in linkages between the aromatic groups. They have a broad molecular weight distribution and high chemical heterogeneity. Dissociation of humic acids functional groups results in the net negative charge of macromolecules in the wide pH range, and determines high affinity to humics toward complexation, as well as high stability of humic colloids in the natural water. Due to their high solubility in water [13], humic acids can easily be transported in the aqueous phase through soil and other natural waters and it is well established that they play an important role in the distribution of contaminants in the environment [14]. Contaminants binding to humic acids also significantly impact the total and free contaminant concentration presenting in the surface and ground waters. The free contaminant concentrations are highly relevant to their bioavailability and toxicity. Furthermore, the mobility of contaminants through ground waters due to fresh water dynamics is an important factor to consider when evaluating the risk associated with contamination. Contaminant solubility and mobility in natural water can either be reduced by binding to precipitated humic matter or increased by binding to dissolve humic matter.

2.2.2 Extraction, Fractionation and Characterization of humic substance

Several methods have been developed and are currently available for extraction and isolation of humic substance from soil to fractionate them before further investigation. Chromatographic, spectrometric, and spectroscopic methods have been used to elucidate their structure and function.

The International Humic Acid Society (IHSS), Soil Science Society of America has published a general procedure for the fractionation and isolation of humic substances. The method recommended that NaOH to be most effective in the quantitative removal of humic matter [34]. The basis and simplified separation scheme is presented in **Fig. 2.2**. Preparation of pure humic acids and fulvic acids require additional refining steps, such as reprecipitation and HCl / HF treatment for the removal of inorganic impurities.

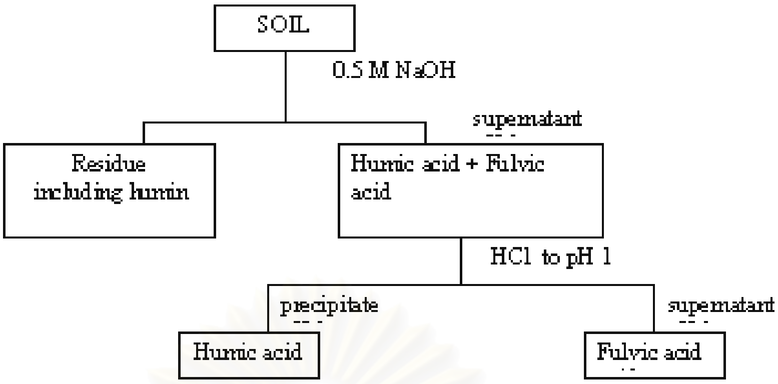


Figure 2.2 Separation scheme for soil humic substances

Separation methods play an important role in the examination of humic substances with heavy metals and others chemical pollutant. Among the chromatographic methods, techniques based on a size –exclusion effects appear to be most useful. Electrophoresis methods provide detailed characterization of humic substances. Gas chromatography with mass spectrometric detection is typically used to identify the products of pyrolysis or thermochemolysis of humic substances. Furthermore, chemical modification has enabled NMR spectrometry to become one of the most powerful analytical tools for revealing and quantitating structural entities [11].

2.2.3 Chemical reactions

2.2.3.1 Chemical reaction towards inorganic species [23, 32-36]

The ability of humic acids to form complexes with metals correlates with the ion potential of the metal, i.e. the greater the metal ion potential value and the higher the rate of complexation of humic substances with those metal ions. The carbonyl groups account for the majority of strong complexing site in the humic molecules. The complexing capability (CC) of humic acids, which are related to the total acidities (TA) of the humic compounds, and a process to define it are as followed: $CC = TA / z$, where z is valence of the cation.

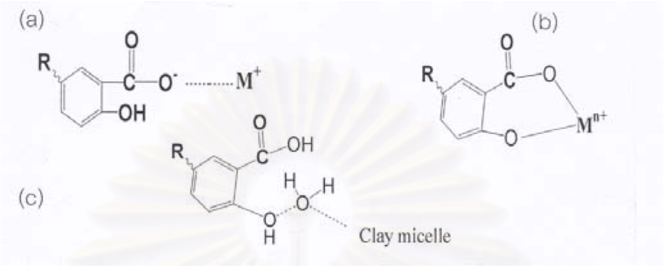


Figure 2.3 (a) Adsorption or electrostatic attraction by humic acid, (b) Complex or chelation reaction, (c) Water bridging or co-adsorption; M^{n+}: cation with charge n+; and R: remainder of the humic acid molecule

A high total acidity value is indicative of a high cation exchange capacity (CEC) and complexing power. The complex formation/ chelation is predicted to take place at pH 4 to 5, and increases gradually, especially at pH = 11, when 99 % ionization of the phenolic- OH is attained. Humic matter is capable of forming soluble and insoluble complexes and chelates. These complexes are in general less soluble than those of fulvic acids and considered to serve as a sink for toxic metals. These may be attributed to the higher molecular weights and lower solubility of humic acids. However, the humo – metal chelates remains soluble when metal/humic ligand ratio is low. In addition, the interaction between metal ions and complexing ligands may result in a complex that is weakly adsorbed either to the soil surface or in a complex that is more strongly adsorbed relative to the free metal ion.

Inorganic anions cannot be immediately bounded with humic acids, but, under certain circumstances, it is possible that positive charges of humic acid caused by the presence of amino groups can be bound to inorganic anions. Humic acid in laboratory studies reduces a variety of metal ions including Hg (II) to Hg (0), Cr (IV) to Cr (III), and U (VI) to U (IV).

Chemical reaction towards organic molecules [37-38]

The chemical structure enables the humic acids to enter into reactions with practically all combinations, occurring in biological systems. Organic cations can be bounded with humic acids by ionic, complex, chelating, and polar adsorption bonds. Nonpolar compounds reacted with charged parts of humic acids less than cationic substances. Main reactions are contributed to acidic carboxyl and hydroxyl groups. Reactions of organic combinations depend on the molecule structure (aromatic, aliphatic, and ionic), that binding mechanism range from van der Waals forces to covalent bond. Because of the detergent character of many humic materials, it is found that their interactions with hydrophobic organics often lead to solubilization.

2.2.3 Water solubility [35]

Among humic substances, only the fulvic acids are water-soluble. The greater the molecule is the more difficulty it is to dissolve in water. One reason is that the number of active hydrophilic groups specifically decreases parallelly with the increase of molecule measurements. Another reason is the lactone ring in the molecule that closes in neutral or acidic environment. This lactone ring opens in alkaline environment and, thus, the number of hydrophilic groups increases (-COOH, -OH). That is why the humic acids are soluble in alkaline environment. Because of the reasons mentioned above, the complexes of humic acids with multivalent metals are not water soluble.

The solubility of the humic acid in water also correlates with its ability to form complexes with metal ions. Fractions of humic acid with high solubility in water are extremely active in complex formation with poly-valence metal ions. Surface tension of humic acid – aqueous solutions depends on the acidity of solution. The higher the solubility of the humic acid fraction, the less the surface tension of its aqueous solution. This means that when the surface activity of such substances is high, they behave in water media like surfactants.

Much as humic substances are the most widespread natural polymers in the biosphere, the redistribution of metals and organic matter in soils and ground water is the main functions of humic substances. Metal ions tend to bind to humic substances restricting their migration to neighboring media. Knowledge of this characteristic of organic matter is of great importance not only for predicting metal migration in the environment, but also for development of efficient methods of control.

2.3 Conclusion

Because the presence of humic substances in soils affected the mobility, and the transport of HM ions. Humic acids were taken into account for an advance of the understanding of the fate, transport, and immobilization of heavy metals in soil by S/S technology. Moreover, the evaluation the long -term effectiveness of this technology in land field scenarios the S/S should be developed by means of leaching tests and modeling to prevent any misused of this technology.

CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Apparatus

Carbon, H, and N compositions of the humic acids were determined by using a Perkin Elmer Series II CHNS/O analyzer, model PE2400. PAS-FTIR spectra of soil sample, humic acids and humic – metals complexes were obtained by using Photoacoustic detector, model 300 and recorded on a Biorad Excalibur FTIR, model FTS 3000 Spectrophotometer. Differential Scanning Calorimetry and Thermogravimetry of humic acids and humic- metals complexes were done on a Labsys ™ (Setaram). The pH of soil solutions, leachants, and leachates were measured by Schott pH-meter CG 825 (reference electrode: Ag/AgCl). A HP 8453 UV-Visible Spectrophometer was used to determine the humification index expressed in term of the ratio of the logarithm of absorption at 465 nm and 650 nm. A Microwave digestion system, Perkin Elmer, was applied for the preparation of soil sample by acid digestion following EPA 3051 Part A method. The elements were determined by an Atomic Absorption Spectrometer, GBC 908AA and an Inductively Coupled Plasma Atomic Emission Spectrometry, JY2002. The compact high speed refrigerated- centrifuger, Kubuta 6930 Model was employed in humic extraction and sorption study. The furnace, Carbolite® was used to determine ash content and loss on ignition of samples. The mixture were shaken mechanically by Multi shaker MMS, Eiela. The compressive strength-testing machine was a hydraulic type (Alfred J. Amsler & Company). Deionized water was prepared by double distillation followed by ultrapure deionized system, Ultima Ultrapure water system, with resistivity 18.2 megohm-cm at 25°C.

3.2 Chemicals

List of chemicals used in the experiments were shown in **Table 3.1**.

Table 3.1 List of chemicals used in the experiments

No.	Name	Company & Grade
1	Aldrich Humic acid (AHA)	Univar, Analytical grade
2	Ammonium acetate	Merck, GR for analysis
3	Barium chloride	Univar, Analytical grade
4	Barium hydroxide	Hopkin& Willium, lab. grade (97%)
5	Boric acid	Univar, Analytical grade
6	Bromo cresol green	Labchem, Laboratory grade
7	Buffer solution for pH measurement	Merck
8	Calcium acetate	Univar, laboratory grade
9	Calcium chloride	Merck, Analytical grade
10	Ethanol	BDH, Analar 99.7 -100 %
11	Ferroin indicator	Labchem, Laboratory grade
12	Ferrous sulfate heptahydrate	Unilab, laboratory grade
13	H-saturated cation exchange (Dowex 50 –X8)	Sigma®Aldrich
14	Hydrochloric acid	Merck, Analytical grade
15	Hydrofluoric acid	Carbo elba, 85% Analytical grade
16	Hydrogen peroxide	Merck, Analytical grade
17	Methyl red	Merck
18	Nitric acid	Merck, GR for analytical
19	Potassium dichromate	(M&B), AR grade
20	KHP	Univar, Analytical grade

No.	Name	Company & Grade
21	Phenolpthaline indicator	Merck, GR for analytical
22	Potassium nitrate	Merck, AR grade
23	Reference Summit Hill soil HA, Cat. No. 1R106H	IHSS, USA
24	Standard metal solution [1,000] mgL^{-1} for AAS and ICP-AES	Merck, AAS grade
25	Silver nitrate	Merck, GR for analytical
26	Sodium chloride	Merck, extra pure
27	Sodium hydroxide	J.T.Baker, A.C.S. reagent
28	Sodium metaphosphate	Univar, Analytical grade
29	IHSS Standard Elliott soil HA, Cat. No. 1S102H	IHSS, USA
30	Sulfuric acid	Univar, Analytical grade
31	Triethylnolamine	Unilab, laboratory grade
32	Glacial acetic acid	Scharlau, Analytical grade (99.7%)

3.3 Soil sampling and Pretreatment

The soil sample was collected by simple random sampling from the King Rama V Dockyard, Royal Thai Navy, Samuthprakan Province at the sampling depth of 0-15 cm of A horizon. Twenty portions of 5- kg of collected fresh soil were air dried and mixed together. Living macroscopic roots, mineral organic, with a diameter larger than 2-mm and all particles were removed by sieving. Then soil sample was divided into four portions for different purposes, including:

Portion I, named here Original Soil (OS); was defined as blank soil subjected to characterize its properties and sorption study. This soil was an ingredient of the cement-based concrete using in concrete formation study.

Portion II, named Metal Spiked Soil (MS). Copper, cadmium, chromium, nickel, lead and zinc solution or salts of nitrate were added to the OS with the aim of producing polluted soil. This MS was used to mold with stabilized agents, to characterize the soil properties and to perform the effects of concentration of metals in concrete materials.

Portion III, named HA added Soil (HS). Commercial HA was added to OS to formulate humic – rich soil. The various concentrations of HA solution were prepared by dissolving HA in deionized water, and then added to the OS. The mixtures were mixed mechanically and incubated for 4 days in dark place at normal room temperature.

Portion IV, named Metal added to humic soil (MHS). Metal and HA solution were mixed for 24 h and then added to OS. Afterwards the mixtures were continuously incubated for 4 days.

All portions were stored in polyethylene bottles (with covers under normal room conditions with minimal temperature and humidity fluctuations). These bottles were shielded from incident light.

3.4 Characterization of contaminated soil

3.4.1 Analytical procedures for Physical, Chemical, and Mechanical properties

3.4.1.1 Soil pH

The degree of acidity or alkalinity in soils is determined by the hydrogen concentration in the soil solution. The H^+ ions may be present in soils as adsorbed H^+ ions on the surface of the colloidal complex, or as free H^+ ions in the soil solution [39-40].

Many other soil properties and processes are affected by soil pH, e.g. clay mineral formation and microbial activity. Soil pH determination is important for fate and transport assessments since the adsorption process is often pH dependent for both organic and inorganic compounds [41].

In the experiment, a glass electrode was employed in pH measurement (Schott pH-meter CG 825). The pH meter was calibrated prior to use with buffering solutions of pH 4.01 and 7.0. Ten grams of the air-dried OS (fraction < 2 mm) was placed in a 100 mL beaker. Then 50 mL of 0.01 $molL^{-1}$ $CaCl_2$ solution was added, equivalent to the liquid/soil ratio of 5. Subsequently, the suspension was mechanically shaken for 5 min, and settled for 1 h before pH measurement.

3.4.1.2 Lime potential [39]

Since pH measurements are affected by the suspension effect and by the activity of electrolytes, especially when the soil is limed with Ca^{2+} and Mg^{2+}, these may cause errors in soil pH readings. To control the errors, the determination of lime potential was used as a correction factor by considering the Ca^{2+} concentration in the calculation of pH. It was completed by using the activity ratio of $(H^+)/(Ca^{2+})^{0.5}$. Using the negative logarithm for this function yields:

$$-\log (H^+)/(Ca^{2+})^{0.5} = -\log k$$

$$pH - 0.5pCa = pK$$

The function *pH -0.5pCa* is called the *lime potential*.

20 g of the OS was placed in a beaker, and 40 mL of the 0.01 $molL^{-1}$ $CaCl_2.2H_2O$ solution was added. The suspension was stirred for 30 min. The suspension was swirled prior to the pH measurement.

Calculation: Lime potential = pH – 1.14

3.4.1.3 Soil water content [39-41]

Since soil water contents determination are essential for fate and transport estimations. Soil moisture has a direct influence on the adsorption processes and should be considered in sorption studies. This test is one used in vadose transport equations to modify water input from infiltration, and to interpret the loss of ignition. The OS sample of approximately 10 g was added to a clean preweighed stoppered weighing flask. The flask with its content was dried at 105 to 110 º C for 24 h in a dry forced draft oven.

Calculation:

$$\text{soil water content (\%)} = \frac{\text{weight of moist soil} - \text{weight of oven dried soil x100}}{\text{weight of moist soil}}$$

3.4.1.4 Cation Exchange Capacity

Clay and humus in soils are colloidal particles with large surface area. Most of the clay particles are electronegatively charged. However, humic and fulvic acids may be positively or negatively charged. A swarm of positively charged ions (cations) usually neutralizes the negative charged ions. These cations are called *adsorbed cations* that can be replaced or exchanged by other cations from the soil solution [39]. The ions involved in the exchange reaction are called *exchangeable cations.* The capacity of soils to hold (adsorb) and exchange cations is, therefore, called *cation exchange capacity (CEC*) [39, 42]. Soil CEC results can be used to approximate the maximum sorptive capacity of a soil for positively charged polar organic compounds and inorganic cationic species. This test was used for both solid waste disposal and remedial assessment projects. It does not generate a soil specific sorption coefficient; however, it provides a screening estimation for potential parameter retardation [41].

Since the adsorption and cation exchange are of great practical in soil chemistry, heavy metals contaminated in soil may be retained and filtered by the adsorptive action of the soil colloids. As such, the adsorption complex (clay and humus) serves the soil as storage and buffering capacity for cations. CEC is a good indicator of soil quality and productivity. Furthermore, the CEC helps to determine the amount of lime to be applied to acid soils. Although, there are numerous methods for CEC determination. The pH 7.0 ammonium acetate CEC method was chosen in this experiment because it has been widely used in the U.S., consequently a large data base exists for soil CEC.

Soil CEC is usually expressed in units of charge per weight of soil. The units are me/100 g (milliequivalents of charge per 100 g of dried soil) and $\mathrm{cmol_c kg^{-1}}$(centimole of charge per kilogram of dried soil). CEC is estimated by the following equation:

CEC = Σ exchangeable Ca, Mg, Na, K, and H^+ (in me/100 g).

Where: *M* is an exchangeable cation, therefore

me Ca /100g soil = (20 x 100 x μg Ca)/(1000 x 40/2)

me Mg /100g soil = (20 x 100 x μg Mg)/(1000 x 24/2)

me Na /100g soil = (20 x 100 x μg Na)/(1000 x 23/1)

me K /100g soil = (20 x 100 x μg K)/(1000 x 39/1)

(a) Exchangeable cation determination [39]

5.0 g of soil (< 425 μm) was placed in a 100 – mL polyethylene centrifuge bottle. 25 mL of 1.0 $\mathrm{molL^{-1}}$ (pH 7.0) NH_4OAc solution was added and mechanically shaken for 60 min. The supernatant solution was then separated from the soil by centrifugation at 2,400 rpm for 30 min. The clear supernatant and the NH_4- saturated soil were both collected. The supernatant was filtered into a 100-mL volumetric flask. The NH_4- saturated soil was gently washed three times with 20 mL 95 % ethanol, by shaking and centrifugation. Each washing of the NH_4- saturated soil was then added to the supernatant in the 100-mL volumetric flask. Then the extracted supernatant was made up to volume with distilled water and used for the determination of exchangeable cations (Ca, Mg, Na, and K) by AAS. The exchangeable H^+ ion concentration was measured separately by $BaCl_2$ method.

(b) Exchangeable H^+ ion determination [39]

The baruim–triethanolamine ($BaCl_2$-TEA) method was conducted to determine the exchangeable H^+. 10 g of OS was placed in a 100 – mL polyethylene centrifuge bottle. 20 mL of 0.2 $molL^{-1}$ $BaCl_2$-TEA solution was added and centrifuged at 2,400 rpm for 30 min. The supernatant solution was then separated and filtered into a 150-mL of Erlenmeyer flask. The wall of the tube was washed with 25 mL of distilled water. The wash water was added to the solution in the Erlenmeyer flask. The washing was done duplicated. Then, 5-8 drops of mixed indicator (a mixture of 0.1 g bromocresol green in 200 ml 90% ethanol and 0.1 g methyl red in 200 mL 90% ethanol in a ratio of 3 :2) were added. The solution was titrated with the 0.05 $molL^{-1}$ HCl solution to a pink endpoint (A mL). A mixture of 20 mL $BaCl_2$-TEA, 30 mL $BaCl_2$ and 40 mL distilled water was used as a blank solution (B mL).

Calculations: Exchangeable H^+ = (B-A) x 0.05 me/10 g soil

= 10 (B-A) x 0.05 me/100 g soil

3.4.1.5 Particle size analysis

The objective of experiment was to classify the texture (class) of soil sample. Particle size information is used to generate soil textural classification for both engineering and descriptive purposes [41]. Soil texture is an important characteristic of soil, affecting drainage conditions, water – holding capacity, amount and size of pores, and plant root development [40]. Consequently, the soil texture may influence the compressive strength of cement- based stabilized soil. Soil scientists subdivide soil (<2 mm) into three fractions. The percentages (by weight) of total sand (2.0-0.050 mm dia.), total silt (0.050-0.002 mm dia.) and total clay (<0.002 mm dia.) are projected in the USDA textural triangle to determine the soil class [39].

The hydrometer method based on Stokes' law, which relates the velocity at which a spherical particle falls through a fluid medium to the diameter and specific gravity of the particle and the viscosity of the fluid [41], was performed to determine the soil class. 50.0 g of OS sample was added into a blender cup. Then the blender cup was filled with distilled water to within 10 cm of the top (rim) and added 10 mL of 4 % w/v sodium metaphosphate solution. The cup was attached to a stirring machine and the suspension was blended mechanically for 15 min. The soil suspension was transferred into an ASTM soil-testing cylinder. The remaining soil residue was washed and transferred to the cylinder by spraying with water. The volume of the soil suspension in the cylinder was made up with water to the 1,130 mL level. The suspension was mixed thoroughly by stirring rod so that all sediment disappears from the bottom of the cylinder. When the stirring was stopped, the exact time (s) was recorded.

A hydrometer was carefully placed into the suspension, after the stirring was stopped for exactly 40 s, and then read to the nearest 0.5 scale division at the top of the meniscus on the hydrometer stem. After that, the hydrometer was removed and rinsed. The suspension was stirred again. The analysis was repeated. The average of the two readings was taken as the result, which equals the amount of silt and clay in grams. The temperature of the suspension was determined and recorded after removing the hydrometer. The suspension was stirred thoroughly again. The suspension was settled for 120 min, and the temperature and hydrometer were recorded. The amount of clay in grams was determined by this reading. The hydrometer must be corrected if the temperature of the suspension is higher or lower than 68 ° F.

3.4.1.6 Bulk density and Particle density

The objective of experiment was to determine the bulk density and particle density of soil sample. Bulk density (D_b) is defined as the mass of soil per volume of undisturbed soil or bulk soil volume (g/cm^3) [39]. Its value depends partly on the mineral and organic matter content, and partly on the amount of pore spaces or soil porosity. Because soil density is an important physical property that affects both agricultural and engineering operations, bulk density values are needed in assessment monitoring programs to convert contaminants concentrations in soil from a weight to weight to a weight to volume basis.

Particle density (D_p) is defined as the mass of soil solid (oven dried) per volume of solid particles (g/cm^3). Estimates of particle density and bulk density can be used to estimate void space as an approximation of porosity. Porosity (P) represents the soil volume available to the air or through which fluids can move [42].

Calculation: $P = 1 - (D_b / D_p)$

(a) The bulk density measurement of disturbed soil [39]

100 g of oven dried OS was filled in a preweighed 100- mL graduated cylinder. The cylinder was compacted by tapping the bottom of the cylinder ten times with the palm. Keep adding soil and tapping the cylinder until a tapped soil volume of 100 ml was obtained. The cylinder containing the soil was weighed. The moisture content of the soil sample was determined separately and the oven dry weight of the 100 mL soil was calculated.

Calculation: $$\text{Bulk density} = \frac{\text{oven dry weight of 100 mL soil}}{100} \quad (\text{g/cm}^3)$$

(b) Measurement of particle density [39]

A graduated cylinder method was used. 40 g of OS was added in a 100-mL graduated cylinder. 50 mL (B mL) of distilled water was added carefully and the mixture was stirred thoroughly with a stirring rod to displace the air. The stirring rod and the inner walls of the cylinder were rinsed the with a measured volume of water (10 ml, B* mL). The mixture was allowed to stand for 5 min. The volume of soil plus 60 mL water in the cylinder was recorded (A mL).

The moisture content of soil sample was determined separately by the gravimetric method. The OS sample of approximately 40 g was added into a clean preweighed stoppered weighing flask. The flask with its content was dried at 105 º C for 24 h in a dry forced draft oven. Water content was determined by the difference between mass of flask before drying and mass of flask after drying (C mL, volume of water in soil). This amount of water must be added to the 60 mL used to obtain the total amount of water used.

Calculation: Volume of water displaced by soil (mL) = A – (B+B*+C)

$$\text{Particle density} = \frac{\text{oven dry weight of soil (g)}}{\text{volume of water displaced by soil (mL)}}$$

3.4.1.7 Loss on ignition [42]

The loss on ignition, expressed as a percentage, is the loss in weight of sample after calcination at 1,100 ° C, in relation to its initial weight (air-dried).

Calculation: $$\text{LOI (\%)} = \frac{(W_{\text{air}} - W_{1100\,^{\circ}\text{C}})}{W_{\text{air}}} \times 100$$

The loss on ignition is made up of three or four separate losses:

- the loss of water contained in the soil, at 105°C, which it is useful to determine for other purpose (Residue water content, RWC at 105° C)

- the loss of all combustible organic matter

- the loss of water in the composition of clay minerals

- if $CaCO_3$ is present, the loss by decomposition of 44% by weight:

$$CaCO_3 \longrightarrow CaO + CO_2,$$

- if $CaMg(CO_3)_2$ is present, there is a loss of 47.9 % through the same mechanism of CO_2 release.

The determination is useful in two circumstances:

- to check that total chemical analysis of the sample adds up to 100 %

- the only way of knowing the true organic matter content for the horizons, which are very rich in poorly- decomposed organic matter. It is impossible to evaluate the total organic matter (Total OM) content by the following equation:

$$\text{Total OM} = \text{LOI} - [\text{RWC} + (0.44 \times \text{total } CaCO_3) + y \times C]$$

Where y is the proportion by weight of the water of constitution held by clay minerals ; which it ranges from 0.05 to 0.13, and C is the clay content (%) [42].

Two expressions of LOI were obtained: LOI-1, and LOI-2. LOI-1 was determined from the weight loss of approximately 5 g of dried soil (105°C) heated at 480 °C for 3 h. LOI-2 was determined from the weight loss of sample used to determine LOI-1 after additional heating at 1,100 °C for 3 h.

3.4.1.8 Determination of Cd, Cr, Cu, Pb, Ni, and Zn in soil sample

Microwave assisted acid digestion method, according to EPA 3051 Part A [43], was applied. Approximately 0.50 g of ground-dried OS was weighed in a microwave digestion vessel, and 10 mL concentrate nitric acid was added. The soil sample was digested in a microwave oven with 2 steps: 30 min at 800 watt and 30 min at 1,200 watt, the final temperature was 175 °C. The sample vessels were allowed to cool. Then the extracted soil was transferred and filtered through filter paper, the filtrate was collected in a 25 mL volumetric flask. The insoluble residue on the filter paper was washed with a minimum of 0.5 $molL^{-1}$ nitric acid. The 25 mL volumetric flask was made up to the final volume with deionized water. The amounts of Cd, Cr, Cu, Pb, Ni, and Zn were determined by ICP-AES.

3.4.1.9 Soil organic matter and Organic Carbon content

Soil organic matter is by definition the organic fraction derived from living organism. It affects the physical, chemical, and biological properties of soil [44]. It is one of the most important soil properties influencing the transport of hazardous compounds. The presence of high organic matter content can also interfere with the S/S process [7-8]. The organic carbon content is obtained by wet oxidation using potassium dichromate in a sulfuric medium. The Walkley - Black Wet Combustion method [39] was conducted in this experiment.

500.0 mg of OS sample was placed in a 500-mL Erlenmeyer flask. 10 mL 1 N $K_2Cr_2O_7$ solution was added with burette. The mixture was swirled gently to mix. Then, 20 mL concentrated of H_2SO_4 was added carefully from a dispenser and swirled again. The suspension was allowed to cool at room temperature for 20-30 min; afterwards 20 mL distilled water was added and swirled again. 5 drops of ferroin indicator was added into a flask. The excess of 1/6 $molL^{-1}$ of chromic dichromate solution in suspension was titrated with 0.5 N of ferrous sulfate ($FeSO_4.7H_2O$) to a clear blue- brown endpoint (T mL). A blank solution was run using the same procedure (B mL).

Calculations: $\% C_{org} = (B-T) \times N \times 3 \times 1.14 \times (100/\text{mg oven dried soil})$

$\%\ \text{Organic matter} = \% C_{org} \times 100/58$

3.4.2 Sorption Study of soil [25, 40]

The objective of this experiment was designed to refine the understanding of the sorption of metals on soil by taking into account sorption isotherm. The sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal or, more correctly, the activity of the free metal in the soil solution. The sorption process can be described by a single coefficient, the distribution coefficient, K_d .

Sorption studies are used extensively in correlation studies to determine the relative importance of a soil's chemical and physical properties for metal retention. Sorption studies also can be used to evaluate the effects that change a soil solution parameter.

Two portions of 25.00 g of OS sample were weighed in 250 mL polyethylene bottles. Then 75 ml of mixed solution of Cd, Cu, Cr, Ni, Pb, and Zn, prepared in deionized water, ranging from 0 to 125 mgL^{-1} were added into bottles **(Table 3.2)**. The mixtures were shaken at 210 rpm for 1 h then centrifuged at 2,500 rpm at 25 º C for 25 min. Afterward, the mixture were allowed to settle for 24 h. After that, 25 mL of the supernatant were filtered, transferred to 100 mL volumetric flask and adjusted to the volume with deionized water for the first portion and with 0.25 $molL^{-1}$ KNO_3 solution for the second one; named here OS, and OS-KNO_3, respectively.

Similarly, two concentrations of HA added to OS to produce the humic-rich soil were 0.25 and 5.0 % w/w. Then 25.00 g of two portions were weighed in 250 mL polyethylene bottles. After that 75.0 mL of mixed solution of Cd, Cr, Cu, Pb, Ni, and Zn, which prepared in deionized water, ranging from 0 to 125 mgL^{-1} were added into bottles. The further steps were performed in the same manner except that the supernatant were adjusted to the volume with 0.25 $molL^{-1}$ KNO_3 named here 0.25% and 5.0 %w/w HS-KNO_3, respectively. The amounts of metal concentration in the supernatant were determined by AAS. All portions shown above were carried out in duplicate and only the mean values were presented.

Table 3.2 Metal concentrations (mgL^{-1}) added to OS, and HSs

Batch number (n=2)	Concentration of each metal spiked to soils (mgL^{-1})	Amount of each metal (mg) in 25 g soil sample*	Amount of each metal spiked to soil sample ($mgkg^{-1}$)
1	0.000	0.000	0.00
2	8.333	0.625	25.00
3	16.666	1.250	50.00
4	33.332	2.500	100.00
5	66.664	5.000	200.00
6	125.00	9.375	375.00

* *These values were defined as the initial concentrations of metal in solutions for determining the Langmiur isotherms.*

It was important to suggest that a 0.25 $molL^{-1}$ KNO_3 solution was used as a background solution, ionic strength equal to 0.25 mol L^{-1}. The idea was to simulate normal soil's solution chemistry and the waste matrix and to equalize the ionic strength across all soil.

In this study, Both Langmiur isotherm and Freundlich isotherm were employed with the aim to compare the relative retention of metals by soil sample. The isotherm which best- fit analysis of the laboratory –soil adsorption was illustrated. The equation that describes the Langmiur system is

$$C_s = (x/m) = (a.b\, C_e) / (1 + b.C_e) \qquad \ldots\ldots\ldots\ldots.. 3.1$$

where:

C_s = metal concentration sorbed on the soil (dimensionless)

C_e = concentration of metal remaining in solution at equilibrium (mgL^{-1})

a = empirical constant

b = saturation coefficient (Lmg^{-1})

x = mass of metal sorbed on the solid phase (mg)

m = mass of soil (mg)

The Langmiur equation may be transformed to a linear expression by inverting equation 3.1 and separating variables: $C_e / C_s = (1/a.b) + C_e/ a$

The empirical coefficients a, and b may be obtained by plotting C_e/C_s as a function of C_e. Using linear regression, the slope equals to 1/a and the y-intercept equals to 1/ (a.b).

The Freundlich model is characterized by sorption that continues as the concentration of sorbate increase in the aqueous phase. The Freundlich isotherm is quantified by

$$C_s = (x/m) = K_F C_e^{1/n} \qquad \text{.....................3.2}$$

Where K_F = Freundlich sorption coefficient

n = an empirical coefficient

3.5 Characterization of humic acids

IHSS's method [34] was slightly modified to extract humic acid from natural soil. Locally collected air dried soil was washed with hydrochloric acid.

3.5.1 Extraction and Purification

10 g of OS (< 2.0-mm) was weighed in a 250 mL polyethylene bottle and equilibrated to a pH value between 1 and 2 with 5 mL 1 $molL^{-1}$ HCl at room temperature. Afterwards, 95 mL of 0.1 $molL^{-1}$ HCl was used to adjust to the final solution. The suspension was shaken for 1 h. The supernatant was separated from the residue by centrifugation at 10,000 rpm for 15 min. Subsequently, the soil residue was neutralized with 5 mL of 1 $molL^{-1}$ NaOH to pH of 7.0 and 0.1 $molL^{-1}$ of NaOH was added to give

100 mL (L/S ratio =10). The mixtures was purged with N_2 gas for 1 min, and allowed to extract for a minimum of 4 h. The alkaline suspension settled overnight and the supernatant was collected by means of centrifugation at 15,000 rpm for 15 min. The supernatant was acidified with 6 $molL^{-1}$ HCl with constant stirring to pH 1.0 and then allowed to stand for 16 h. The mixture was purged with N_2 gas for 1 min once more. Precipitated HA was obtained by centrifuging the mixture at 15,000 rpm for 15 min. To purify the precipitated HA, HA fraction was redissolved by adding a minimum volume of 0.1 $molL^{-1}$ KOH, and KCl (solid) to attain a concentration of 0.3 $molL^{-1}$ K^+, then centrifuged at 15,000 rpm for 15 min to remove the suspended solids. The HA was reprecipitated by adding 6 $molL^{-1}$ HCl with constant stirring to pH of 1.0. The suspension was allowed to stand again for 16 h and centrifuged at 10,000 rpm for 10 min. The supernatant was discarded. The precipitated HA was suspended in 0.1 $molL^{-1}$ HCl / 0.3 $molL^{-1}$ HF solutions in a plastic container and shaken overnight at room temperature. The suspended HA was centrifuged at 10,000 rpm for 10 min and the HCl / HF treatment was repeated until ash content drops below 1%. The precipitated HA was washed with 50 mL of 0.1 $molL^{-1}$ NaOH. This HA solution is then purified further by stirring with 30 g of a H-saturated cation exchange Dowex -50x for 15 min then filtered on a sintered glass funnel. The filtrate solution was collected and then centrifuged at 10,000 rpm for 15 min. The supernatant was discarded. The precipitated HA was dried at 80 °C, weighed, and stored in an amber-colored flask. The amount of HA in soil sample (g kg^{-1}) was determined in closing stages.

3.5.2 Fractionation

Humic fraction can be fractionated into two fractions by shaking in ethanol. The dissolved fraction is called hymatomelanic acid, whereas the undissolved part is called α-humic acid. Hymatomelanic fraction contains polysaccharide components in ester linkages [23]. Each fraction was determined in the percentage by mass.

1.00 g of SHA was placed in a weighed 25 mL Erlenmeyer flask. 25 mL of 95 % ethanol was added in the flask and then stirred for 15 min. The undissolved fraction was collected and dried at 80 º C.

3.5.3 Determination of acidity of soil humic acids [39]

The present experiment examined the amount of two types of acidity functional groups in HA. As the sum of carboxylic and phenolic-OH contents equals the total acidity of soil HA that reflects the negative charge or the cation exchange capacity of humic compound. The following methods for determining of carboxylic and phenolic-OH contents were:

(a) Carboxyl content by Calcium acetate method

This method based on the formation of acetic acid, may be expressed as follows:

$$2R\text{-}COOH + Ca(CH_3COO)_2 \longrightarrow (RCOO)_2Ca + 2CH_3COOH$$

The carboxyl content is then determined by titration of the acetic acid with a standard base.

About 20 mg of finely ground SHA was added in a 125-mL ground-stoppered Erlenmeyer flask. Afterwards 10 mL of 0.2 N Ca $(OAc)_2$ solution was added. This solution was diluted with 40 mL of CO_2 free distilled water. After shaking the flask for 24 h with a wrist-action shaker, the mixture was filtered through a clean Erlenmeyer flask. The filtered residue was washed once with CO_2 free distilled water. The solution was titrated potentiometrically with the standardized 0.1 N NaOH solution to a pH of 9.0 (T mL). A blank solution was run with the same procedure (B mL).

Calculations: me COOH/g = (T-B) x N x (1000/ oven dried HA)

(b) Total acidity of SHA

Barium hydroxide, $Ba(OH)_2$ method was conducted. Humic acid is saturated with a known excess of Ba^{2+}. The unused fraction of $Ba(OH)_2$ is back-titrated with a standard acid.

20.0 mg of finely ground SHA was added in a 125-mL ground-stoppered Erlenmeyer flask. Afterwards, 10 mL of 0.2 N $Ba(OH)_2$ solution was added. This solution was displaced the air in the flask by bubbling N_2 gas. The flask was closed airtight and shaken for 24 h with a wrist-action shaker at room temperature. The mixture was filtered through a clean Erlenmeyer flask. The filtered residue was washed once with CO_2 free distilled water. The solution was titrated potentiometrically with the standardized 0.2 N HCl to a pH of 8.4 (T mL). A blank solution was run with the same procedure (B mL).

Calculations: me Total acidity /g SHA = (B-T) x N x (1,000/ weight of HA)

The phenolic-OH concentration was determined by the difference between the total acidity and the COOH content.

Calculation: me Phenolic -OH/g = me Total acidity /g – me COOH/g

3.5.4 Elemental analysis

The objective of this experiment was to investigate the chemical composition of HAs, and the relationship between ratios of element toward their structure and properties.

Carbon, H, and N contents were determined with an elemental analyzer. The experiment was carried out with chormatographically separation of gaseous humic products feeding by pyrolysis in high purity oxygen by frontal analysis with quantitatively detection by thermal conductivity detector. The HA samples were AHA, SHA, Reference soil HA, and Standard soil HA. The results were shown as individuals form and ratios of element.

3.5.5 Ash content

The objective of the experiment is to verify whether the extraction and purification of soil HA according to IHSS's procedure success, which evaluated from low ash content. This experiment ash content of HA samples were inorganic residues after the destruction of organic matter by calcinations at 500 ° C.

0.2 g of SHA was placed into a preweighed alumina crucible in an oven at 500 ° C for 4 h. After the ashing was complete, the crucible was cooled in a desiccator in the presence of silica gel.

$$\text{Ash content (\%)} = \frac{\underline{\text{oven dry weight of SHA (g)}} \times 100}{\text{initial weight of SHA (g)}}$$

3.5.6 Humification index [23]

Degree of humification can be expressed in terms of optical density values, extinction, or absorbance. By plotting the logarithm of the absorbance against the wavelengths in the visible light range, an absorbance spectrum of humic acid is usually produced in the form a straight line. The slope of such line or curve is taken as a characteristic for the differentiating humic substances [45]. It can be formulated in terms of quotient of absorbance at two arbitrary selected wavelengths. The small value (3-5, or lower) of the ratio indicates a high degree humification. The HAs with high molecular weights (M.W. >30,000) have lower E_4/E_6 (the ratio of the logarithm of absorption at 400 nm and 600 nm) values (4.32-4.45) than HAs with lower molecular weights (M.W.>15,000). The values of D_4/D_6 (the ratio of the logarithm of absorption at 465 nm and 665 nm) seem to agree by showing a range of 4.1-4.8 for HAs. In this experiment, the electronic spectra of SHA samples were recorded at the D_4/D_6 ratios.

About 10 mg SHA sample was dissolved in 100 mL of 0.05 $molL^{-1}$ NaOAc and adjusted pH to 4.01 and 11 by 0.1 $molL^{-1}$ acetic acid and NaOH 0.1 $molL^{-1}$, respectively.

3.5.7 PAS-FTIR Spectra of Humic acids, Soils, and Metal-HA complexes

The related objective of this experiment was to compare the PAS-FTIR spectra of HA samples, soils, and Metal-HA complexes that difference in sources and preparations (**Table 3.3**). PAS-FTIR spectra were achieved by using a MTEC Photoacoustics (PA) technique, and recorded on a Biorad Excalibur FTIR, model FTS 3,000 spectrophotometer. Operating parameters for FTIR – PAS measurement with a fast scan were 8 cm^{-1} resolution, open source aperture, 32 numbers of scans, 0.1 cms^{-1} mirror velocity, and helium detector gas atmosphere. The FTIR beam splitter was a Zincselenide (ZnSe) type accomplished to scan the spectrum in range of 400 to 4000 cm^{-1} [46-47]. The normalized spectrum was obtained with a MTEC carbon black reference standard.

3.5.8 Thermal Analysis

Differential scanning calorimetry (DSC), and thermogravimetry (TG) of HA

OS sample was subsampled into seven portions shown in **Table 3.4**. Approximately 15 mg of sample was analyzed. In this experiment, the sample was placed in an alumina (Al_2O_3) crucible, using empty crucible as the reference. Enthalpy variation (ΔH) value was determined from the peak area of the DSC curve, using the indium fusion enthalpy as the reference (T_f= 429.76 K; (H_f = 28.5 Jg^{-1}) [39, 48-50].

All thermal analyses – differential scanning calorimetry (DSC), and thermogravimetry (TG) - were done on a Labsys ^{TM} (Setaram).

Table 3.3 List type of samples and their forms for PAS –FTIR

Portion	Type and sample preparation
1	Original dry soil (oven 80ºC)
2	2.5 % w/w Metal- 1.0 % w/w AHA -soil (complex 2)
3	2.5 % w/w Metal- 0.1% w/w AHA –soil (complex 1)
4	0.1 % w/w AHA added soil
5	2.5 % w/w Metal spiked soil
6	Purified –soil HA (by Cation exchange H^+ resin)
7	IHSS soil HA reference 1R106H, Summit Hill soil
8	IHSS soil HA standard 1S102H, Elliott soil
9	Soil HA (extracted by 0.1 N NaOH)
10	AHA (Sodium salts form), Aldrich

Table 3.4 Type and sample preparation for thermal analysis

Portion	Type and sample preparation
1	Original dry soil (oven 80º C) whole soil, was ground to < 2-mm
2	OS was ground to <2-mm and treated with 30% H_2O_2, washed with distilled water, dried and ground again to pass a 2-mm sieve
3	5 g of 2-mm ground OS was incubated with 1 % w/v AHA solutions for 24 h, dried and ground to pass a 2-mm sieve
4	5 g of 2-mm ground OS was incubated with 5 % w/v AHA solutions for 24 h, dried and ground to pass a 2-mm sieve
5	5 g of 2-mm ground OS was incubated with 2 mL of totally (125 mgL^{-1}) mixed heavy metal solution for 24 h, dried and ground to pass a 2-mm sieve
6	5 g of 2-mm ground OS was incubated with 2 mL of totally (125 mgL^{-1}) mixed heavy metal solution and 2 mL of 5 % w/v AHA solution for 24 h, dried and ground to pass a 2-mm sieve
7	SHA, ground to < 2-mm

3.6 Study of Solidified/Stabilized Soil

The purpose of this experimental section was to characterize the factors affecting the effectiveness of concrete by mean of compressive strength and leaching tests [18, 22, and 51].

The study's focus of interest was the use of Type I Portland cement as a binder for contaminated soil treatment [7]. In order to characterize the solidified waste materials, the standard test for compressive strength of hydraulic cement mortars was applied to concrete specimens [52].

Concrete blocks, measuring 53-mm x 60-mm x 46-mm dimension, were prepared of which the approximate area of loaded surface (specimen face) and their volume were 3,153 mm^2 and 145.34 cm^3, respectively. In order to prevent the formation of air voids during mixing, concrete blocks were compacted by tapping in two layers and sealed. All batches of concrete mortars were performed at room temperature and ambient humidity level. The curing time was 28 days in the molds. This period was selected in order to get mature and well-hydrated cement pastes [29]. The methods for measurements of physical properties of the monolithic S-OS were shown in **Table 3.6**. The compressive strength for concrete blocks in term of MPa can be calculated as follow:

$$f_m = P/A$$

where: f_m = compressive strength in MPa

P = total maximum load in N (kg m s^{-2}), and

A = area of loaded surface in mm^2

The variables affecting the compressive strength of concrete were investigated including binder to waste ratio, humic acid concentration, and metal concentrations.

3.6.1 Influence of binder to waste ratio

The primary objective of this experiment was to set up the concrete composition for utilizing as a **model block**. The cement- based stabilized soils were prepared with Portland cement to OS mass ratios ranging from 0.25 to 1.0. Water was added sufficiently to produce a hardened paste. The studies were conducted with blocks prepared in five batches, of which percentages of water, cement, and soil were shown in **Table 3.5**. Data were analyzed quantitatively through the use of mean values.

The blocks were removed from the molds after 28 days-curing time. Then the blocks were measured the physical properties.

All specimens were submitted to a compressive strength test. Only the cement to soil ratio that obtained the highest compressive strength was taken for the further experiments. Furthermore, the fragmented concrete of the highest compressive strength was homogenized, and prepared according to the extraction procedure requirements for leaching tests. Concentrations of metals in this fragmented concrete were designed as concrete blank.

3.6.2 Influence of humic acid concentration

Since humic acids affect the water retention, retardation of cementation and on the treatment of municipal solid waste [23]; the objective of this experiment was to investigate the effects of HA in contaminated soil on compressive strength of concrete. These effects were examined with emphasis upon the amount of HA added to soil.

Stock solution of AHA was prepared by dissolving 25 g of air- dried AHA in 250 mL of deionized water with stirring for 30 min. The AHA solution was added to OS at percentage by mass of AHA to soil ranging from 0.10 to 5.00 % as shown in **Table 3.7**.

These replicates of each batch were carried out. After 28 days curing period, concrete specimens of each batch were subjected to compressive strength test. The fragmented concrete of each batch was also collected, homogenized, and prepared to perform the extraction test **(section 3.6.4)**.

Table 3.5 Composition of the mixture used to manufacture the stabilized soil (S-OS)

Batch Number (n=3)	**Water** (% w/w)	**Cement to soil (C/S) ratio**	**Weight of concrete** (g)
1	40	1/1	228.9
2	44	1/1.5	219.4
3	47	1/2	195.5
4	55	1/3	193.8
5	55	1/4	189.5

Table 3.6 Measurement of physical properties of monolithic S-OS

Physical properties	**Method /Description**
-Density (kg m^{-3})	- Ratio of weight of concrete block to bulk volume
-Bulk volume (cm^3)	-Apparent volume
-Moisture content (%)	-Loss of water during oven drying at 105 °C for 2 h, ratio of mass of water (g) to mass of concrete
-Specific surface area (m^2)	-Contact surface areas of concrete block
-Water absorption capacity , WAC (%)	-Amount of water (cm^3) sorbed into the concrete matrix to its solid mass, performed by immersing a monolith in deionized water (L/S=20) for 14 days.
-Pore volume (cm^3/block)	-Volume of voids = bulk volume to volume of sorbed water ratio

3.6.3 Influence of metal concentrations

The objective of this experiment was to examine some aspects of the association of the compressive strength of concrete with the concentration of metals in contaminated soil. The experiment designed for the examination was carried out in which the absence of HA added to soil, besides the independent variable was concentration of metals.

Stock solution of mixed metal salts was prepared in a 250 mL beaker by dissolving 6.86, 9.51, 11.44, 12.383, 3.49, and 11.37 g of $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, $Cr(NO_3)_3$, $Ni(NO_3)_2.6H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2.4H_2O$, respectively, in a 100 mL of deionized water with stirring for 1 h.

The concentration of each metal ion was 2.5 % w/v. The studies were conducted with blocks prepared in six batches, in which each batch consists three specimens. The percentages of spiked amount of metals were shown in **Table 3.8**. The preweighed OS was moistened with sufficient deionized water in a 500 mL PE bottle, and then it was spiked with the metal solution and stirred mechanically for 24 h at ambient temperature.

After 28 days curing period, concrete samples of each batch were subjected to compressive strength test. The fragmented concrete of the hardest mortar was homogenized, and stored for further extraction test.

3.6.4 Leaching study

In order to evaluate the efficiency of stabilized soil, factors affecting the leaching of metals into the environmental surrounding were investigated by batch-leaching tests [7, 51]. To ascertain the stable period of the solidified cement/soil concrete in the landfills, it is required to study the leaching behavior of heavy metals from the matrix. The experiments were designed and used to explore if, and how, different factors affect the metal retention. The five batch leaching methods were carried out to determine the amount of available leached metals including:

(1) The influences of factors on metal retention of crushed stabilized soils (e.g. L/S ratio, type of leaching medium).

(2) The influence of pH on the metal solubilization was performed to determine the neutral acid capacity (ANC) of inorganic constituents from a waste material by addition of acid or base [18, 19, and 22].

(3) The Monolithic leaching test (ML) designed for investigating the leaching behavior of monolithic concrete under static conditions that were renewed periodically by leachants. The serial batch test was renewed after fixed contact time to avoid approaching saturation of the solution and thus preventing a solubility-control phenomenon in the leachate [18].

(4) The Pore water test (PW) designed for evaluate the initial equilibrium composition of the pore solution and the soluble species Maximum mobile fraction (MMF) for leaching [18].

(5) The TCLP testing was carried out to ensure that the leached metals were under regulated level of metals assigned by US EPA [7].

For leaching study, the fragmented stabilized soil samples following compressive strength test were used in **section 3.6.4.1-4 and 3.6.4.6**. The samples were ground (<2 mm) and dried at 80 ° C for 4 h and kept in a desiccator prior to undergoing leaching tests. In the experiments, all leachates were filtered through Whatman no.42 filter paper, re-acidified to pH around 2 by nitric acid addition. Each batch was carried out in duplicate.

3.6.4.1 Influence of liquid to solid ratio

Since, metal leachability may depend upon the liquid to solid (L/S) ratio. The objective of this experiment was to investigate whether there were significant differences in the leachability as compared to ratios of liquid to solid (L/S).

Table 3.7 Percentage of AHA added to the OS to make stabilized –humic soil (S-HS)

Batch Number (n=3)	**AHA** (% w/w)
1	0.00
2	0.10
3	0.25
4	0.50
5	1.00
6	2.50
7	5.00

Table 3.8 Amounts of metal spiked to the OS to make stabilized-metal added soil (S-MS)

Batch Number(n=3)	**Amount of each metal spiked** (mg /kg soil)	**Amount of six metals spiked** (mg /kg soil)
1	0	0
2	75	450
3	150	900
4	300	1,800
5	600	3,600
6	1,200	7,200

25.00 g of S-OS was placed in a 250 mL centrifuge bottle. The leaching were conducted in five batches with different L/S ratios, shown in **Table 3.9**, and each batch was run in duplicate. The utilized leachant was 0.1 molL^{-1} acetic acid solution with pH of 2.88. Each batch was shaken mechanically for 18 h at 25 º C. Then the mixture was allowed to settle for 1 h. The supernatant was pipetted and filtered through Whatman no.42 filter paper. The clear solution was subjected to metal analysis by ICP-AES.

Table 3.9 Liquid to solid (L/S) ratio and volume of leaching medium used

Batch Number (n=2)	**Liquid to solid (L/S) ratio** (v/w)	**Volume of leaching medium used** (mL)
1	3	75
2	4	100
3	5	125
4	8	200
5	18	450

3.6.4.2 Influence of type of leaching medium

In order to study of the long –term leaching of landfill contaminants, in particular heavy metals, the physico- chemical and biological processes associated with the real scenarios of leachants were taking into account. Research in this area has consistently shown that changing conditions (e.g. composition and pH of leachate) during humic phase may lead to a substantial change in the mobility of heavy metals.

Consequently, the objective of this experiment was to monitor the alteration of leachate compositions. Three types of leaching medium were investigated. There were distilled water; 0.1 and 0.5 mol L^{-1} acetic acid; and 1.0 and 2.5 % AHA solution. Acetic acid solution was a representative of leachates in the first decades after disposal of stabilized materials, which generated during decomposition of organic matter under anaerobic landfill condition [29]. The leachant containing humic acid was a representative of leachates in the humic phase.

A portion of 20 g of 2 mm ground S-MS (batch no.1 and no.3) was placed in a 250 mL PE bottle. The leaching medium was then added with a L/S ratio of 5. The static extraction was achieved for 30 min, followed by centrifuging at 10,000 rpm at 25 º C for 10 min. The suspension was settled for 3 days. The amounts of metal were determined by an ICP-AES spectrometry.

3.6.4.3 Influence of humic acid in contaminated soil on metal retention in concrete

The experiment aims to study the effect of humic acid in contaminated soil on the retention of metals by means of extraction test.

25.00 g of 2 mm ground - fragmented concrete **(section 3.6.2)** was incubated with 0.5 $molL^{-1}$ acetic acid (75 mL, L/S ratio = 3). All of the mixtures were shaken mechanically for 30 min and then kept in a dark place at room temperature for 4 days. The supernatant was separated from the solid by high-speed centrifugation at 10,000 rpm for 25 min, afterward filtered through Whatman no.42 filter paper into a 250 mL volumetric flask, and then diluted to the mark with 0.5 $molL^{-1}$acetic acid. The amounts of Cd, Cr, Cu, Pb, Ni, and Zn in the solution were determined by ICP-AES spectrometry. The results were compared with their total amount in concrete obtained by digestion with aqua regia solution.

3.6.4.4 Influence of pH on metal solubilization

The pH dependent solubilization of various metal species has an important effect on the leaching behavior of material. The experimental study of metal solubility according to the leachant pH was carried out on finely- homogenized, crushed materials in order to rapidly reach solid/liquid steady state conditions in sealed PE bottles. Contact solutions using maintained at various pH values between 0.54 and 12 by addition of nitric acid or sodium hydroxide solutions, regulated the L/S ratio of 10. Since the alkaline leachant (pH>12) was typically considered as non-aggressive for the cement matrix, the leachant with pH higher 12 was not under taken.

About 5.0g of 2 mm ground S-OS and S-HS (5%w/w HA added) was weighed in 75 ml PE bottle. Then 2 molL^{-1} 25 mL of nitric acid solution was added into bottle. After that, the mixture pH was potentiometrically adjusted to maintain equilibrating at values ranging from 3 to 12 by addition of 0.5 molL^{-1} nitric acid/sodium hydroxide, regulated the L/S ratio of 10 (total volume = 50 mL). This mixture was mechanical shaken for 30 min. The suspension was settled for 7 days. After that, the mixture was filtered two times through Whatman no.42 filter paper. The filtrate finally was measured the pH and re-acidified to pH around 2 by nitric acid addition. The amounts of metal were determined by an ICP-AES spectrometry. Each batch was run in duplicate.

3.6.4.5 The monolithic leaching (ML) test

The concrete formula giving the highest compressive strength obtained from part **3.6.3** was chosen to prepare 22 testing specimens for leaching test, TCLP tests, and the total chemical analysis. The S-MS (1,500 mg kg^{-1} metals added soil) was removed from the molds, left curing for 28 days and submitted to a batch-leaching test. A monolith concrete was immersed in a medium at a liquid/solid contact surface = 3.0 m^3/m ^{2}. The initial pH of each leaching mediums was determined before leaching step. The leachants were sequentially renewed after 8, 16, 24, 72 hours, 1, 1, 3 weeks and then every month up to a cumulative leaching period of 100 days **(Table 3.11)**. The leaching mediums were listed in **Table 3.12**. The leaching was carried out in an unsealed 1.5 L PET bottle and leaching medium was exposed to carbon dioxide gas from the atmosphere. The leachate of each batch was collected after a period of time.

The pH of leachate was monitored for all of the cumulative leaching periods. The leachate was filtered through Whatman no.42 filter paper, and then re-acidified to pH around 2 by nitric acid addition. The amounts of metal were determined by an ICP-AES spectrometry.

3.6.4.6 Pore water (PW) and Maximum mobile fraction (MMF) Test

The test allows the assessment of constituents of solubilization at steady state conditions between fine crushed materials and deionized water in closed vessels and for different L/S ratios at room temperature (25 ± 1 °C) during 7 days of continuous stirring. The materials were crushed to < 1 mm and samples were put into contact with deionized water, for L/S ratios: 200, 100, 50, 10, 2, and 1 ml g^{-1}(dried material). The closed vessels were agitated for 7 days by mechanical shaker. After filtration (Whatman no.42 filter paper) the solution were analyzed. The plotting of pH according to the L/S ratio, as well as the plotting of metal concentrations (mgL^{-1}) vs. L/S ratio gives useful information on the available quantities and solubility of different elements.

Seven portions of S-OS, and S-HS (5% w/w HA added soil) were set according to **Table 3.10**. Each portions of dried-crushed materials was placed in 250 mL PE bottles, and added deionized water which their established L/S ratios. The mixtures were continuously agitated for 7-days by a mechanical shaker at 100 rpm. After that, all portions were filtered two times using Whatman no.42 filter paper. All leachates were measured pH. The amounts of Ca, Na, Cd, Cr, Cu, Pb, Ni, and Zn were determined by ICP-AES. All batches were done in duplicate.

3.6.4.7 TCLP test

The objective of this experiment was to determine whether there were significant differences in leachability of heavy metals derived from the differences in composition of concrete as compared to the regulated level presented by US EPA. The different of prepared concrete samples were shown in **Table 3.13**.

After 28 days curing period, the concrete of each batch were fragmented, homogenized to 9.5 mm, and subjected to leaching test. A portion of 25 g S-OS, S-MS, S-HS, and S-MHS, were placed in a 500 ml PE bottle. Afterwards, 500 mL of 0.1 $molL^{-1}$ AcOH (pH 2.88 ± 0.05) was added, giving L/S equal to 20. The granular solid was immerged in leaching medium for a week. The mixture, then, was shaken by a mechanical shaker at 30 rpm. The equilibrium extraction time was 18 h. After that, the mixture was filtered twice by using 0.2-μm glass filter. The amounts of Cd, Cr, Cu, Pb, Ni, and Zn were determined by ICP-AES. The concentration of each metal was compared with the regulated level of metals assigned by TCLP test.

3.7 Analysis of leachate

The objective of the present experiment was to investigate the retention of chemical species by the analysis of leachate that serve as a link among the effectiveness of stabilized concrete, as an input parameters for leaching model and the their application to predict the long- term behavior of concrete in the landfill.

3.7.1 Determination of Sodium and Calcium

Each period, the leachate was collected and filtrated though a Whatman no.42 filter paper. The elements Na and Ca were determined by direct aspiration into an air –acetylene flame and a nitrous oxide –acetylene flame AAS, respectively.

Table 3.10 Liquid to solid (L/S) ratio, volume of deionized water and weight of crushed material used

Batch Number (n=2)	**Liquid to solid (L/S) ratio** (v/w)	**Volume of deionized water** (mL)	**Weight of concrete materials** (g)
1	200	50	0.25
2	100	50	0.50
3	50	50	1.00
4	10	50	5.00
5	2	50	25.00
6	1	50	50.00

Table 3.11 Leaching time of each period and cumulative of contact time for batch leaching test of S-MS (monoliths) in an unsealed PET bottle (h: hour, d: day, w: week, m: month)

Period	1	2	3	4	5	6	7	8	9
Leaching time	8 h	16h	24h	3d	1w	1w	3w	1m	1m
Cumulative time (d)	0.25	1	2	5	12	19	40	70	100

Table 3.12 Types and concentrations of leachant taken into account for influence of contact time on S-MS samples

Type of leachant	**KNO_3** ($molL^{-1}$)	**AcOH solution** ($molL^{-1}$)				**HA solution** (mgL^{-1})				
Concentration	0.25	0.05	0.10	0.20	0.40	10	20	40	200	400

3.7.2 Determination of Chloride ion by Argentometric method [53]

25 mL of leachate was pipetted into a 250 mL volumetric flask. The leachate was adjusted pH to 7-10 with H_2SO_4 or NaOH. Then 1.0 mL of K_2CrO_4 indicator solution was added. Afterwards the solution was titrated with the standardized 0.01 N $AgNO_3$ titrant (N) to a pinkish yellow endpoint (A mL). The deionized water was run as blank solution (B mL).

$$\text{Calculation: } Cl^{-}\ mgL^{-1} = \frac{(A\text{-}B) \times N \times 35450}{25} = C \quad mgL^{-1}$$

$$Cl^{-} \text{ leachate mmol kg}^{-1} \text{ concrete} = \frac{(C \times 500)}{(35.5 \times \text{weight of monolithic concrete, g})}$$

3.7.3 Determination of metals in leachate

Each period, the leachate was collected, filtrated though a Whatman no.42 filter paper and re-acidified by nitric acid to leachate pH around 2. The amounts of heavy metals were determined by ICP-AES; while the others by AAS.

Table 3.13 Composition of the mixture used to manufacture concrete blocks for TCLP test

Concrete	**Cement to soil ratio by mass**	**Six Metals spiked to soil** (mg kg^{-1})	**AHA added to soil** (% w/w)
S-OS	1/1.5	-	-
S-MS	1/1.5	1,500	-
S-MHS	1/1.5	1,500	5.0
S-HS	1/1.5	-	5.0

3.7.4 pH measurement of leachate

In the experiment, a glass electrode was employed in pH measurement. The pH meter was calibrated prior to use with buffering solutions of 4.01, and 9.00.

All leachants were submitted to measure the initial pH prior to put into the leaching container. Each of contact time, the leachate was collected and filtrated through a Whatman no.42 filter paper.

3.8 Total chemical analysis of stabilized soils

Total amount of metal (Na, Ca, Cd, Cr, Cu, Ni, Pb, and Zn) in the stabilized concrete was determined after the digestion by aqua regia using ICP-AES. A portion of 3.0 g ground air dried S-OS, S-HS and S-MHS as shown in **Table 3.13** were weighed into a round- bottom flask and 21 mL concentrated HCl and 7 mL concentrate HNO_3 were added to each flask. The concrete samples were digested with reflux unit for 2 h. After the samples had cooled, the solution was quantitative transferred into a volumetric flask, diluted with deionized water to a final volume of 250 mL, and passed through Whatman no.42 filter paper. Each batch was run in duplicate.

Total chloride ions (Cl^-) in stabilized concrete was carried out with the similar manure for determining chloride ion in leachate. About 3.00 g of ground air-dried concrete was weighed into a round- bottom flask and added 10 mL concentrated HNO_3. The concrete samples were digested with reflux unit for 2 h. After the samples had cooled, the solution was quantitative transferred into a volumetric flask, diluted with deionized water to a final volume of 250 mL, and passed through Whatman no.42 filter paper. Then each batch of the solution was run by the similar manure as described in **section 3.7.2**.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of contaminated soil

4.1.1 Physical, Chemical, and Mechanical properties

The air-dried soil at the sampling depth of 0-15 cm of A horizon was characterized. The A horizon was chosen because it is associated with biological activity, and therefore generally enriched with organic matter –humic accumulation. An average pH of soil was 7.34, indicating a very slightly alkaline character [39-40]. The soil pH was related to a value of lime potential of 6.2. The soil sample contained approximately 3.7 % of organic matter with 6.8 % of water content. Concentration of organic matter in this range can have a significant influence on the sorption of organic and inorganic hazardous chemicals. The main physical, chemical, and mechanical characteristics of the soil were shown in **Table 4.1**. The concentrations of heavy metals in soil were 4.45, 42.32, 27.72, 48.61, 33.70, and 82.75 gkg^{-1} for Cd, Cr, Cu, Pb, Ni, and Zn, respectively as illustrated in **Table 4.2**. The amounts of HM found in the soil sample were much higher than the typical values of apparently safe soil [5, 44]. These indicate that the soil had been contaminated by the six elements. The distribution of mineral particles < 2 mm according to size classes was expressed in **Table 4.3**. The soil texture was classified as a *clay* according to the US Department of Agricultural classification scheme [39, 40].

Table 4.1 The physical, chemical and mechanical characteristics of contaminated soil sample

Properties	calculated	Properties	calculated
Soil Water content (%)	6.8	CEC (me/100g)	10.08
Soil texture	clay	Bulk density (g cm^{-3})	0.95
pH	7.34	Particle density (g cm^{-3})	1.06
Lime potential	6.2	Porosity	0.14
Organic Carbon (%)	1.5	Loss on ignition (%) (n=5)	
Organic matter (%)	3.7	LOI-1 at 480 °C	63.42
Humic acid (%)	0.376	LOI-2 at 1,100° C	18.84

Table 4.2 Total concentration of Cd, Cr, Cu, Pb, Ni, and Zn in soil performed by ICP – AES and common range of metals in soils

Metals	**Mean g kg^{-1}***	**Range founded, g kg^{-1}**	**Typical range, mg kg^{-1}**
Cd	4.45 ±6.58	1.3-17.9	0.01-7
Cr	27.72 ±3.21	36.7-48.8	5-1,000
Cu	42.32 ±5.29	24.8-32.0	2-100
Pb	33.70 ±7.38	40.4-59.6	2-100
Ni	48.61 ±8.24	28.6-44.4	10-1,000
Zn	82.75 ±6.45	76.4-91.3	10-300

** Mean values ±s.d. (n=6)*

Table 4.3 Particle size analysis of a contaminated soil sample of A horizon

Scale of particle dimensions (µm)	<2	2-50	50-2,000
Subdivision of particle size classes	Clay	Silt	Sand
(%)	47.3	35.7	17.0

Table 4.4 Exchangeable cations (Ca, K, Mg, and Na) by AAS and exchangeable acidity

Exchanged ions	Ca	Mg	Na	K	Exchangeable H^+
Concentration, me/100g soil	0.702	0.190	8.209	0.962	0.017

$\sum$ Exchanged cation capacity = 10.08 me/100g soil

The sand content in soil assumed as an aggregate was approximately 17%, which might influence on the strength of waste concrete due to a less amount of sand to clay mineral ratio of solid grain soil. The data in **Table 4.3** also indicated that the soil sample seemed to be permeable resulting from the large and continuous pores of sand.

Based on the investigating of the characterization of soil sample, physical, chemical, and mechanical properties interpreted that the implementation technology based on cement –stabilized soil should be considered carefully. The major findings of potential interference on the effectiveness of S/S treatment were in following:

(1) The great amount of particle size distribution of sample soil affected an amount of medium bulk density of soil. This influenced the difficult mixing of the S/S agents with

the contaminated soil. A loosened soil sample with an increase total pore was efficiency mixed with S/S agents simply.

(2) The percentage of 47.3 clay fraction in soil with decreased total soil porosity indicated that soil had a high water retention capacity and reduced the water permeability. This soil was also capable of cations adsorption and/ or complexation. Thus, clay fraction might hinder the hydration reactions of the Portland cement as S/S agents.

(3) Although the organic matter content of this soil sample is only 3.85% by mass, the active colloidal behavior of soil organic matter can affect soil physical and chemical properties. Consequently, the presence of organic matter might hinder the solidification of the cement structure during curing period. However, a low content of 10.08 me/100g soil cation exchange capacity (CEC) were found, as shown in **Table 4.4**. Because of the CEC of a soil change in pH, the various hydroxyls of clays and organic acids were more ionized in basic environment. Thus, the found CEC value was also interrelated to the clay texture and soil reaction (pH) of soil sample [40]. In addition, the low CEC values was revealed a low total acidity of organic matter content, and implied that a minimum sorptive capacity for inorganic cationic species of soil.

4.1.2 Sorption of metals on soil sample

The adsorption experiments utilized a L/S ratio of 3, and equilibrium time for 24 h as previously explained in **section 3.4.2**. The Langmiur adsorption isotherm were illustrated in **Figs. 4.2- a, b, c, and f,** that contaminated soil samples have adsorption ability toward metal ions. Because this experiment was designed as a way to investigate the complexation ability of humic acid onto solid/liquid phases, the stability constant of humic-metal binding (K_f) can be estimated by sorption studies.

The adsorption experimental results were illustrated by Langmiur isotherms. This isotherm was applicable to physical adsorption (monolayer) within a low concentration range [25, 41]. It was verified that the adsorption of cations corresponded to the Langmiur and not the Freundlich isotherm (applied the obtained experimental data to Langmiur and Freundlich equations), the better coefficients of correlation were frequently obtained for the Langmiur model. However, the Freundlich isotherms of metal sorption were available to estimate the *distribution coefficient*, K_d , and the obtained K_d were shown in **Table 4.5**.

The amount of sorbed metals gradually decreased as metal concentration in the test solutions were increased. This gave a chance for more soil-metal saturation that closed to the CEC of soil at a given pH following to raise its equilibrium concentration in the system. There was a significant relationship between the presence of HA, as well as soil organic matter, in soils with a 0.25 $molL^{-1}$ KNO_3 and the adsorption ability. For OS sample, and OS-KNO_3, soils have rather high adsorption capacity comparable with that of HS. This was explained that HA influenced on the increasing of solubility of metal attributing to metal complexation. Charge sites (mainly COO^- groups) facilitated HA to retain cation in nonleachable but exchangeable forms that were mobile. In the presence of HA, the adsorption coefficient (K_d) of soil towards metal ions decreased with respect to the formation of water-soluble complexes between these ions and humic acid; a postulated reaction between M^{+2} and HA function groups shown in **Fig. 4.1**. The bonding was partly covalent, particularly when the charge was neutralized by transition metal cations (e.g. Ni^{+2}, Cu^{2+}, and Zn^{+2}).

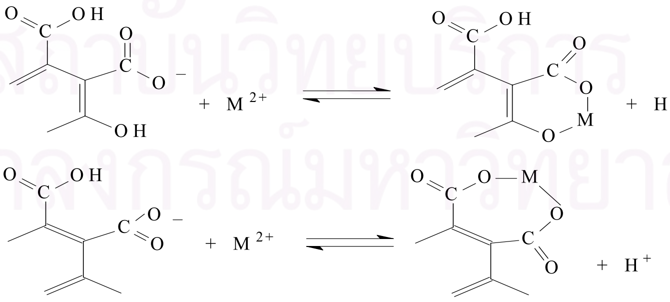


Figure 4.1 Postulated reactions between M^{2+} and humic acid function groups influencing a water-soluble complexation [44]

The complexes increased the mobility and water solubility in soil matrixes associated with the K_d value of soil adsorption decreased as shown in **Table 4.5.**

$$\mathrm{Soil}_{(s)} + aM^{n+}_{(aq)} \xrightleftharpoons{K_d} \mathrm{Soil}\ (a\text{-}b)M_{(s)} + bM^{n+}_{(aq)}$$

$$\mathrm{HA\text{-}Soil}_{(s)} + aM^{n+}_{(aq)} \xrightleftharpoons{K_d} \mathrm{Soil}(b)M_{(s)} + \underset{\text{water soluble complex}}{\mathrm{HA}(a\text{-}b)M^{n+}_{(aq)}}$$

where a, and b: mole of metal ions (a >b), M^{n+} : metal ion with n charge

The K_d value for each metal ions were estimated from the slope of Freundlich isotherm in the lower region of the highest linearity, which the correlation coefficient (R^2) closed or equal to 1.

$$C_s = x/m = K_F C_e^{\ 1/n}$$

Where n =1, K_F an equation above can be replaced by K_d then yielded

$$K_d = C_s/C_e \qquad (\mathrm{L\ mg^{-1}})$$

This estimation of K_d based on the assumption that the concentration of metal species were low, and the established equilibrium time at 24 h was achieving.

Table 4.5 The values of soil distribution coefficient, K_d under various soil sorbents

Sorbents	K_d ($\times10^{-3}$ L mg^{-1})					
	Cd	**Cu**	**Cr**	**Ni**	**Pb**	**Zn**
OS-deionized water	9	9	6	6	13	13
OS-KNO_3	20	20	6	7	9	9
0.25% w/w HS-KNO_3	7	7	7	6	11	11
5.0 % w/w HS-KNO_3	8	8	6	7	8	8

The values of K_d for cadmium and copper of OS-KNO_3 were significantly decrease comparing to those of 0.25 and 5.0 % w/w HS-KNO_3. No comprehensible of K_d values for chromium, nickel, lead, and zinc were observed.

As described previously, the Langmiur isotherm employed the coefficients of correlation. Their isotherm profiles of cadmium, copper, chromium, and zinc sorption were relatively similar for all cases (**Figs. 4.2-**a, b, c and f) While nickel, and lead –Langmiur sorption isotherms were different (**Figs. 4.2-**d and e), and worthy of particular consideration. The maximum adsorption capacities for these metals were observed at initial concentration of each metal in test solution at 66.67 mgL^{-1} (5 mg Ni and Pb per 25g soil) for 0.25 and 5.0 % w/w HS-KNO_3

As regard to the various hydroxyls of clays, humic acids, and organic acids in soil ionized H^+ into soil solution; thereby producing the negatively charged cation exchange sites. The high CEC in soils, especially in humic added soil, the more negatively charged cation exchange sites that heavy metals were almost all adsorbed [40]. The maximum amount of metals adsorbed corresponded to the number of cation exchange sites. The excess amount of metals dissolved in the soil solution in free ions forms. It was observed that low metal concentration, the percentage of adsorbed metal highly increase around 95%. While in the case of high metal concentration, no amount of adsorbed metal was observed especially in case of lead and nickel. Moreover, these metal species were dissolved by the test solution. At just less than 2.5 mg metal in the solution, more than 50% of metal was adsorbed onto HA added soils. The results illustrated that the amounts of sorbed metals of which range from 50 to 95% were observed for OS samples. Influence of added HA was obvious at concentration above 0.625 mg of each metal in the test solutions for 25 g soils. In addition strong ionic strength affected the metal adsorption; as shown in **Figs. 4.2-** a to f. It was also observed for all metal ions with maximum equilibrium concentration (C_e) rising.

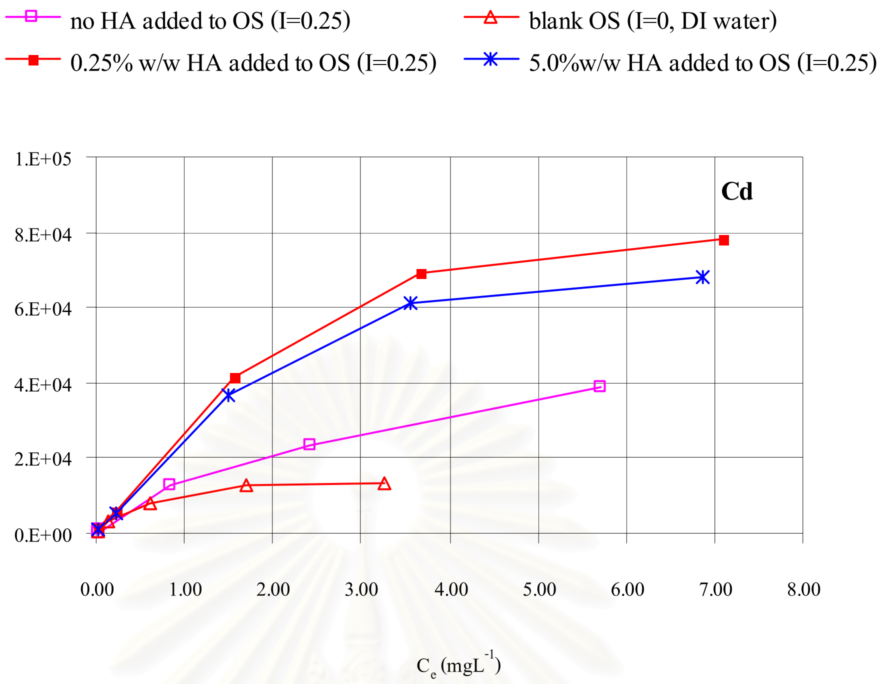


Figure 4.2-a Langmiur isotherm of adsorption of cadmium onto soil samples at 25 °C

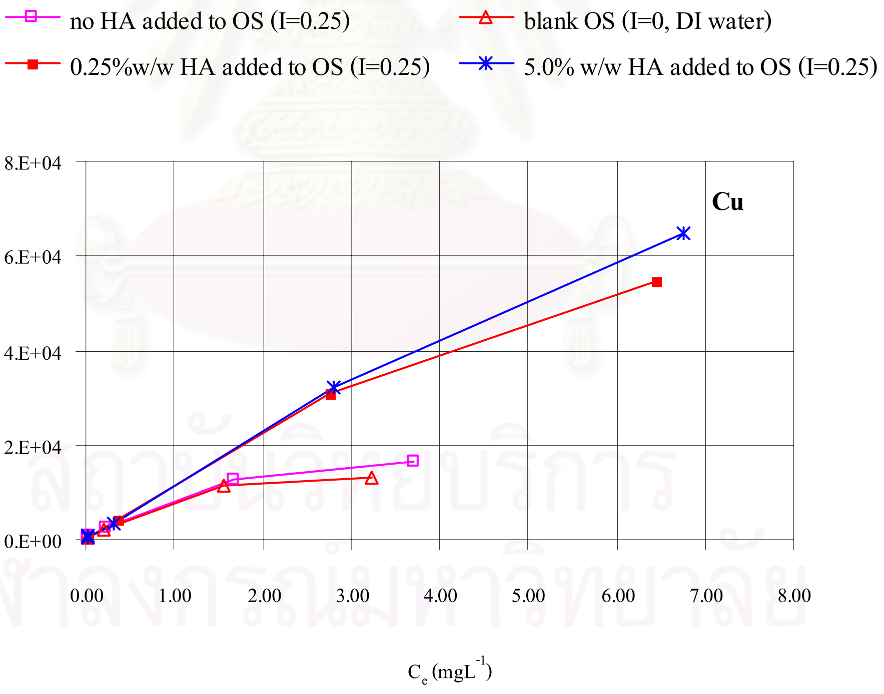


Figure 4.2-b Langmiur isotherm of adsorption of copper onto soil samples at 25 °C

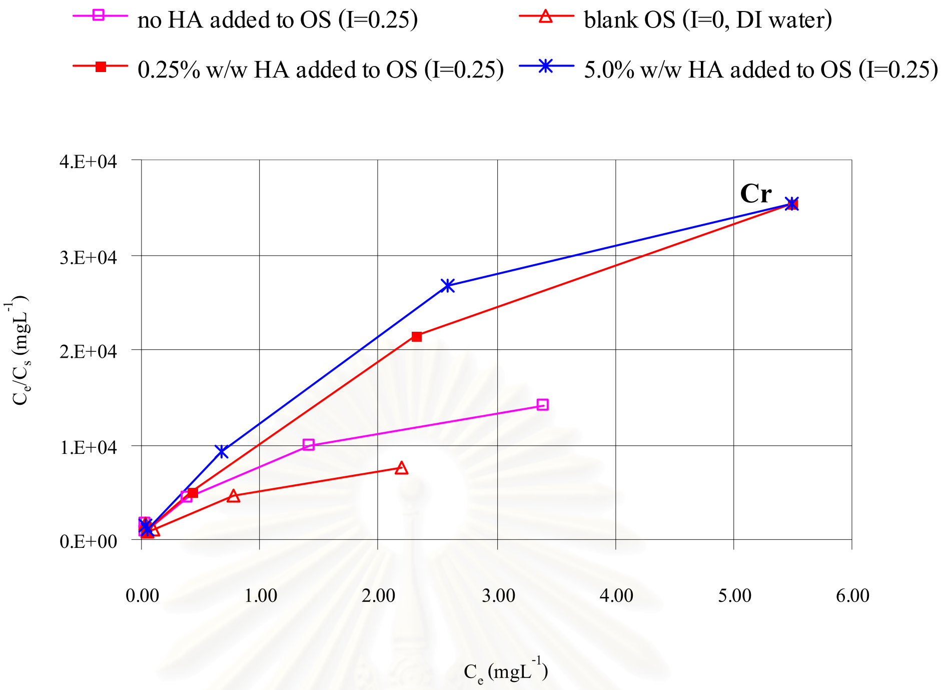


Figure 4.2-c Langmiur isotherm of adsorption of chromium onto soil samples at 25 °C

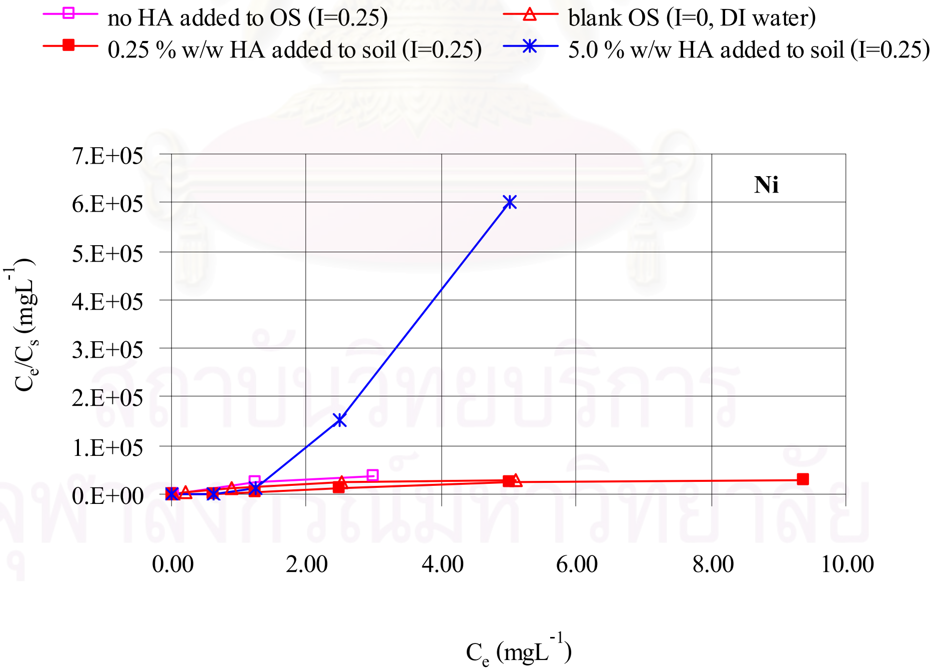


Figure 4.2-d Langmiur isotherm of adsorption of nickel onto soil samples at 25 °C

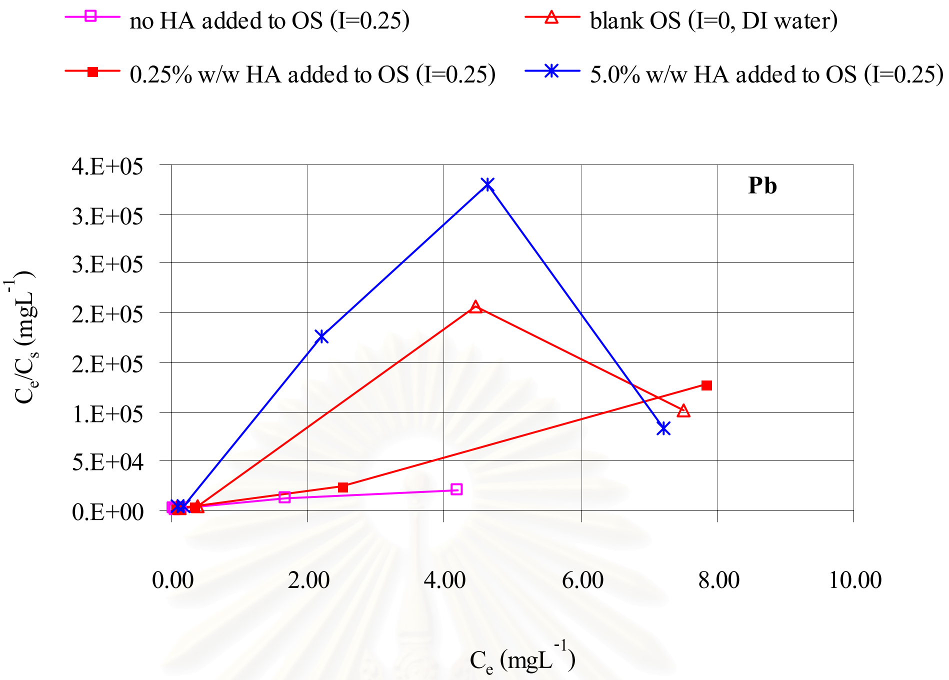


Figure 4.2-e Langmiur isotherm of adsorption of lead onto soil samples at 25 °C

The adsorption of lead on to soils as shown in **Fig. 4.2**-e and **Figs. 4.3- 4.6**, it found that lead sorption onto the OS-KNO_3 increased with increasing of the initial metal concentration for all of the test solutions. On the contrary, the maximum amount of sorbed lead ions was approximately 2.1, 2.5, and 1.1 mg for 25 g OS, 0.25 and 5.0 % w/w HS-KNO_3, respectively. In case of lead concentration was higher for the later soils, the sorption decreased suddenly. It was expected that sorption mechanism had been changed concerning the desorption of weak metal ions-soil-humic bindings. However, the experiment result for lead sorption was different to the results reported by Pulse and his coworkers that lead sorption not forever increased with ionic strength. The significant relevant factors at this point were a high concentration of metal ions and pH of the test solutions. It was important to notify that higher percentage amount of HA added to soils, results in higher pH of the test solution. This affected lead desorption from soil matrix to the solution.

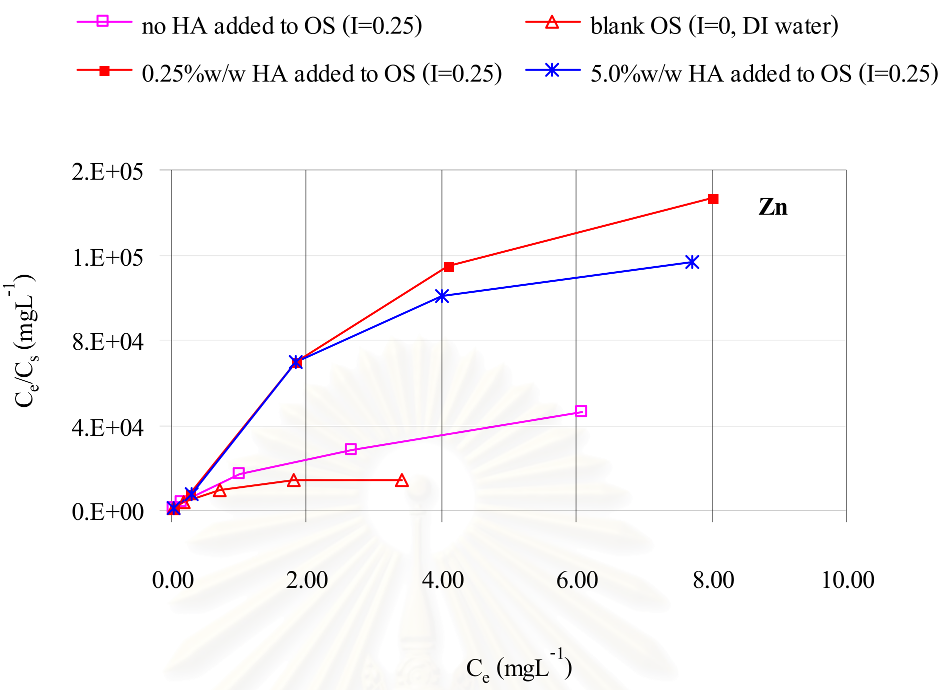


Figure 4.2-f Langmiur isotherm of adsorption of zinc onto soil samples at 25 °C

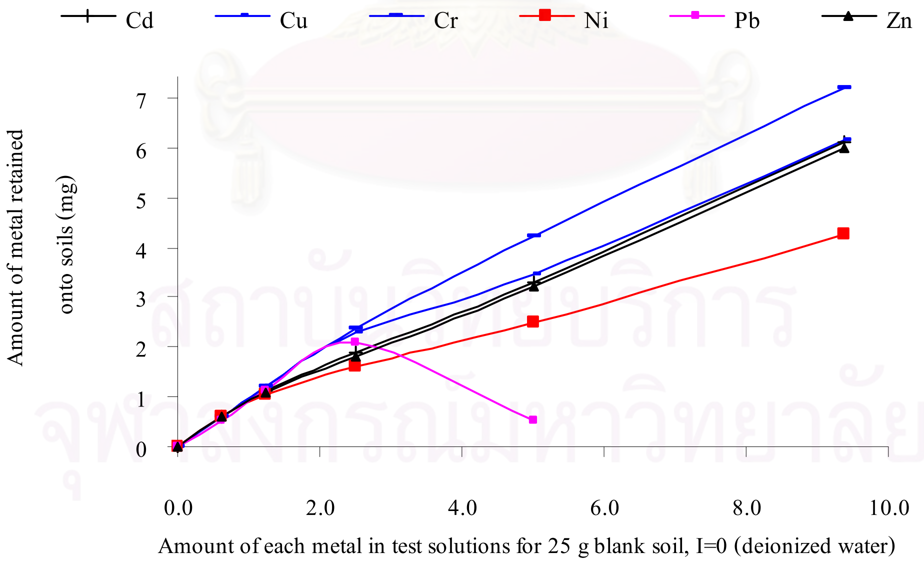


Figure 4.3 Adsorption of 75 mL of metal concentrations of various metals onto 25 g OS

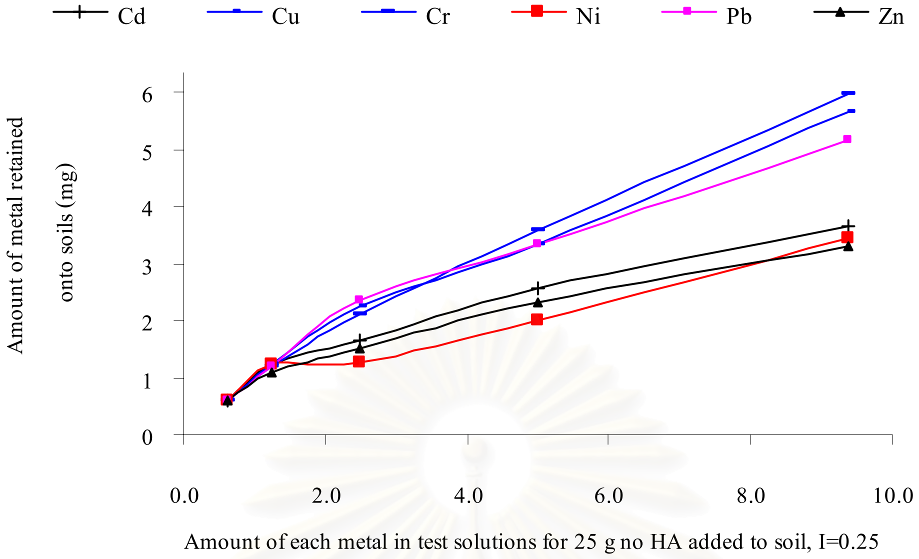


Figure 4.4 Adsorption of 75 mL of metal concentrations of various metals onto 25 g OS – KNO_3

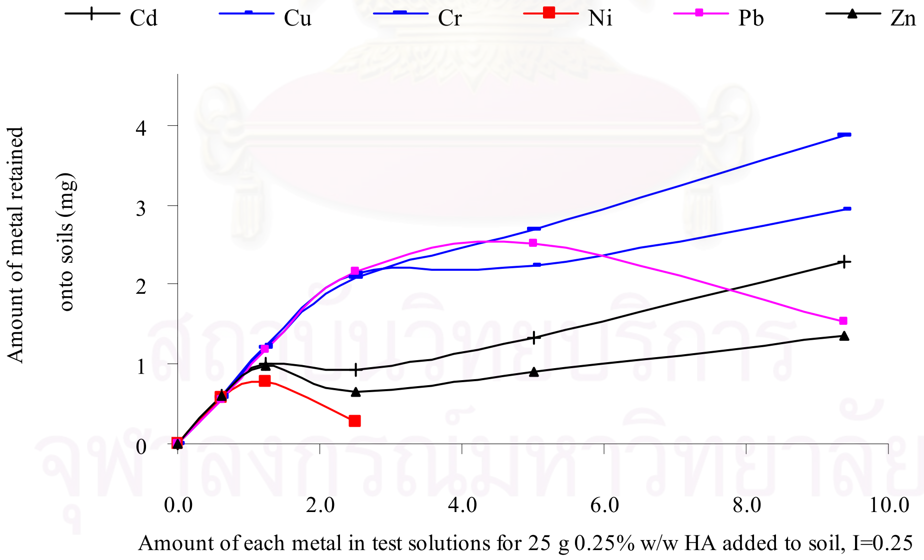


Figure 4.5 Adsorption of 75 mL of metal concentrations of various metals onto 25 g of 0.25% w/w HS-KNO_3

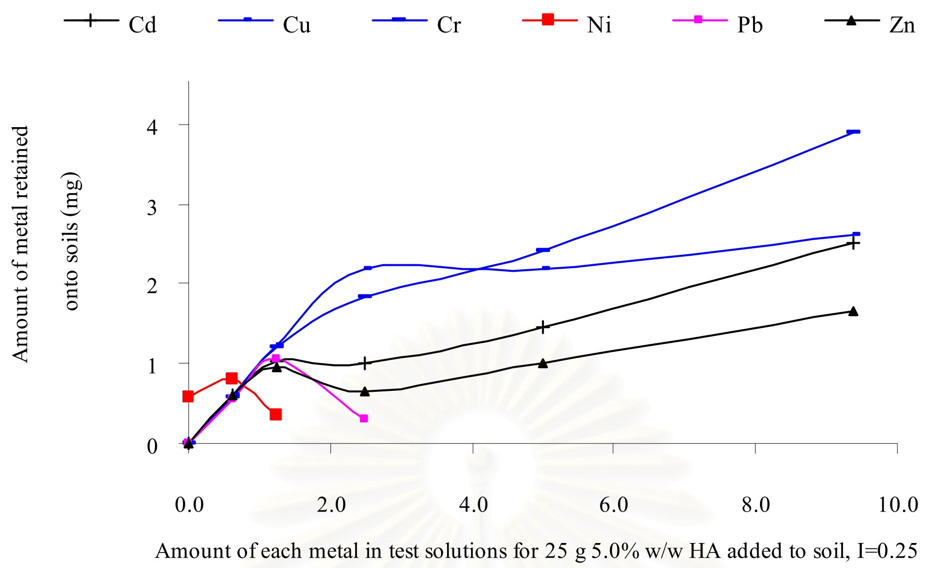


Figure 4.6 Adsorption of 75 mL of metal concentrations of various metals onto 25 g of 0.25% w/w HS-KNO_3

In addition, the maximum and minimum selectivity of metal adsorption in each medium might be explained based on affinities of soils with humic materials (AHA).

Table 4.6 Sorbents and maximum affinities for studied metals

Sorbents	Low [M] in the test solution[#]	High [M] in the test solution[#]
OS-deionized water	Cr, Cu, and Zn	Cr, Cu, and Zn
OS-KNO_3	Cd, Cu, Cr, and Zn	Cr, Pb, and Cd
0.25% w/w HS-KNO_3	Pb, Cu, and Zn	Cr
5.0 % w/w HS-KNO_3	Cr, and Cu	Cr

[#] *Low concentration: 0.625 – 5.0 mg of each metal for 25 g soil.*

[#] *High concentration: 5.0 – 9.375 mg of each metal for 25 g soil.*

Table 4.7 Sorbents and minimum affinities for studied metals

Sorbents	Low [M] in the test solution [#]	High [M] in the test solution[#]
OS-deionized water	-	Pb
OS-KNO_3	-	Cd, Ni, and Zn
0.25% w/w HS-KNO_3	Ni	Zn, and Pb
5.0 % w/w HS-KNO_3	Ni, and Pb	Zn

[#] *Low concentration: 0.625 – 5.0 mg of each metal for 25 g soil.*

[#] *High concentration: 5.0 – 9.375 mg of each metal for 25 g soil.*

The results from the **Tables 4.6-4.7** showed that sorption medium have different affinities for metals. Chromium and copper were retained on soil strongly to all soil-sorbents for both low and high metal concentration in the test solutions. Whereas minimum affinities of nickel and lead ions sorption were observed in the 0.25 and 0.5% w/w HS-KNO_3 samples taken part at low metal concentration, zinc ions adsorption showed a fewer minimum affinities.

In conclusion, the K_d values were available and considered one of the input parameters for leaching models. The affinities of soil to metal adsorption can estimate the leachability of each metal which one being critical metals for the stabilized soil especially in the presence of HAs.

4.2 Characterization of humic acids

The yield of dried humic acid extracted from soil sample based on the IHSS's method was 3.76 gkg^{-1}. The soil was classified as nonhumus soil. The extracted humic acid was fractionated into two parts in ethanol solution. The amounts of dissolved part (hymatomelanic acid) and undissolved part (α- humic acid) were 11.46 %, and 88.54%, respectively. The laboratory procedures by means of molecular spectroscopy, and thermal analysis were conducted to characterize SHA comparing with AHA, IHSS soil HA reference 1R106H, and IHSS soil HA standard 1S102H. Elemental composition of the SHA was C, 41.77%; H, 4.03 %; and N, 0.48 % as showed in **Table 4.8**. The C and H contents of SHA were similar to those reported by IHSS and references except for N content, which was less than those values. The chemical properties of humic acids were presented below.

4.2.1 Elemental composition of humic acids and ash contents

The compositions of SHA were similar to those of the other reference sources. By comparison with elemental composition expressed in term of atomic percentages, the variation was relatively small. However, it was important to notice here that variation in the composition was affected by variability in soils, humic acids, isolation and extraction techniques, and errors in sampling and analyses. The results of the determination of ash content, SHA and AHA yielded 2.113 and 3.194% ash, respectively. There was a significant amount of mineral as shown by the ash content and the presence of Si-O band (1035 cm^{-1}) [46] in the PAS-FTIR spectrum. These were caused by the high content of clay fraction and/or insufficient purification of humic acids.

4.2.2 Acidity of the humic acids

The acidity values were reported in milliequivalents per gram (meq/g) in **Table 4.9**. The results showed that phenolic-OH acidity was significantly larger than the carboxylic COOH acidity for both of SHA and of AHA. Thus, the negative charged- sites of phenolic functional groups were much more than of the once. The presence of high phenolic content might be effective on chelation and complexation reactions.

Table 4.8 Elemental composition, atomic ratio of HA samples and their ash contents

Sample	%C$^{\#}$	%H$^{\#}$	%N$^{\#}$	H/C	N/C	%ash content
SHA	41.77	4.03	0.48	0.10	0.01	2.113
AHA references [23]	49.8	4.7	2.3	0.09	0.01	-
AHA	3.69	2.70	0.38	0.73	0.10	3.194
	(38.28)	(4.71)	(0.63)	0.12	0.02	-
IHSS soil HA reference	48.60	5.35	4.60	0.11	0.11	nd.
1R106H	(54.00)	(4.84)	(5.13)	(0.10)	(0.10)	(1.41)
IHSS soil HA standard	51.94	3.69	3.75	0.07	0.07	nd.
1S102H	(58.13)	(3.68)	(4.14)	(0.06)	(0.07)	(0.88)
Average percentage form various sources[23]	53.8-58.7	3.2-6.2	0.8-4.3	-	-	-

$^{\#}$ *calculated on dry ash free matter basis, nd: item was not determined, values in the bracket: obtained by the reference which reported by IHSS, USA.*

Since the carboxyl content in soil humic acid were in the range of 2.4 to 5.4 meq/g, which obtained by the Calcium acetate method reported by Stevenson [39]. The obtained values from the experiment were out of the range for COOH. The phenolic-OH content in SHA was over range of 1.5 to 4.4 meq/g, which noncorrespond with values reported by Schnitzer [23].

4.2.3 Humification index

The typical absorption spectra of the SHA solutions at pH 4 and 11 were shown in **Fig. 4.7**. For spectrum of others humic acids the curves looked similarly; such two wavelengths were selected in studying of the humification index streaked in strength lines from the near visible region (465 nm) to the far visible region (650 nm). The SHA had the smallest the value of the logarithm of absorbance ratio, corresponded to steep absorbance curves, this related to the highest degree of humification of soil sample [23]. Moreover, this soil humic acid tended to possess a longest lifetime. As a whole, because of large broadness of absorption bands covering all λ values, presumably related to nature of humic acids, identification of chromophores in traditional meaning might be impossible. Therefore, the absorption spectrum was featureless with absorption increasing at lower wavelength due to the overlapping absorption spectra of the functional groups.

Table 4.9 Total, carboxylic and phenolic acidities of the HA samples in meq/g HA; # calculated by difference of column 2 and 3

Sample	Total acidity	Carboxylic acidity	Phenolic acidity #
SHA	7.71	1.10	6.61
AHA	5.57	1.10	4.47
HA	6.7	3.6*	3.1**

** mean values of COOH acidity for Soil humic matter, ** mean values of phenolic-OH acidity for Soil humic matter[23].*

Table 4.10 The logarithm of absorbance ratios (D_4/D_6) at 465 and 650 nm of SHA samples in 0.05 mol L^{-1}NaOAc buffer solution in pH 4 and 11 against the blanks

Sample solution	D_4/D_6 pH 4	D_4/D_6 pH 11
SHA	0.85	0.96
AHA	3.22	3.37
IHSS soil HA reference 1R106H	6.14	12.81
IHSS soil HA standard 1S102H	2.52	3.99

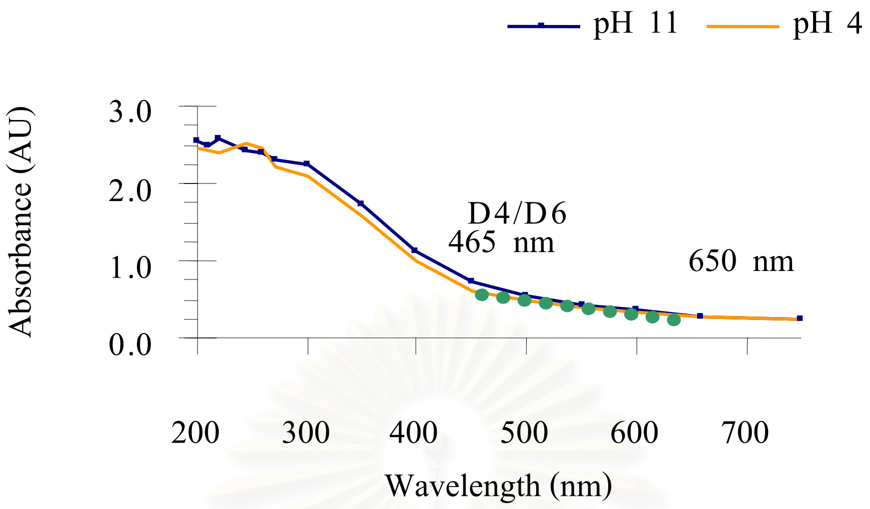


Figure 4.7 UV-Visible Spectra of SHA in an acetate buffer solution at pH 4 and 11

From the experimental results shown in **Table 4.10**, the D_4/D_6 ratios at pH 4 and 11 were not identical for all kinds of HA. This indicated the effect of pH on absorbance ratio of humic acid. These phenomena were usually related to the higher negative charge attributed to the dissociation of protons in phenolic-OH functional groups of humic molecule as illustrated in **Fig. 4.8**.

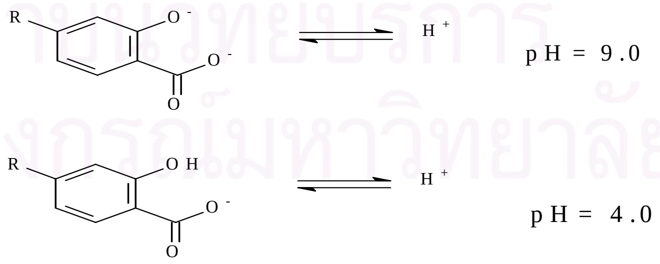


Figure 4.8 Development of variable charges in a humic molecule by dissociation from carboxyl groups at pH 4.0, and from phenolic-OH groups at pH 9.0

The present experimental results implied that the complexation reactions take placed at pH 4.0 to 8.0 in natural soil environments. As the pH of sample soil was 7.34, the metal-humic complexes can occur. Particularly in condition of S/S by cement that pH of alkaline matrix was higher than 12, the chelation reaction would be dominant at this pH value, because the ionization of phenolic-OH will be reached at this pH.

4.2.4 PAS-FTIR spectrum of humic acids and soils

To ascertain that metal-humic complexes occur, the PAS-FTIR spectrum was taken under investigations. The soil and humic acid samples were listed in **Table 3.3** obtaining PAS-FTIR spectra. The spectra of the soils and humic acids were shown in **Figs. 4.9-4.10**. Interpretation of the spectra was based on the following literature: Perez et al, 2003 [11]; Tan, 2003 [23]; Nakanishi et al, 1977 [47].

The most interesting bands, in which oxygen-containing functional groups carboxylic and phenolic-OH were accounted for, were: a broad band around 3397 cm^{-1} (H-bonded OH group); a sharp peak at 2913 cm^{-1}(aliphatic CH stretch); a well pronounced broad band at 1680 cm^{-1} (aromatic C=C, C=O, and/or C=O of bonded conjugated ketones, quinone, C=O stretch of amide I); and a peak at 1060 cm^{-1} (C-O stretching of polysaccharides like substances, Si-O of silicates). The sharp peak at the 1035 cm^{-1} was found that attributed to Si-O vibrations of clay impurities and indicated the presence of clay material that was not completely removed during the purification process of the experiment (ca. 2.1 % ash content). The FTIR spectra of SHA (**Fig. 4.9**/portion 9) were similar for other HA samples obtained from the IHSS (portions 6, and 7).

Besides, PAS - FTIR spectra of the OS (dried), shown in **Fig. 4.10** was found that a very strong band at 1587 cm^{-1} (C=O stretch of $RCOSiR_3$ either water band) was shifted to 1643 cm^{-1} (C-O^- symmetrical stretch) during the addition of metals and humic acid. The PAS-FTIR spectra of OS showed a weak band at 950 cm^{-1} corresponded to Al-OH vibration, a weak broad band at 3680 cm^{-1} corresponded to OH vibration, and to vibration of octahedrons in silicate minerals. A sharp strong band at 2644 cm^{-1} was attributed to OH vibration of carboxylic acid which confirmed by the existent of a band at 1701 cm^{-1} corresponded with C=O stretching vibration. The soils in which added humic acid and/or heavy metals had a slightly similar PAS-FTIR spectrum by comparison the position of the OS spectra of a very strong broad band at 3600 cm^{-1} to 3400 cm^{-1}(OH stretching vibrations connected to intermolecular H-bonding of polymeric OH in the molecules); 1632 cm^{-1} and 1400 cm^{-1} ($C-O^-$ antisymmetry and symmetry stretching of carboxylate group); 1020 cm^{-1} (Si-O stretching vibration that intense and very broad; and at about 770 cm^{-1} (aromatic C-H vibrations), respectively. Shoulder peaks were observed at 3000 and 3480 cm^{-1} for the addition of metal and humic acid to OS both at C_2 and at C_1 levels (portions 2, and 3). These shoulder indicated the presence of the complexes of metal humic linkages.

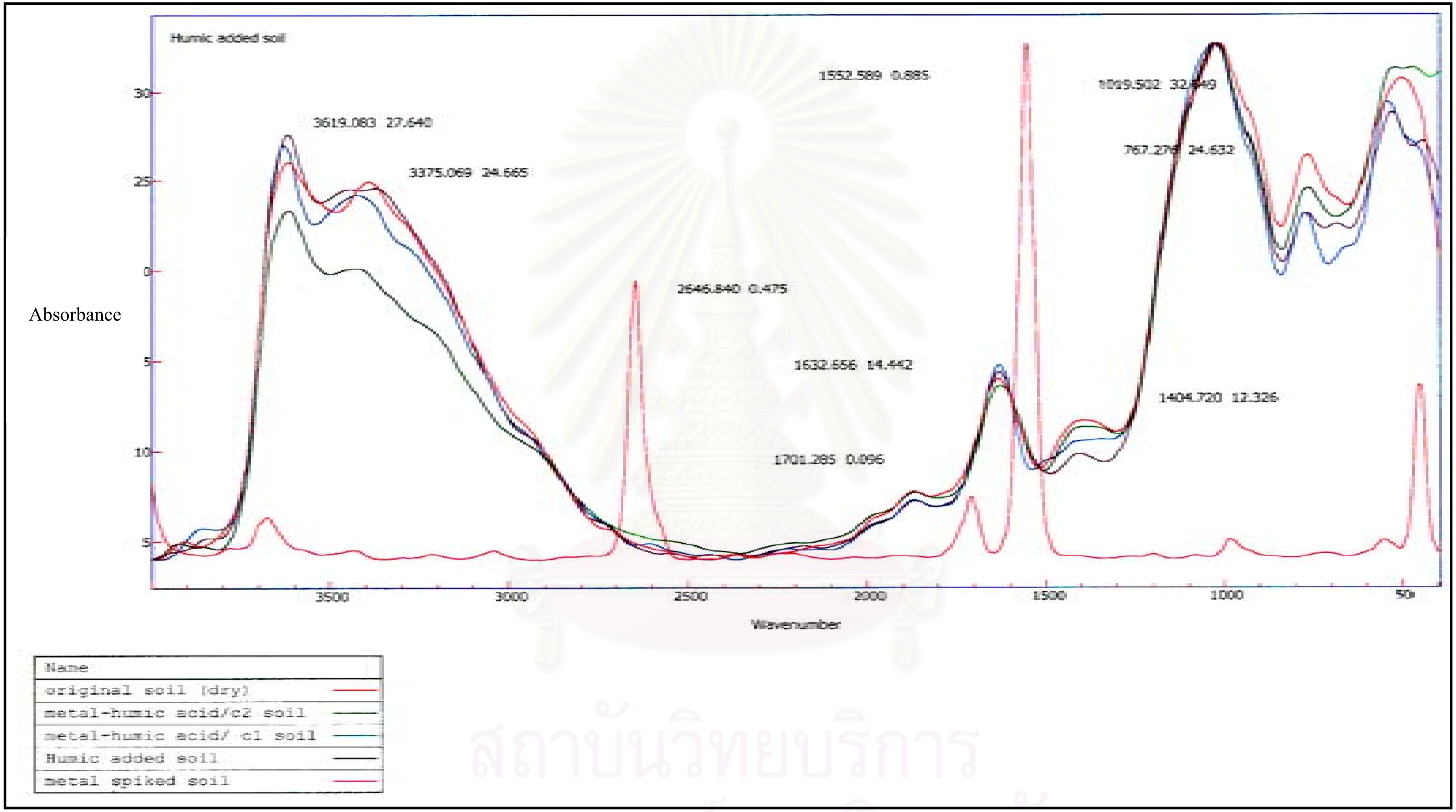


Figure 4.9 PAS-FTIR spectra of soil and humic acids

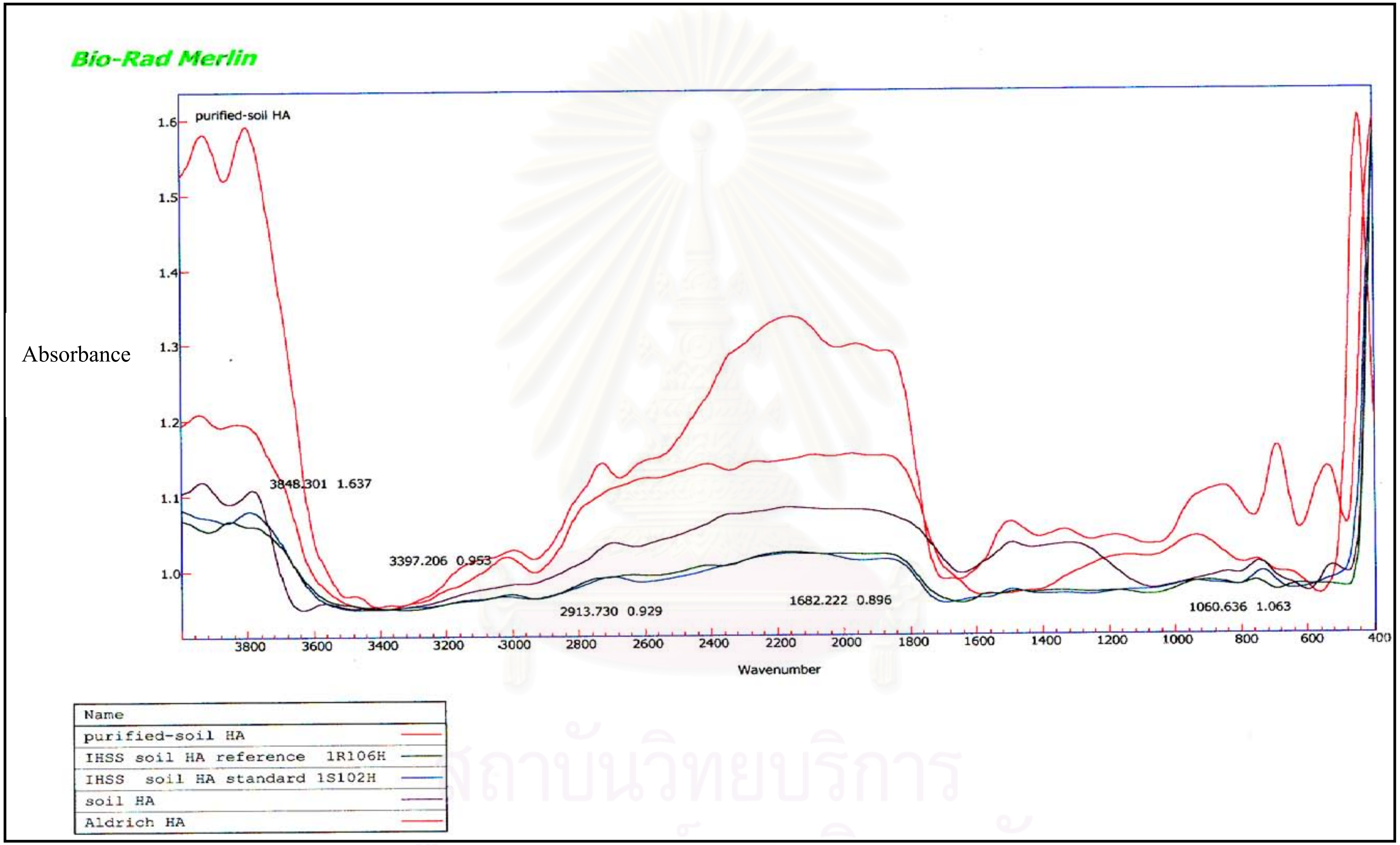


Figure 4.10 PAS-FTIR spectra of humic acids

4.2.5 Thermal analysis [39, 48-50]

The thermogram of soil samples and SHA listed in **Table 3.4** were obtained. Thermal analyses data were shown in Table 4.11.he DSC thermogram of the whole OS sample with and without the decomposition of organic matter by 30% w/w H_2O_2 solution were shown in **Figs. 4.11-**a and b , respectively. The DSC thermogram showed that a smaller amount of the heat of enthalpy of endothermic peak at about 300°C (+15.46 μVs.mg^{-1}) and 500 °C decreased for the decomposed organic matter-OS sample. This observation indicated that organic matter content in soil, including humic acid, was stable to the chemical oxidation. These may implied that metal species had stability to chemicals and environmental conditions. The heat of enthalpy of endothermic peak at about 520 °C increased with significant increase of metal addition (**Fig. 4.11-**e) by comparison to the DSC thermogram of whole soil (**Fig. 4.11-**a) in the same sample weight. The addition of metal solution to soil minerals and/or humic-soil, Occurring reactions could be described by several mechanisms, including humic complexation of metals, yielded the getting higher of heat of enthalpy. It was importantly noticed herein, that there were two endothermic peaks at around 300°C and 320°C possibly attributed largely to humic acid addition (**Figs. 4.11-**c and d). The excess of humic acid added soil might be not so much by chemical bonding but rather by sorption on the soil surface, without metal addition. Therefore, as mention previously, HA-DSC thermogram was also shown in a region of endothermic peak at about 300 °C including at about 520 °C. **Fig. 4.11-**d indicated that the addition of 2 mL 5 % w/w HA solution to 5 g OS caused a broad endothermic peak at about 300 °C to 320 °C. DSC thermogram in **Figs. 4.11-**d, e, and f showed that the heat of enthalpy based on the same mass at 125 °C soil decreased with increasing of amount of added humic acid and metal solution.

Fig. 4.11-g DSC thermogram of SHA sample showed well-defined thermal events. The DSC curve showed endothermic peak attributed to dehydration and loss of peripheral polysaccharide chains (temperature at 125 °C) with ΔH of + 26.25 μVs.mg^{-1}. Although,

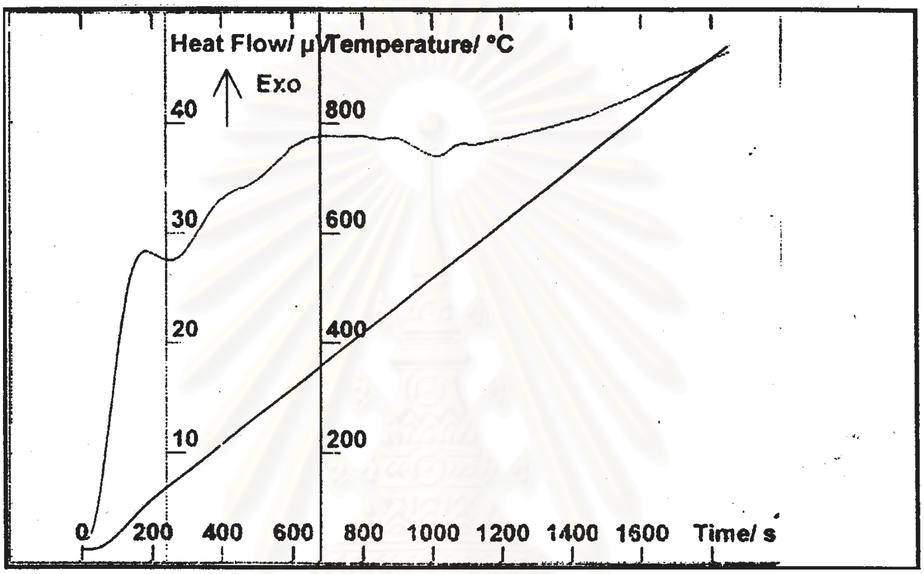
dehydration of SHA sample was performed by dried at 80°C and kept in desiccator in the presence of silica gel prior to run. However, a very sensitive to adsorb water of humic acid yielded a strong endothermic peak at 125 °C. The thermogram also found a strong endothermic peak at about 525 °C with the ΔH of + 22.83 µVs.mg^{-1}, attributed to the decomposition of humic molecule. These released energy suggested the presence of a significant number of strong bonds in the soil humic acid. The bonding was expected to the intermolecular organo-mineral linkages yielded thermostable materials.

Table 4.11 Thermal analysis data DSC of the samples

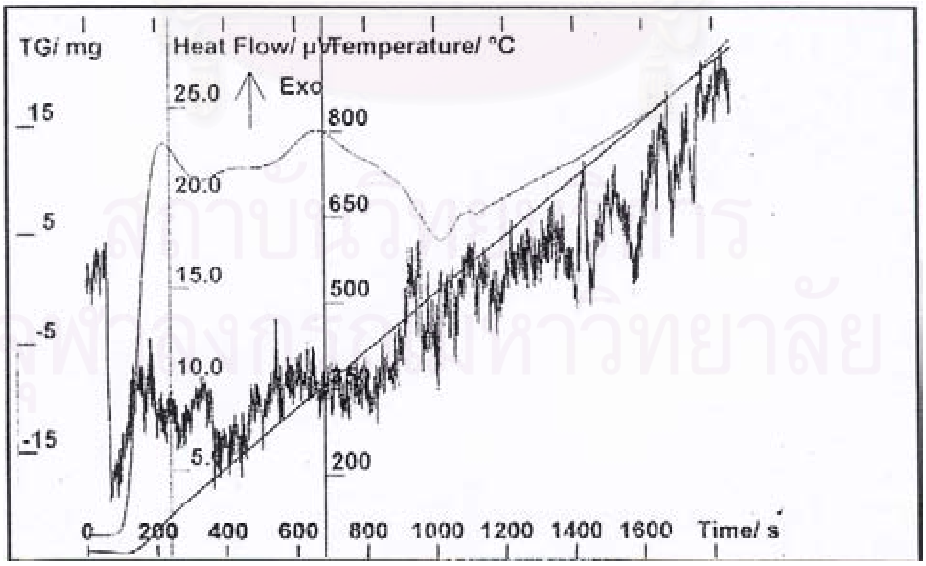
No.	Samples	Thermal events of DSC at the 1st endothermic peak	
		Tg °C	Enthalpy µVs.mg^{-1}
1	Whole soil	123.74	15.46
2	Whole soil + H_2O_2	179.46	9.71
3	Metal spiked soil	160.94	28.10
4	1% w/w HA added to soil	160.42	31.42
5	5% w/w HA added to soil	151.14	24.14
6	Metal added to 5% HA soil	171.60	11.83
7	SHA, ground to < 2-mm	147.41	22.83

Figs. 4.11-a, and e shows the TG-DSC thermogram of OS and metal spiked soil sample, respectively. The phases of metal oxides appeared at about 350°C with rapidily increasing and followed by gradually reducing of mass caused by heating up. The decomposition of soil minerals that the heat flow (about 31 µV) of OS sample was higher than of metal spiked soil. In experimental results of TG-DSC thermogram shown in **Figs. 4.11-**c, d, and e, the available consequences were only focused on the change of curves and their characteristic in the range of temperature around 125 °C to 900 °C. Generally, the

curve profiles (**Figs. 4.11-**c, and d) were slightly different in size, but were identical in the tendency of the mass variation. These implied that the soil-humic interactions were independence of concentration of humic content in soil. However, in the presence of metals that were spiked to humic-soil, the DSC/TG thermogram (**Fig. 4.11-**f) implied that the metal-humic soil's interaction affected to the variation of mass that gradually change.

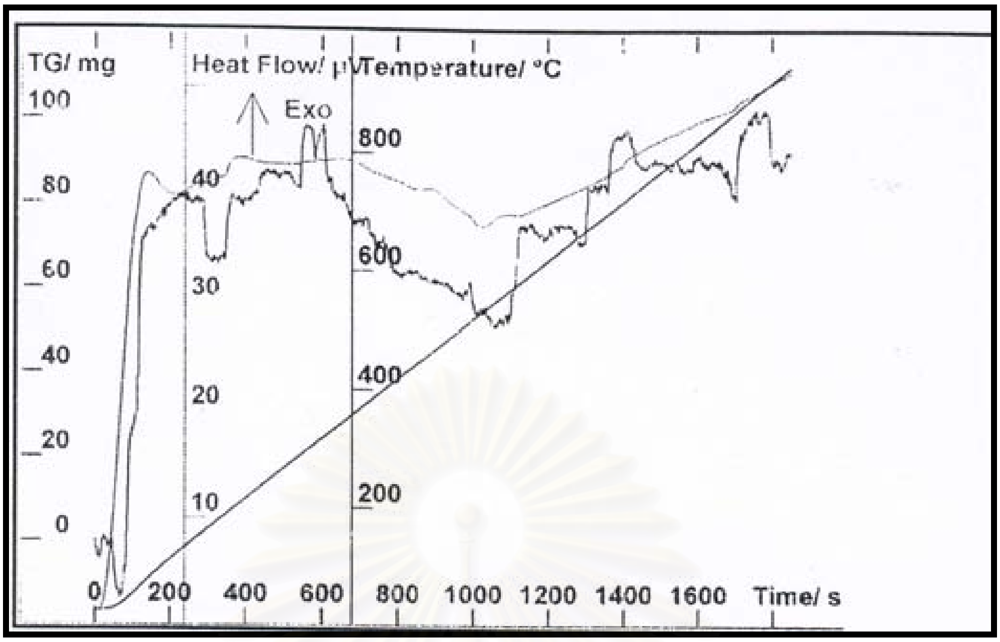


(a)

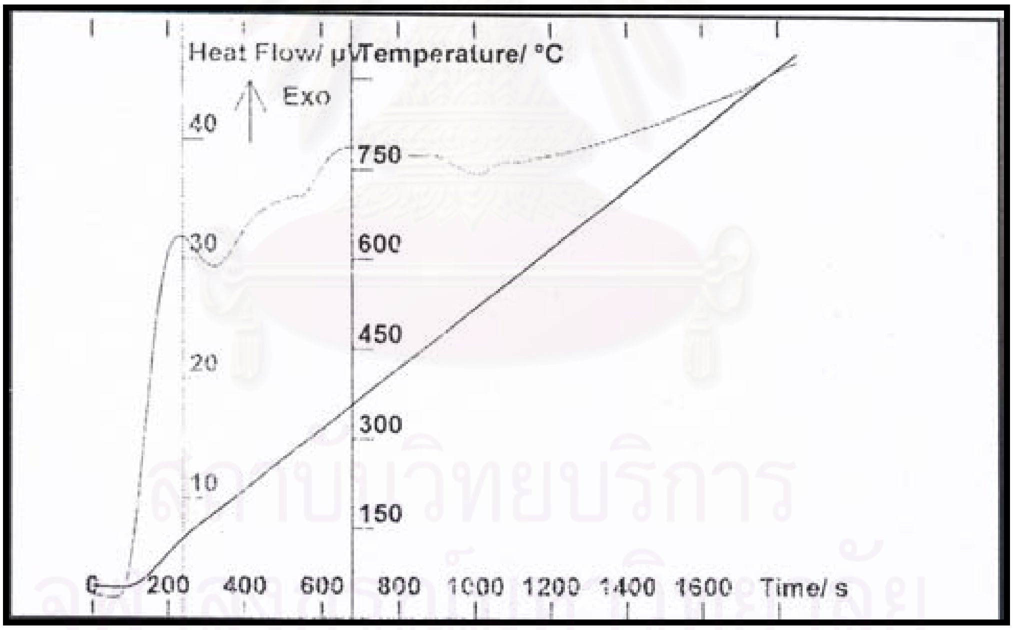


(b)

Fig. 4.11 DSC/TG thermogram (a): whole soil, (b): OS treated with 30 % w/w H_2O_2

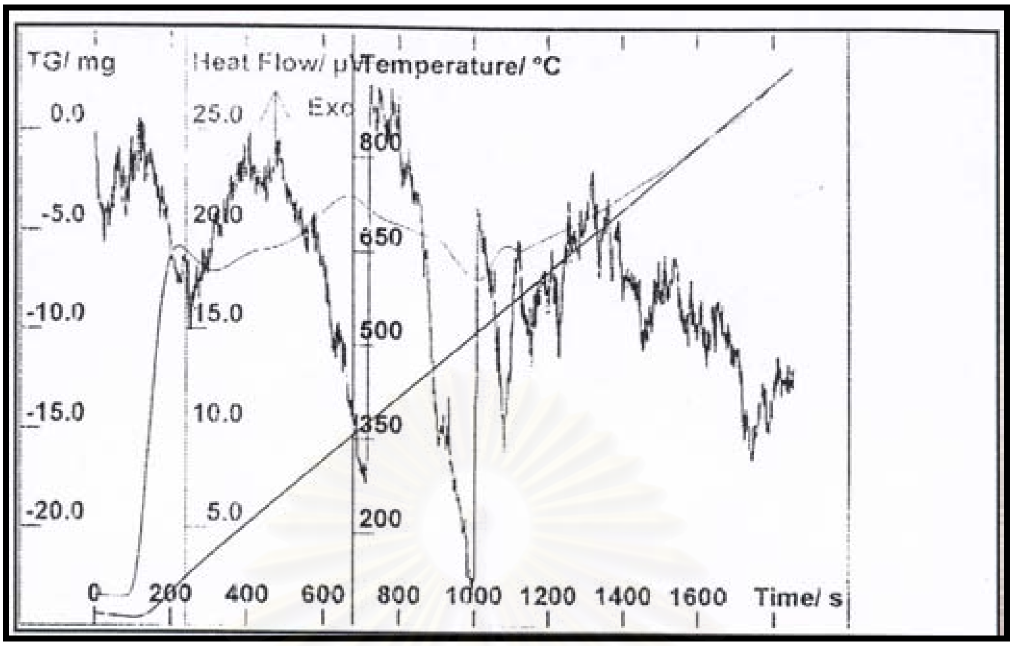


(c)

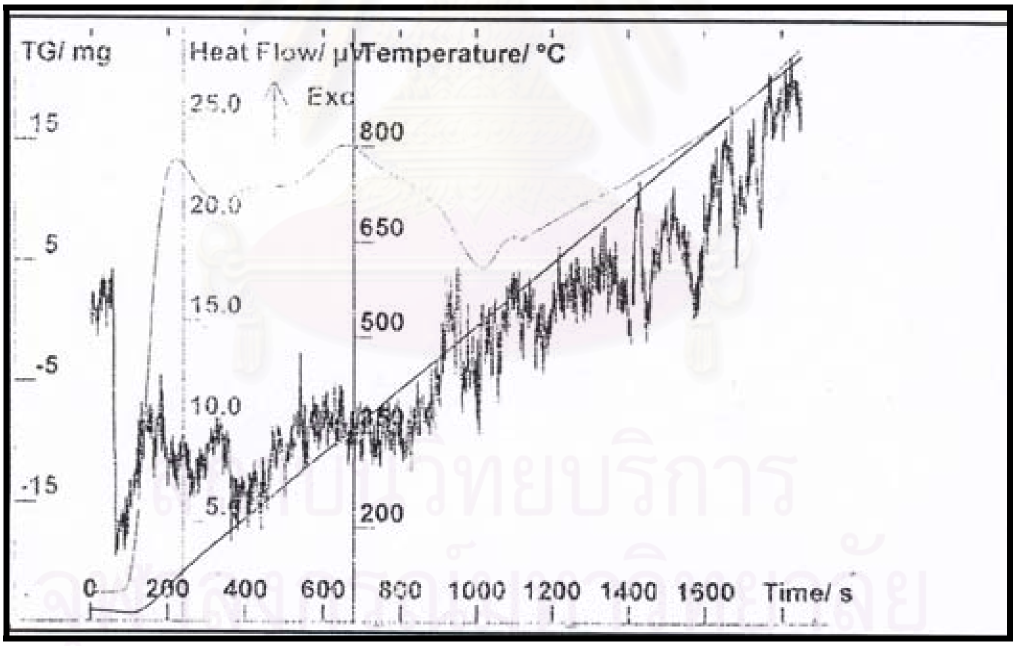


(d)

Fig. 4.11 DSC/TG thermogram (c): soil incubated with 1% w/v AHA solution, (d): 5% w/v AHA solution

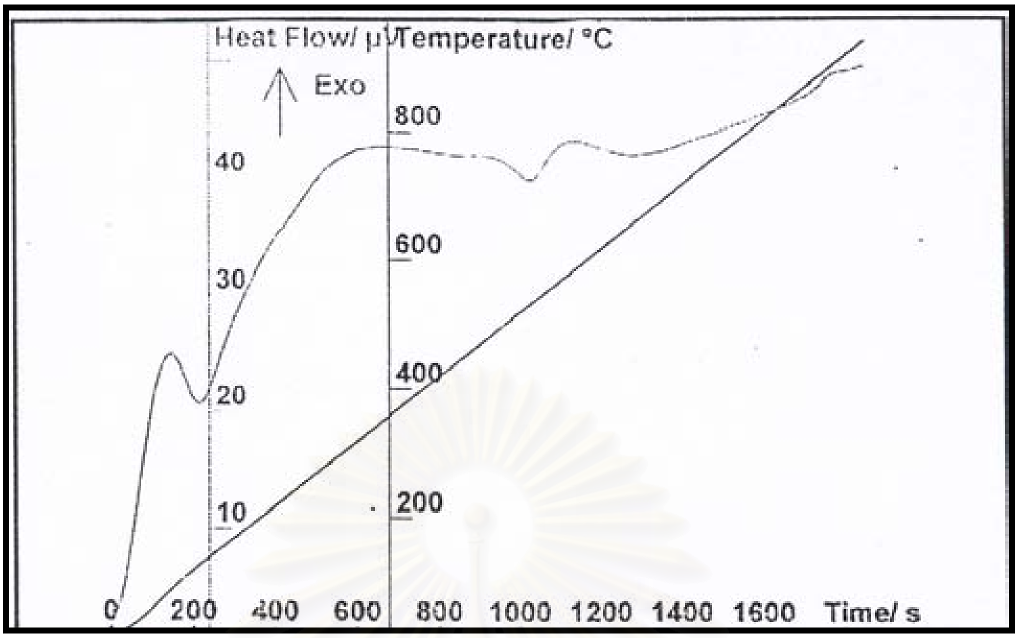


(e)



(f)

Fig. 4.11 DSC/TG thermogram (e): soil incubated with 2 ml of 125 mgL^{-1} heavy metals solution, (f): soil incubated 125 mgL^{-1} heavy metals solution and 5 % w/v AHA



(g)

Fig. 4.11 DSC/TG thermogram (g): SHA

4.3 Study of Stabilized/Solidified of Soil Sample

4.3.1 Influence of binder to waste ratio

The study of concrete formation was the primary objective conducting with blocks prepared in five batches, of which percentage of water, C/S ratios were shown in **Table 3.5**. For all batches, blocks with a curing time of 28 days were submitted to a Compressive Strength (CS) tests. The CS and density (D) of the S-OS were shown in **Table 4.12**. The CS and D diminished significantly with decreasing the C/S ratio. The low C/S ratio was influenced by the solidification of the S-OS because a large amount of soil affecting the weakening bond between soil particles and cement. At the C/S of 1/1, the CS is the highest. With the material used, increasing the water content from 40% to 55% had less effect on the CS of concretes than the decrease of the C/S ratio.

Table 4.12 Compressive strength and bulk density of S-OS

Batch number	Cement to soil (C/S) ratio	Density (D) of concrete, g cm^{-3}	Compressive strength (CS), MPa
1	1/1	1.565	1.16
2	1/1.5	1.500	1.03
3	1/2	1.336	0.59
4	1/3	1.325	0.19
5	1/4	1.295	0.19

The treatment S-OS, batch no.2 had been established for the further experiment as a **model block**. The concrete formation of a model block was shown in **Fig. 4.12**. Bulk density of concrete model was 1.500 gcm^{-3}. Its bulk density was inversely proportional to the C/S ratio and directly corresponded to its CS. In addition, bulk density can be used to estimate differences in compaction of a given concrete mortar. The C/S ratio changes through the addition of soil content influenced the bulk density. In this part, it can be explained by considering that a large amount of soil particle refined the pore space. A non-compacted mortar with increased total void space may influence the increased leachability of metals in pure water, and significant increase in permeability.

Although S-OS, batch no.2 had not presented the highest CS comparing with batch no.1. Supported reasons why the batch no.2 selected being a model block were in followings:

1.) If we considered the cost of S/S treatment, cost of C/S ratio of 1/1.5 was lower than those of C/S ratio of 1/1, especially for the large scale- treatment.

2.) Other chemicals, e.g. aggregates, additive mixed-polymers and/or some metals contaminated in soils could improve the CS of C/S ratio of 1/1.5 [8]. In contrary, it is believed that replacement of Portland cement by pozzolonic, increase the strength, and durability of the solidified waste forms [20].

Overall, it was observed from the results that the CS of all batches was outlying of proper applications. On the contrary, the great value of CS was probably not a sign of an effectiveness of S/S treatment, unless a new approach was replaced to improve physical characterization of the wastes concrete for engineering purposes e.g. a superplasticizer addition as part of raw material [30].

The monolith-stabilized soil models were measured for their physical properties as shown in **Table 4.13**.

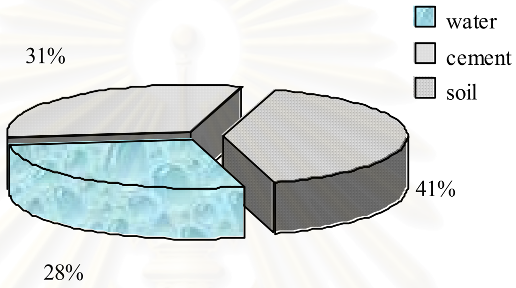


Figure 4.12 Concrete formation of a model blocks

4.3.2 Influence of humic acid concentration

Fig. 4.13 illustrated the effects of S-HS on the CS. The CS of concrete gradually decreased with increasing of AHA added original soil amount. The reduction from the CS resulted in the inhibition of crystallization or cementation of metal oxides and hydroxides. It also implied that a fraction of cement or binder required for cementation should be higher in the presence of humic acids. In addition, the hydration of cement requires the large amount of water much more than stoichiometric ratio as expressed in the following reaction equations: [7]

$$2(3CaO.SiO_2) + 6H_2O \overset{\text{moderate}}{\rightleftharpoons} 3CaO.2SiO_2.3H_2O + Ca(OH)_2$$

$$2(2CaO.SiO_2) + 4H_2O \overset{\text{slow}}{\rightleftharpoons} 3CaO.2SiO_2.3H_2O + Ca(OH)_2$$

These reactions are more time-consuming. This resulted from the high water-holding capacities of humic acids. Attributable to the amorphous- thick fiber like structure; friable in consistencies; and the hydrophilic of humic acid, these basis help to explain why such a less CS of concrete was associated with humic matter enriched soil.

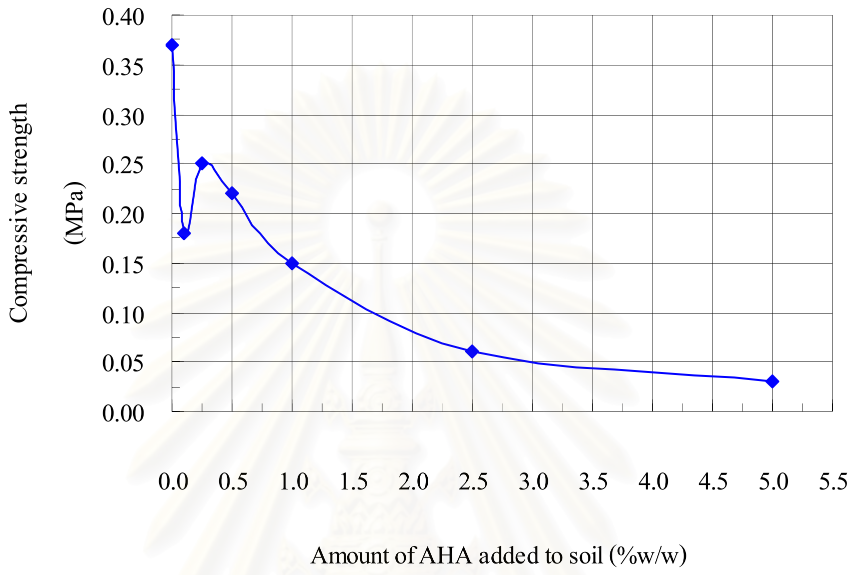


Figure 4.13 Effect of humic acid on compressive strength of S-HS

4.3.3 Influence of metals concentration

The S-MS with variation of metal concentration shown in **Table 3.8** were conducted by CS tests. **Fig. 4.14** showed that metal concentration significantly affected the solidity of concrete under studied conditions. The CS of S-MS samples, on the other hand, increased with increasing of metal concentration. However, at the added metals concentration was higher than 900 mgkg^{-1} the CS was slightly decreased. The effect of concentration related to the incorporation of metals in compacted, crystalline, and insoluble matrices. Soil's slurry retarded the setting, and caused swelling and cracking within inorganic matrix, which were observed at the highest of metal concentration given. The cracked and swelled S-MS were exposed more surface area to leaching. Therefore, the reduced CS of stabilized concrete was caused by a large variation of setting time, and reduced dimensional stability of the cured matrix [8]. Furthermore, some metal spiked soil under high alkaline environment of cement might be resolubilised enhancing the soluble metal ions. The normal hydration reactions were blocked by the adsorption process of these ions on the surface of cement matrice.

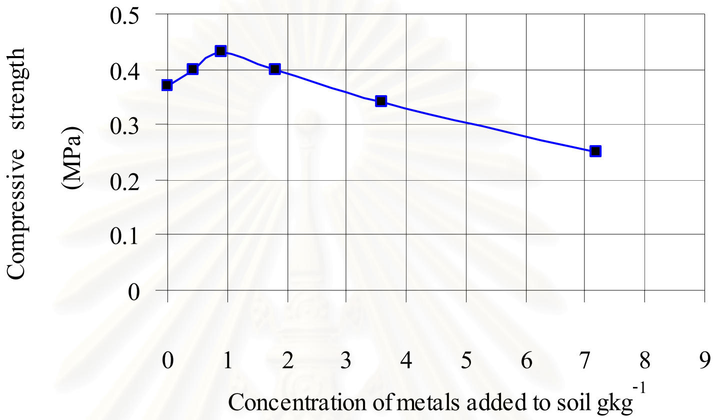


Figure 4.14 Effect of metals concentration added to soil on the compressive strength

4.3.4 Leaching study

4.3.4.1 Influence of liquid to solid ratio

The fragmented–homogenized of S-MS was submitted to leaching for L/S analysis. The result in **Fig. 4.15** indicated that there was no significant difference in the amount of leached metals between those, which performed in a low L/S ratio of 3-5. The high L/S ratio comprehensible affected the leachability of metal types. The result could well explain the relationship of metal release as a function of L/S ratio.

Although, the L/S ratio ranging from 3 to 5 proved that there was no significantly difference in the amount of leached metal for all types. The L/S ratio of 5 was chosen which it was the highest L/S ratio for the further experiments (**section 3.6.5.2**).

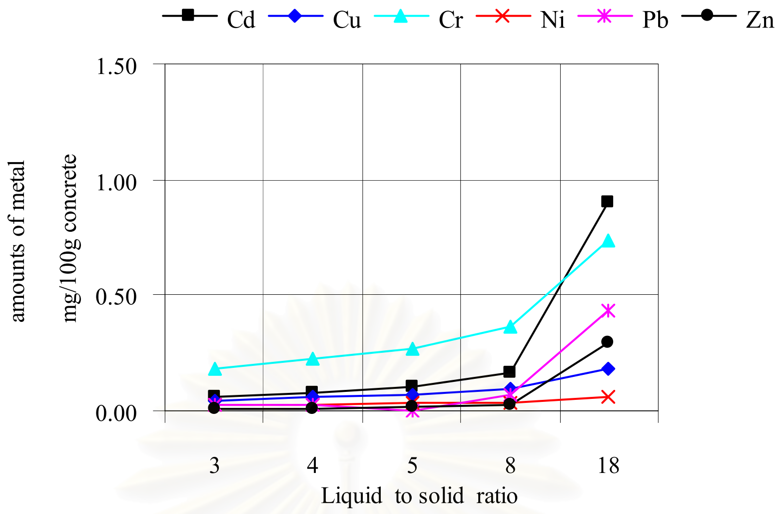


Figure 4.15 Relationship of metals release as a function of liquid to solid ratio, leachant of 0.1 mol L^{-1} AcOH with pH of 2.88

4.3.4.2 Influence of type of leaching medium

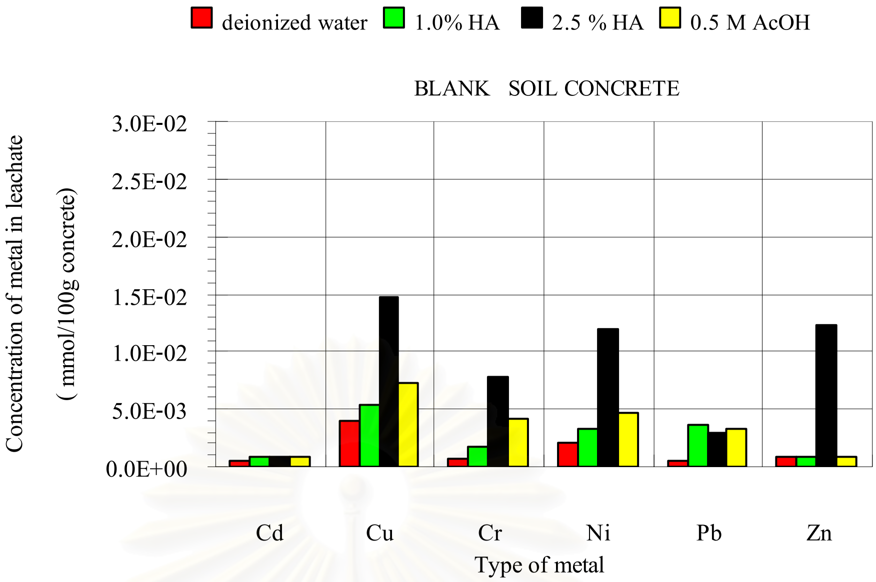
The fragmented–homogenized of S-OS and S-MS (900 $mgkg^{-1}$ metals added to soil) were submitted to batch leaching using various aqueous based- media. The amounts of released metal were compared in the same L/S ratio of 5. **Figs. 4.16** a, and b showed that metal leachability strongly depended on metal types in and types of leaching medium. It was important to notify here that free metal-Aldrich humic acid and acetic acid were used, thus leached metals were only from stabilized soil.

It was observed that the amount of leached cadmium was quite low, compared to other metals in all leachates for both S-OS, and S-MS. Because cadmium ion was classified as soft acid metal [54], in the condition of hard bases as given leachant (**Table 4.14**) it was not reacted with those hard bases ion. Consequently, it had the lowest leachable fraction from concrete metrics.

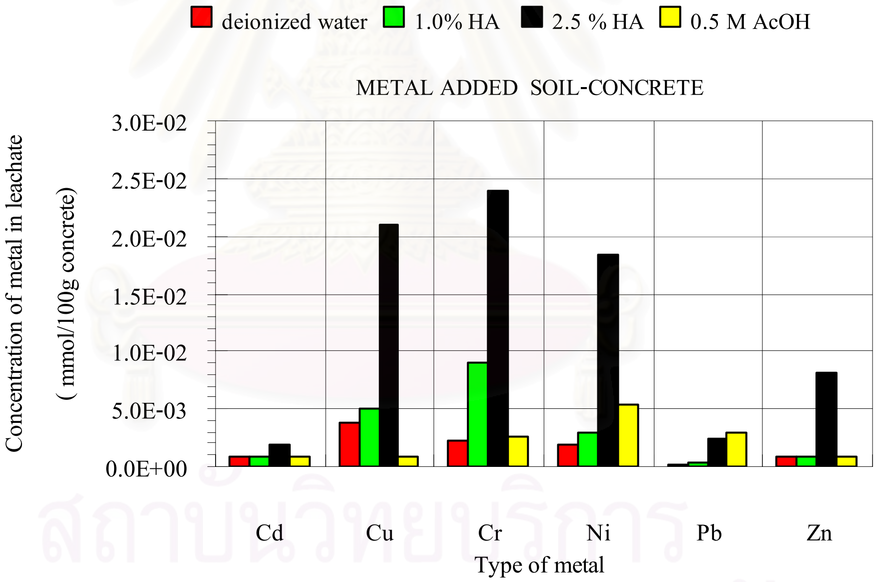
While, copper appeared to be the highest released species. If the types of leachant taking into account it was distinguished that 2.5% w/v HA solution increased the metal leachability for copper, chromium, nickel, and zinc (except for cadmium and lead species). This solution was prevailing metal leachable than 0.5 molL^{-1} AcOH, L/S=5. Besides the higher concentration of humic acid solution, the more increasing of leached metal was observed. For S-MS, amounts of metal releasing in case of deionized water, 1% HA w/v and 0.5 mol L^{-1} AcOH were not different in level of mmol/100 g concrete. However in case of amounts of leached metal for S-OS were higher than those of S-MS; e.g. copper for 0.5 molL^{-1} AcOH and zinc for 2.5 %w/v HA; This difference amounts are in $1x10^{-3}$ mmol level, thus their were incomprehensible measuring. Since, ion mobility may higher in diluted solution [55]. These errors were negligible within the confidence level. It was important to report that the amounts of Cu, Cr, Ni, and Zn release were much increased for S-MS, in 2.5 % HA solution compared to other leaching mediums. Even thought the amounts of each spiked -metal was 6.249 mg/100 g of concrete, excluded the original metal contamination. However, more than 80% of metals were chemical bounded in the solid phases.

Table 4.13 Measurement of physical properties of monolith S-OS

Physical properties	Mean values ± s.d. (n=3)
Bulk density (kg m^{-3})	1500 ±42
Volume (cm^3)	145.34 ±0.83
Moisture content (%)	4.76 ±2.37
Specific surface area (m^2)	0.0167
Water absorption capacity (%)	25.42 ± 0.13
Pore volume (cm^3/block)	50.05 ± 2.50



(a)



(b)

Figure 4.16 Relationship between types and concentrations of leachants, and amounts of metals (mmol of each metal per 100 g of concrete);S-OS, (b): S-MS

Table 4.14 Physical and chemical properties of ions that influenced ion mobility

\# *For coordination number: 6*, [54]

ion	Electronic configuration	Ionic radii, pm #	Charge to mass ratio	Type of hard/ soft acid/base
Cd^{+2}	d^{10}	109	0.0178	Soft acid
Cr^{+6}	d^{5}	58	0.1154	Hard acid
Cu^{+2}	d^{10}	87	0.0315	Border line hard acid
Ni^{+2}	d^{8}	83	0.0852	Border line hard acid
Pb^{+2}	d^{10}	133	0.0097	Border line hard acid
Zn^{+2}	d^{10}	88	0.0306	Border line hard acid
$RCOO^-$, RO^-, H_2O, OH^-		-		Hard bases

4.3.4.3 Influence of humic acid in contaminated soil on metal retention in concrete

The fragmented–homogenized concrete for S-OS and all S-HS listed in **Table 3.7** were submitted to the extraction test; using 0.5 mol L^{-1} acetic acid solution and L/S equal to 3, in dark place, and equilibrium extraction time of 4 days. The amounts of released metals were taken into account. **Table 4.15** summarized the amounts of leachable metals in S-OS, and S-HS. Although humic acid retarded the solidification of concrete as described previously (**section 4.3.2**), the results indicated that nearly all portions of heavy metals were restricted in cement matrixes. This was because the total concentration of each studied metals containing in S-OS was very much higher than portion of those metals released for both S-OS and S-HS. To elucidate the portion of those metals released, moreover, **Fig. 4.17** also elucidated that leached metals were less than 4 % of total amount of each metal (**Table 4.15**).

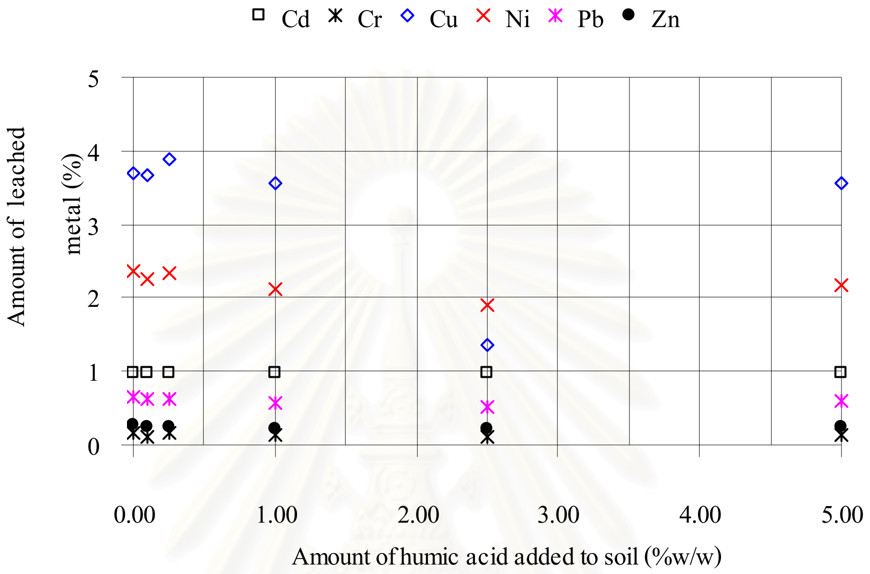


Figure 4.17 Amount of leached metals (%) in the S-HS by varying the amount of humic acid added to soil

Generally, alkaline matrices of concrete decreased the solubility of metal [7]. On the contrary, the humic–metal complexation might be increased the mobility [23], the complexes were well restricted in pores of crystallizing cement. It was proposed that the formation of a large humic complex took place. These phenomena expected that clays materials in soil physico-chemically interacted with added humic acids and metals forming occlusion compounds. Thus, the metal species were capable of retaining efficiently in the stabilized soil.

In conclusion, there was no significant difference between the amount of leached metals and humic levels, which based on the studied condition of the studies. Data analysis using analysis of variance analyzing (ANOVA) at 95% confident limit was facilitated to verify this conclusion.

Table 4.15 Total amount of metal in S-OS (mg/100g) by acid digestion, and leached metals in fragmented concretes containing humic acids

Element	Total amount	**Amount of leached metal** (% w/w)					
			Amount of AHA added to soil (%w/w) for S-HS				
	S-OS	S-OS	0.10	0.25	1.00	2.50	5.00
Cd	6.89	0.068	0.068	0.068	0.068	0.068	0.068
Cr	24.77	0.041	0.029	0.042	0.033	0.024	0.035
Cu	10.37	0.383	0.381	0.404	0.370	0.331	0.370
Ni	10.83	0.257	0.244	0.253	0.231	0.205	0.236
Pb	13.23	0.640	0.612	0.627	0.574	0.514	0.590
Zn	10.50	0.257	0.238	0.210	0.229	0.248	0.267

4.3.4.4 Influence of pH on metal solubilization

The fragmented of S-OS and S-HS (5%w/w AHA added soil) crushed to 2 mm were contacted for 7 days with solution of various pH (liquid to solid mass ratio equal to 10). The effectiveness of the metal fixation has been established by using contact solutions maintained at various pH values between 1.5 to 12 by additions of nitric acid or sodium hydroxide. The leaching of calcium from crushed mortar at various pH values was shown in **Fig. 4.18**. Its solubilization decreased with pH increasing and became negligible for pH >12 [18].

The extent of metal solubilization depended on the pH, degree of complex ability of humic acids, and the nature of chemical pollutants. For S-OS, the amount of released metals increased as the pH of the system was decreased. In principle, this will be related with the solubility constant, K_{sp}. For all studied -heavy metals, they were encouraged as they had some similarities in their chemistry in solution that depends on pH. However, the shapes of the solubilization curves were different as seen in **Figs. 4.18- 4.24**. The amounts of Ca, Cd, Cu, Ni, Zn, and Pb (except for Cr) being leached from the S-HS were relatively lower than form S-OS under the leachant pH of 6-8.

These results also indicated that metals in the concrete matrix were strongly retained in such a solidified matrix. For S-HS, the leached amount of cadmium proportional decreased with increasing of leachant pH (**Fig. 4.19**). The solubilization of nickel species was comparable to the cadmium one; however, under alkaline condition its solubilization was invariable (**Fig. 4.22**).

In the case of lead solubilization under different pH conditions presented in Fig. 4.23, there was a valley feature. The least aggressive leaching (pH $\approx$ 12) resulted in more increasing of lead release caused by a high pH maintained at the surface. Owing to the amphoteric characteristic of lead at high and low pH of leachant, its solubilization was low for the natural pH-leachant. It indicated that releasing of lead was prone to the chemical conditions. The chromium solubilization under different pH conditions was presented in **Fig. 4.20**; the solubilization vs. pH relation was a hill features (pH of 5-12); contrasting to lead one. The amount of leached chromium increased as the pH of the system was downward to about 5, then leached amount increased with pH increasing up to 10 followed by descending of leached amount again. These features were also observed in the copper, lead, and zinc releasing illustrated in **Figs. 4.21**, **4.23**, and **4.24**, respectively.

In the last, it can be concluded that the metal solubilization in stabilized soil was a function of pH of leaching medium.

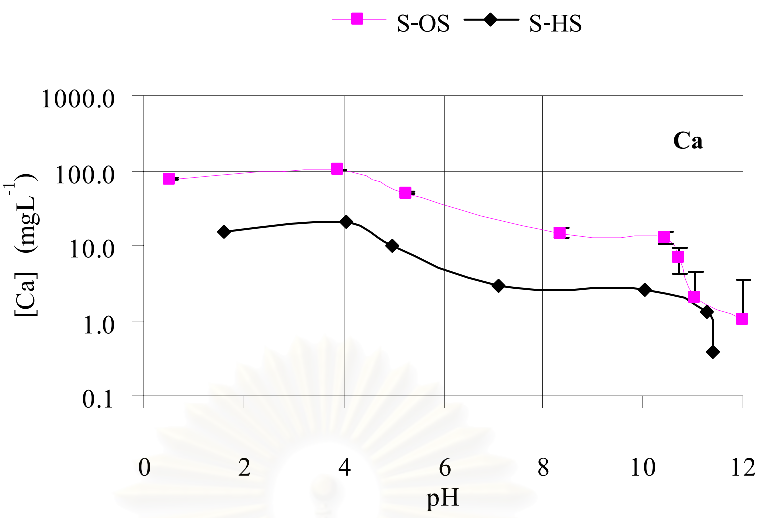


Figure 4.18 Influence of pH on dissolved calcium for stabilized soils

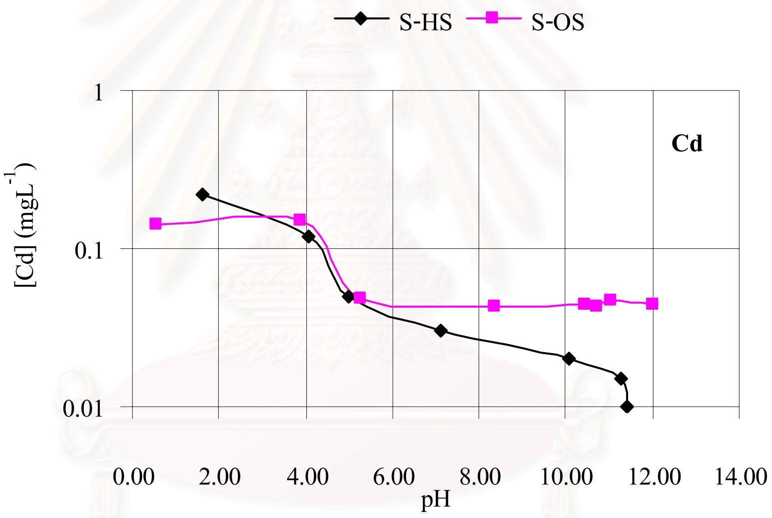


Figure 4.19 Influence of pH on cadmium solubilization of stabilized -soils

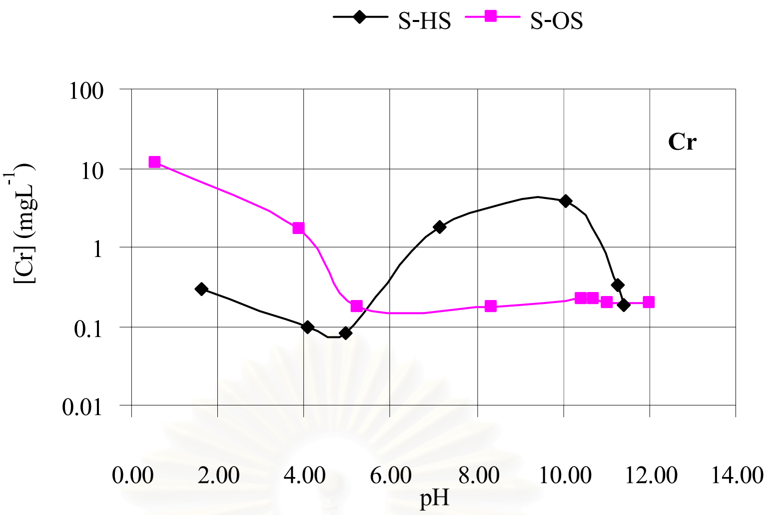


Figure 4.20 Influence of pH on chromium solubilization of stabilized -soils

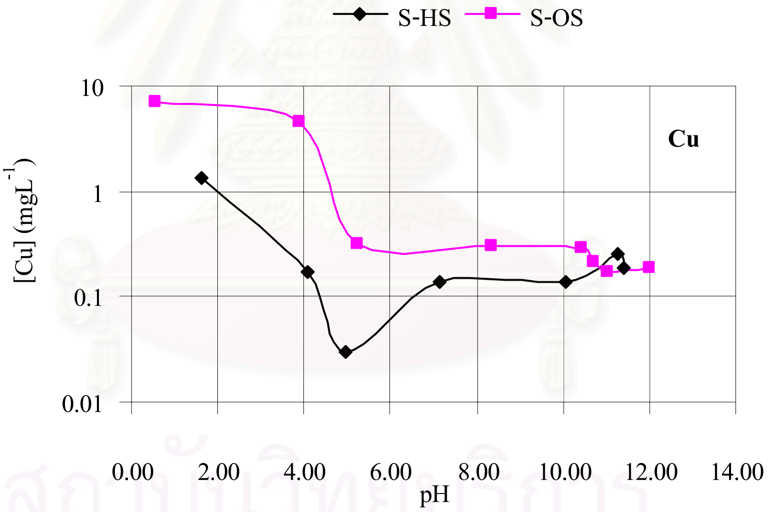


Figure 4.21 Influence of pH on copper solubilization of stabilized -soils

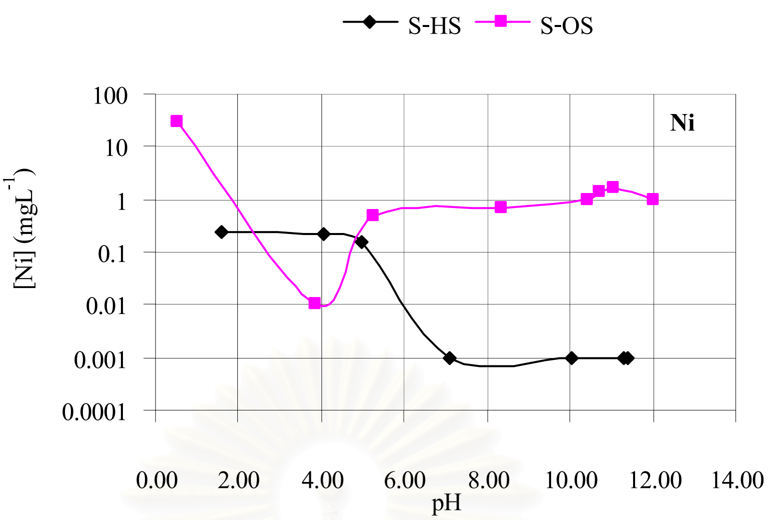


Figure 4.22 Influence of pH on nickel solubilization of stabilized- soils

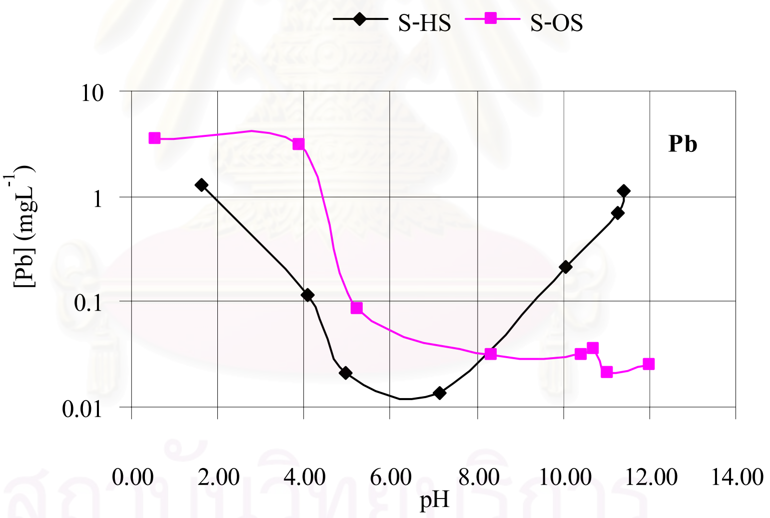


Figure 4.23 Influence of pH on lead solubilization of stabilized -soils

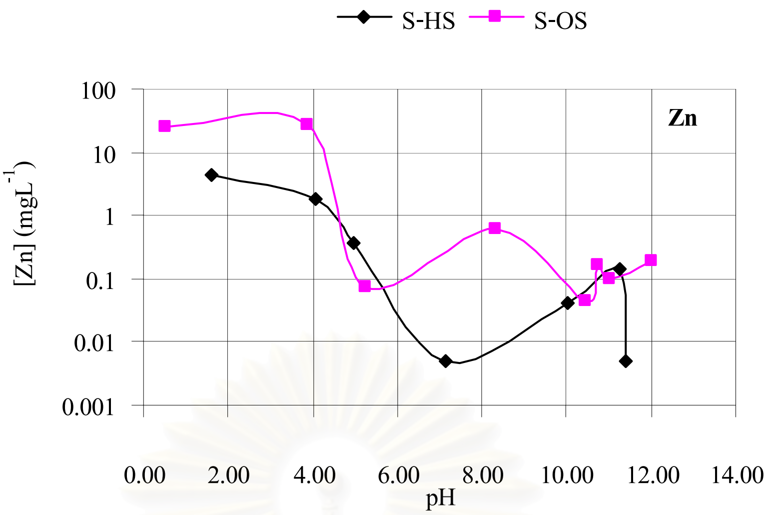


Figure 4.24 Influence of pH on zinc solubilization of stabilized soils

4.3.4.5 The monolithic leaching (ML) test

The influence of contact time was investigated by the monolithic leaching (ML). The ML tests were conducted on S-MS (1,500 mg kg^{-1} metal added soil) of 4.6 x 6.0 x 5.3 cm^{3}, contacted with leachants (**Table 3.12**) at a L/S contact surface = 3.0 m^{3}/m^{2} (500 mL/167.16 cm ^{2}). The solid-solution contact time were shown in **Table 3.11** for each sequence. The results were presented in three graphic forms:

- Relationship between cumulative contact times (day) and pH of leachates as showed in **Figs. 4.25**-a, and b.

- Plot of cumulative amount of the different species (mmol kg^{-1}) against cumulative contact time (day) showed in **Figs. 4.26-4.34**.

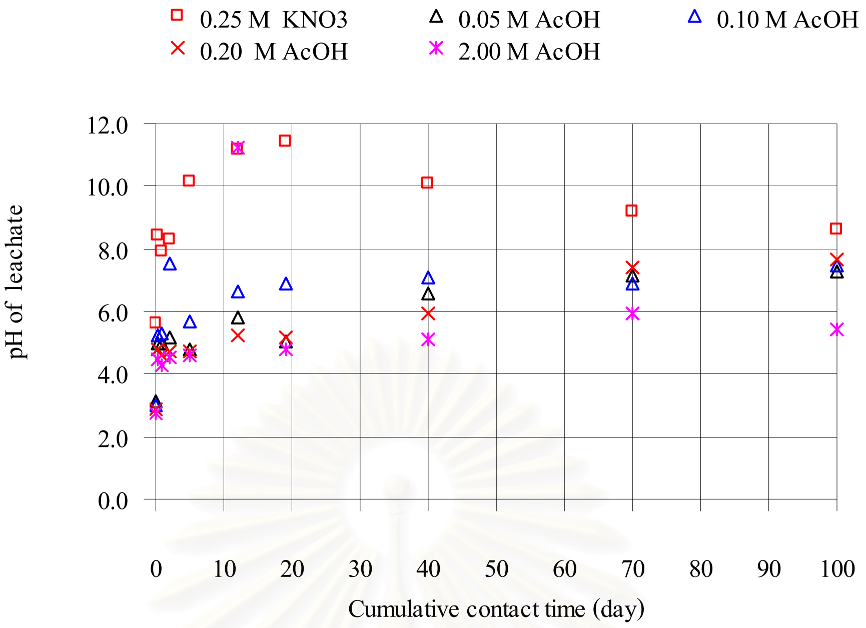
- Released molar fluxes of the different species mmol/m^{2}s showed in **Figs 4.44-4.52**.

For chloride determination, the leachates of each sequence contact time were analyzed after filtration (Whatman no.42) and neutralized by sulfuric acid if leachate pH was greater than 10 or by sodium hydroxide if the pH was less than 7; chloride ions were determined by Argentometric method. For metal analysis, the leachates of each sequence contact time were analyzed after filtration (Whatman no.42) and re-acidified by nitric acid to leachate pH around 2; metal species (amounts of Na, and Ca were determined by AAS; and amounts of Cd, Cu, Cr, Ni, Pb, and Zn were determinated by ICP-AES)

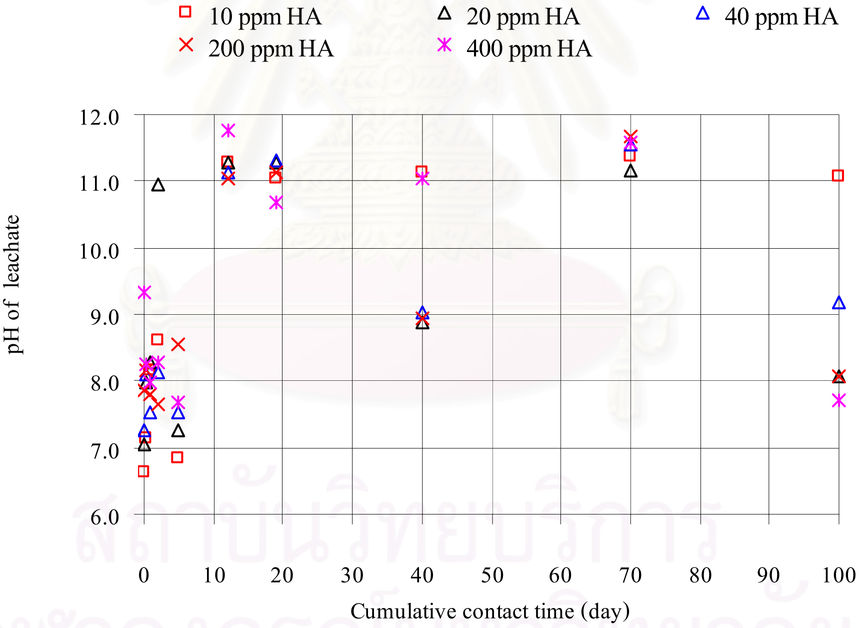
(a) Alteration of pH in leachates

The leachate pH was measured by electrometric procedure at 25 °C, before and after leaching of each sequence contact times. Due to the pH dependence, experiments were designed to cover important differences in pH environment to which the materials were exposed to as well as for an assessment of the buffering capacity of the material neighboring of humic acid medium. A CO_2 feature, which makes a monolith-leaching model sensitive to externally pH variations, was take part to consider particularly in the leaching for long period.

The relationship between cumulative contact time and pH of leachates were shown in **Figs. 4.25-**a**,** and b for potassium nitrate and acetic acid solutions, and humic acid solutions, respectively. The pH of leachate with adding potassium nitrate in leachant was the highest comparing to pH of acetic acid. For humic acids in leaching medium, the pH of leachate increased with increasing the amount of humic acids. For humic acid in leachants (**Fig. 4.25-**b), it was observed that cumulative contact times were divided into two periods; the first one for initial to five days, and the one for the contact time up to a hundred days. The pH of leachates decreased and remained constant during the first contact period following by reaching the highest pH around 12. Afterward, pH of leachates fluctuated during the past 12 days and then streaked to neutral pH of 7 gradually.



(a)



(b)

Figure 4.25 Relationship between cumulative contact times and pH of leachates, (a) potassium nitrate and acetic acid solutions, and (b) humic acid in leachants.

The results also indicated that concrete material resisted to pH changes under the influence of all acidic solutions, and CO_2 uptake from the air. This is because of its acid neutralization capacity. After 5 days leaching it was observed that pH of leachate was increased rapidly up to pH 12 for 2.00 mol L^{-1} AcOH, and HA solutions, because the increase of the dissolution of alkaline matrix (Ca, and Na ions). It was expected that the pore water of concrete were in saturated environment. Hence, the species can diffuse through a torturous -continuously pores to liquid/solid surface contact which increase pH to around 11.

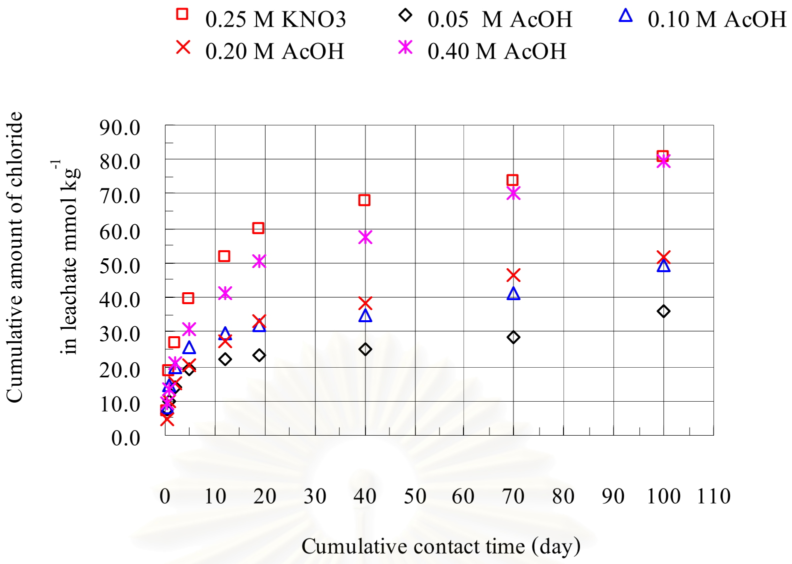
Due to entirely dissociation of phenolic groups of humate at pH 11, they played a role in buffering the pH of leachant downward to 9. In case of 400 mg L^{-1} HA leachant, it was found that pH of leachate were not much changed. This was because the liquid/solid contact surface was covered by a brown- humate blocking the dissolution /precipitation.

(b) Chloride ions in leachates

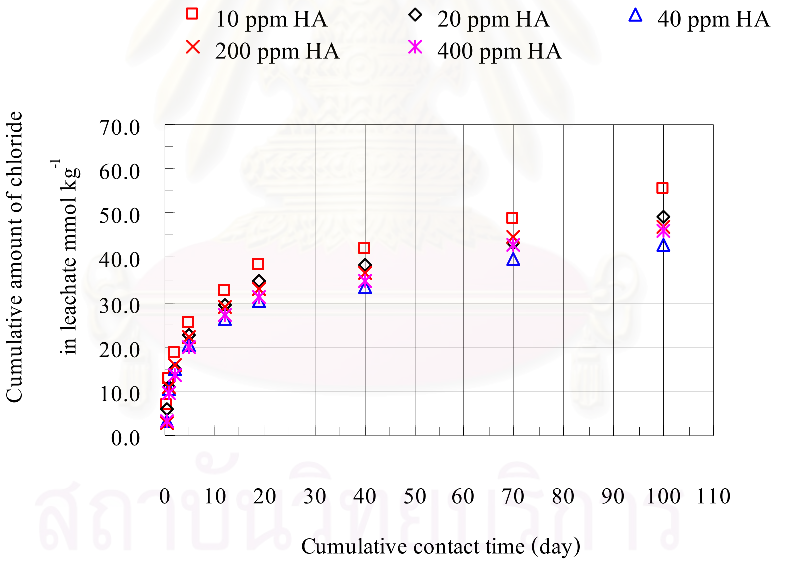
The cumulative amounts of leached chloride depended on the type of leaching medium. As shown in **Fig. 4.26**. The much difference of leached amount of chloride was observed in case of the increase of acetic acid concentration comparing to humic acids. The amount of chloride in leachate with added potassium nitrate in leachant was the highest among the leachants.

(c) Sodium in leachates

Like the chloride, the cumulative amount of leached sodium depended on the type of leaching medium. About six orders of magnitude increase of sodium in leachate was observed in the present of 0.05 mol L^{-1} acetic acid in leachant (**Fig. 4.27**). This result of the acetate ion was in equilibrium of sodium ions and acted as buffer solution. These verified by the less change of pH for 0.05 mol L^{-1} acetic acid as leachant comparing to the others (**Fig. 4.25**). On the contrary; the amount of leached sodium in all humic acid concentrations, potassium nitrate, and all acetic acid excluded 0.05 mol L^{-1} were similar.

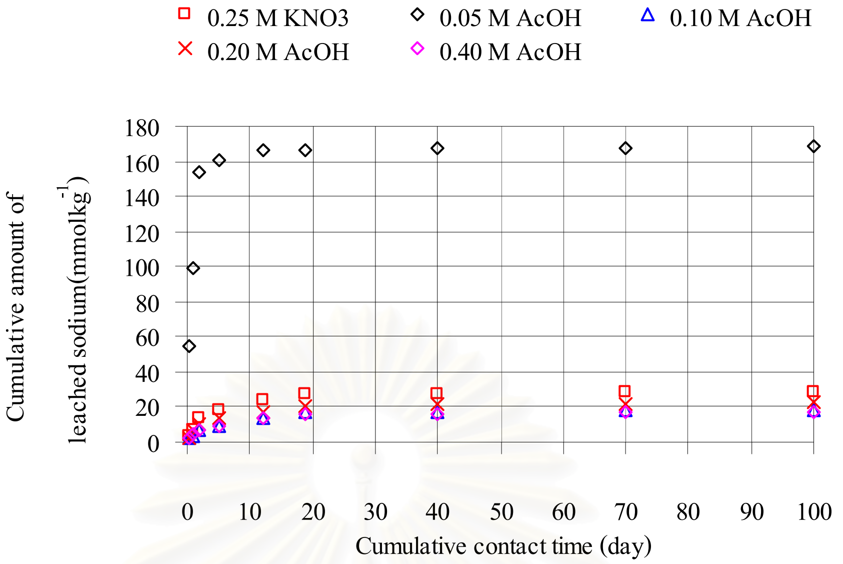


(a)

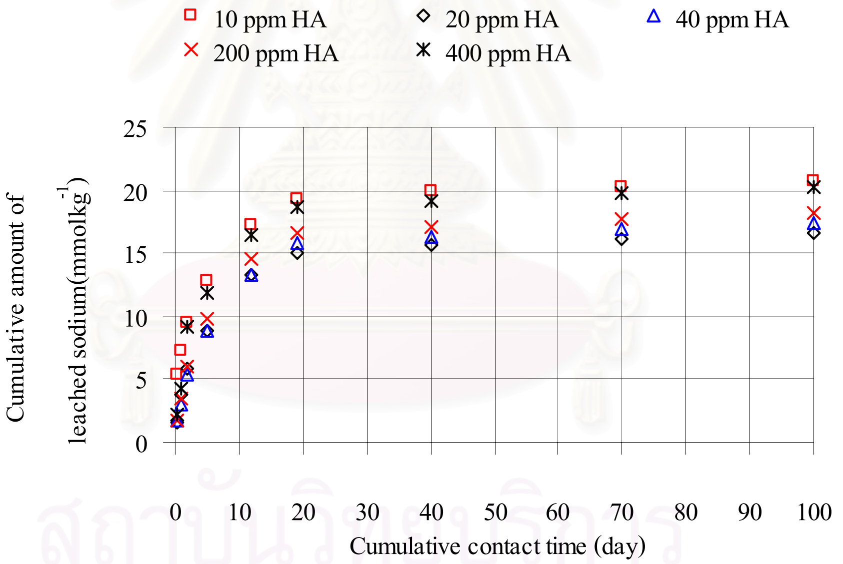


(b)

Figure 4.26 Relationship between cumulative contact time (day) and cumulative amount of leached chloride ion (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration (a) potassium nitrate and acetic acid solutions and, (b) humic acid in leachants.



(a)



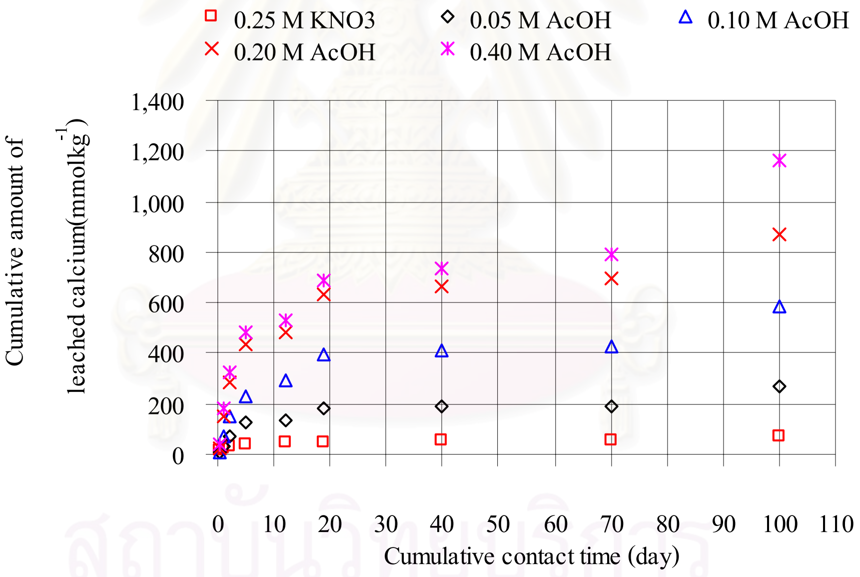
(b)

Figure 4.27 Relationship between cumulative contact time (day) and cumulative amount of leached sodium (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of (a) potassium nitrate and acetic acid solutions and, (b) humic acid in leachants.

(d) Calcium in leachates

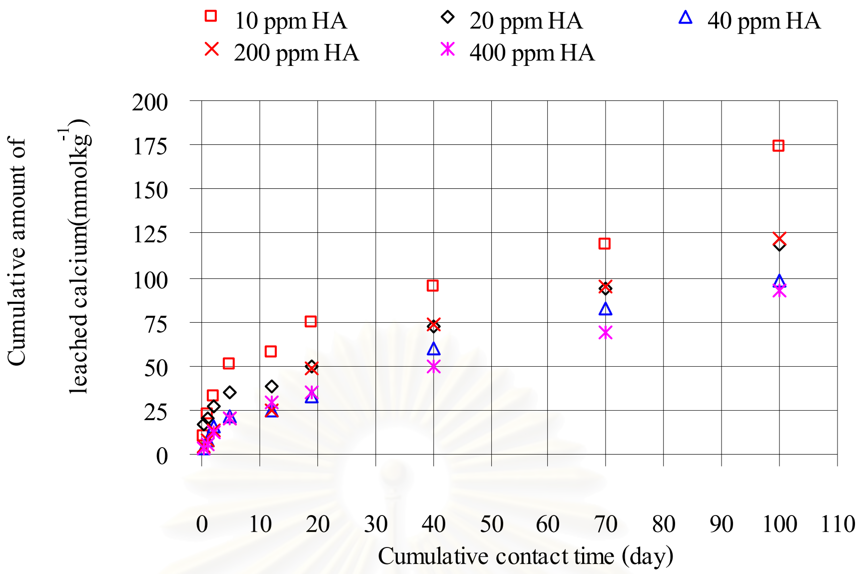
The cumulative amounts of leached calcium extensively depended on pH and the type of leaching medium. The increasing of leached sodium in leachate was observed in the present of acetic acid in leachant (**Fig. 4.28**). The higher concentration of acetic acid the higher amount of calcium released. The acidity of leachant promoted the dissolution of calcium species (i.e. Ca (OH)$_2$, Calcium silicate hydrate (CSH) of concrete matrix.

For humic acid as leachants, the amount of leached calcium was decreased with in creasing the humic acid concentration. The results were corresponded to the former results (**Section 4.3.4.4**).



(a)

Figure 4.28 (a) Relationship between cumulative contact time (day) and cumulative amount of leached calcium (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of potassium nitrate and acetic acid solutions.



(b)

Figure 4.28 (b) Relationship between cumulative contact time (day) and cumulative amount of leached calcium (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of humic acid in leachants.

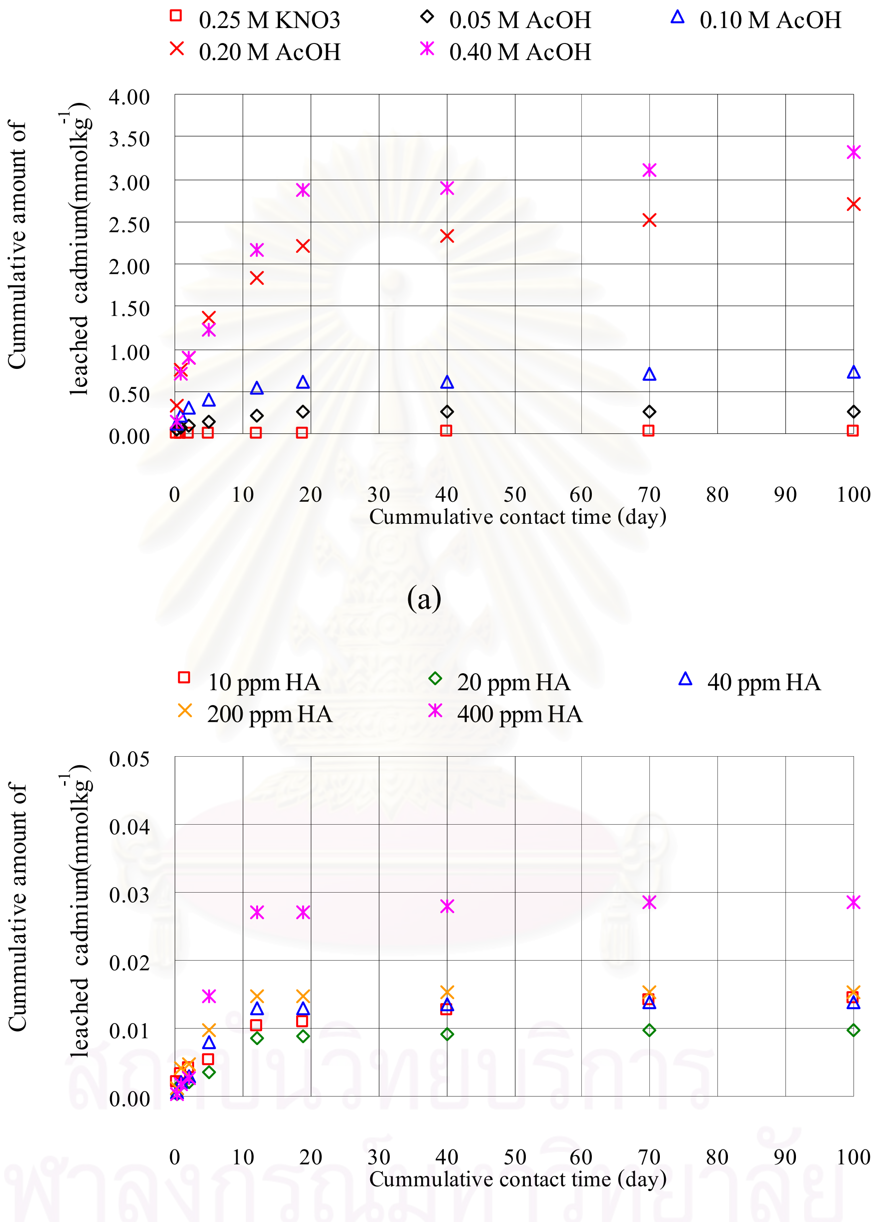
(e) Cadmium in leachates

The cumulative amount of leached cadmium increased similarly to calcium in case of acetic acid and potassium nitrate (**Fig. 4.29**). The amount of leached cadmium was the least one comparing to other metals when humic acid was used as leachant.

For humic acid as leachants, the amount of leached calcium decreased with increasing humic acid concentration. The results were corresponded to the previous results (**section 4.3.4.4**).

(f) Chromium in leachates

The cumulative amount of leached chromium increased similarly to calcium in case of acetic acid and potassium nitrate, except for the two last concentration of acetic acid (**Fig. 4.30**). The cumulative amount of leached chromium for 0.20 mol L^{-1} acetic acid was higher than those of 0.40 mol L^{-1} acetic acid within 70 days of leaching.

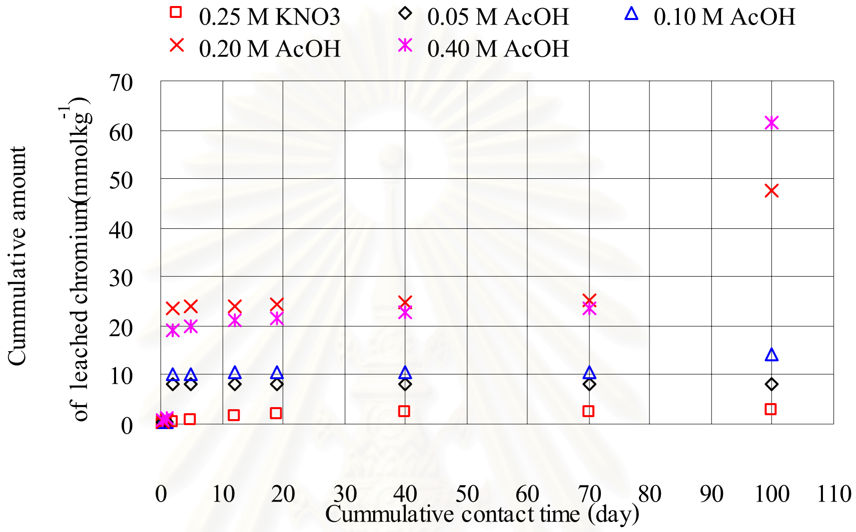


(a)

(b)

Figure 4.29 Relationship between cumulative contact time (day) and cumulative amount of leached cadmium (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of (a) potassium nitrate and acetic acid solutions and, (b) humic acid in leachants.

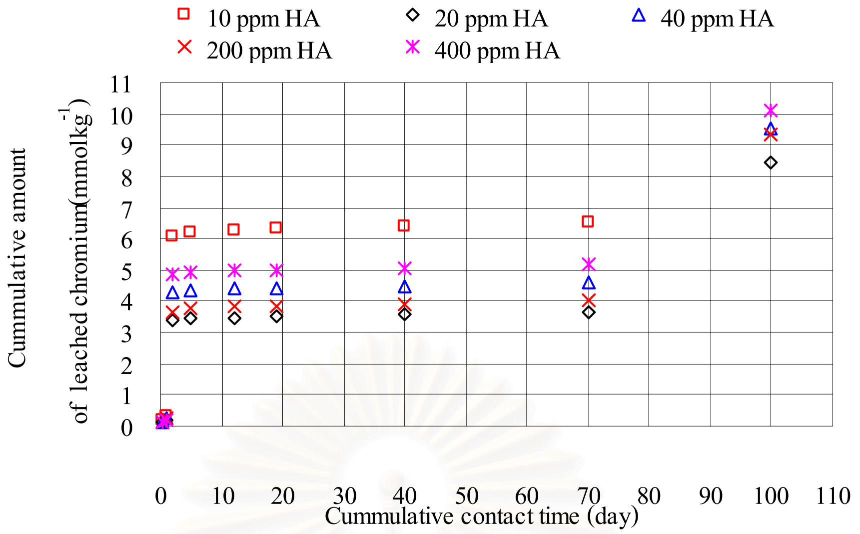
All of acetic acid mediums the leached chromium were higher than humic acids. Less than 15% were leached chromium from the stabilized soil comparing to its total content. The overall releases of chromium by acetic acid were more than that by humic acids.



(a)

Figure 4.30 (a) Relationship between cumulative contact time (day) and cumulative amount of leached chromium (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of potassium nitrate and acetic acid solutions.

For leachants containing humic acids (**Fig. 4.30-**b), the cumulative amount of chromium during the first 70 days increased about two times after a hundred days of leaching approached. The increase of cumulative amount of chromium was not proportional to the cumulative time. In the first period the lowest cumulative amount was observed in 20 mg L^{-1} humic acid in leachant, the highest amount was observed in 10 mg L^{-1} humic acid; while during the second period, the highest amount of chromium were found in 400 mg L^{-1} humic acid.



(b)

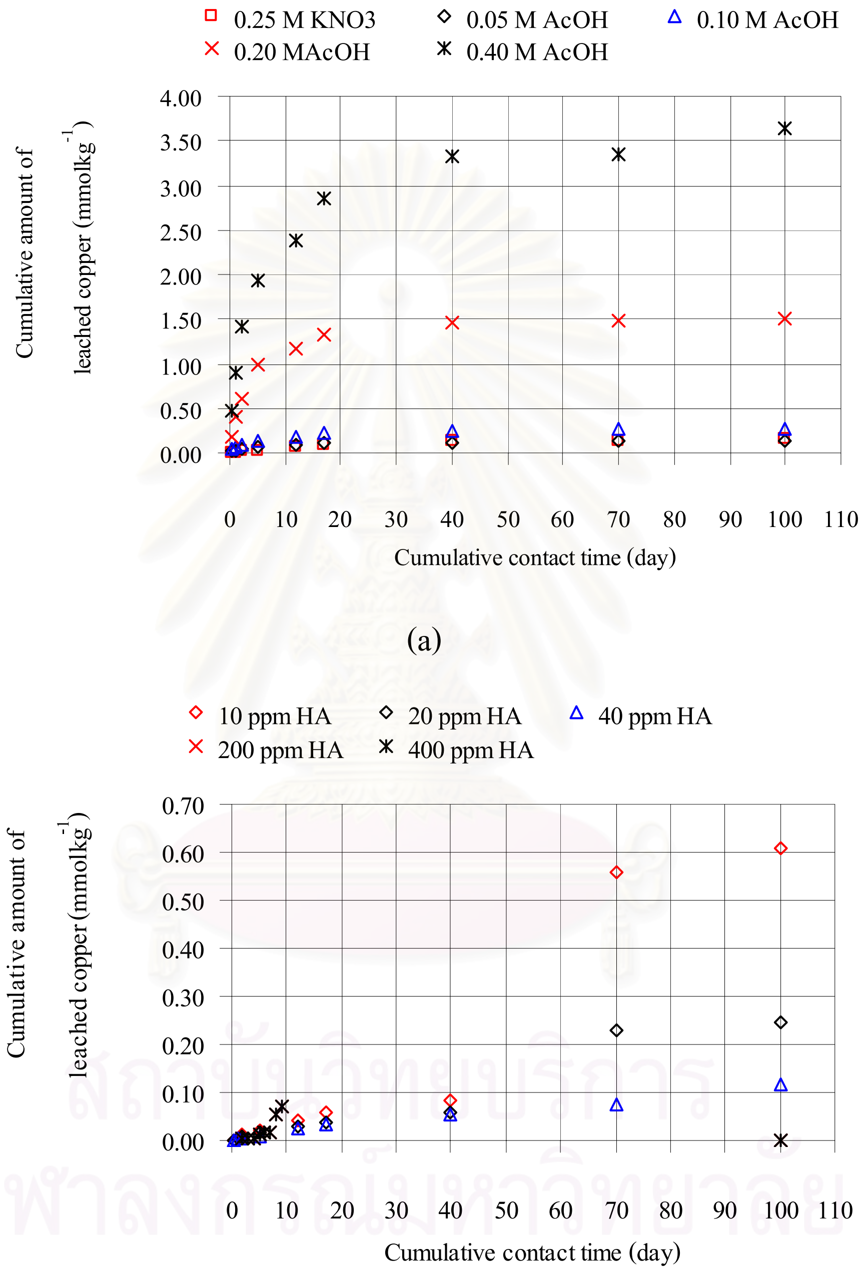
Figure 4.30 (b) Relationship between cumulative contact time (day) and cumulative amount of leached chromium (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of (a) potassium nitrate and acetic acid solution and, (b) humic acid in leachants.

(g) Copper in leachates

Similarly, the cumulative amounts of leached copper and cadmium depended on the type of leaching medium. The copper cumulative amount in leachate was the highest in the presence of 0.40 mol L^{-1} acetic acid in leachant (**Fig. 4.32**-a). This was because the copper releasing was significantly pH- dependent. For humic acid in leachants (**Fig. 4.32**-b), the highest of the cumulative amount was observed at 10 mg L^{-1} humic acid resulting the highest of pH (≈11) in leachate for a hundred days, although the initial pH of 10 mg L^{-1} humic acid was the lowest (**Fig. 4.25**-b).

(h) Nickel in leachates

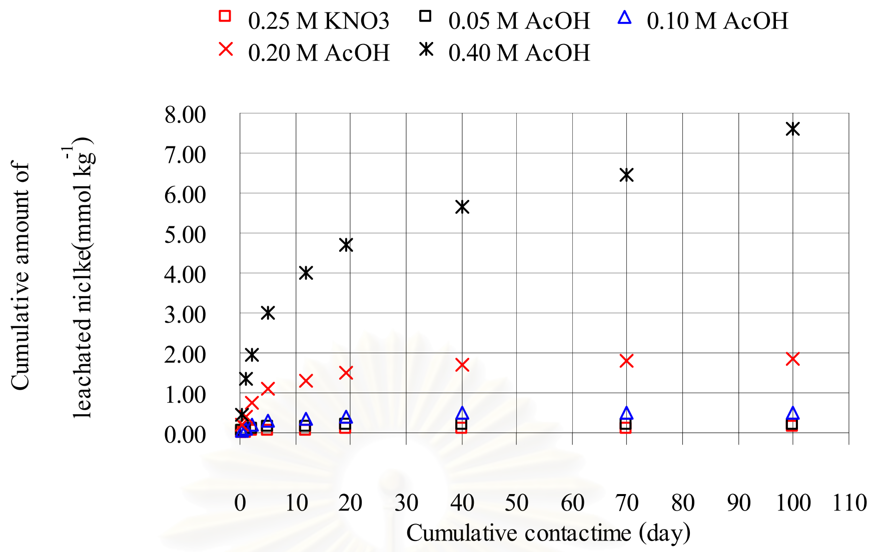
In the similar increasing trends of the cumulative amount of nickel to calcium, cadmium and copper was observed both for acetic acid and for potassium nitrate as leachants (**Fig. 4.32**).



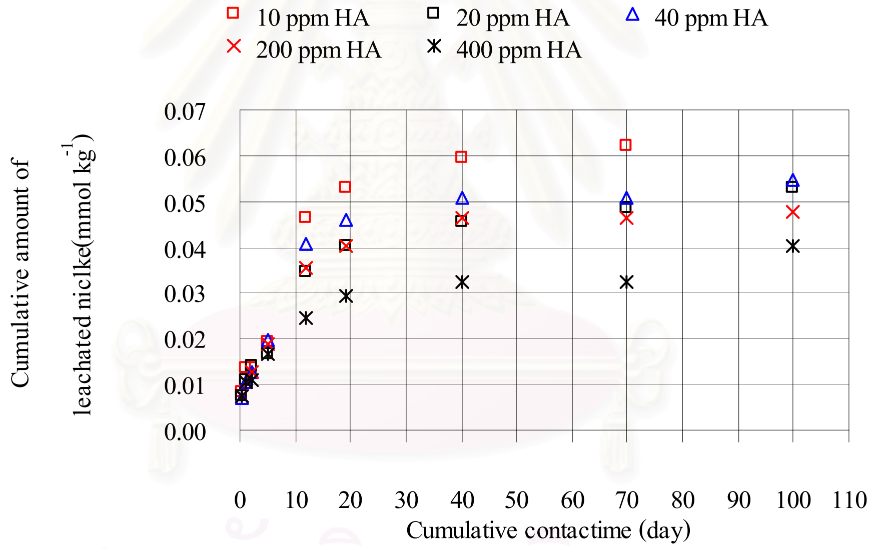
(a)

(b)

Figure 4.31 Relationship between cumulative contact time (day) and cumulative amount of leached copper (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of (a) potassium nitrate and acetic acid solutions and, (b) humic acid in leachants.



(a)



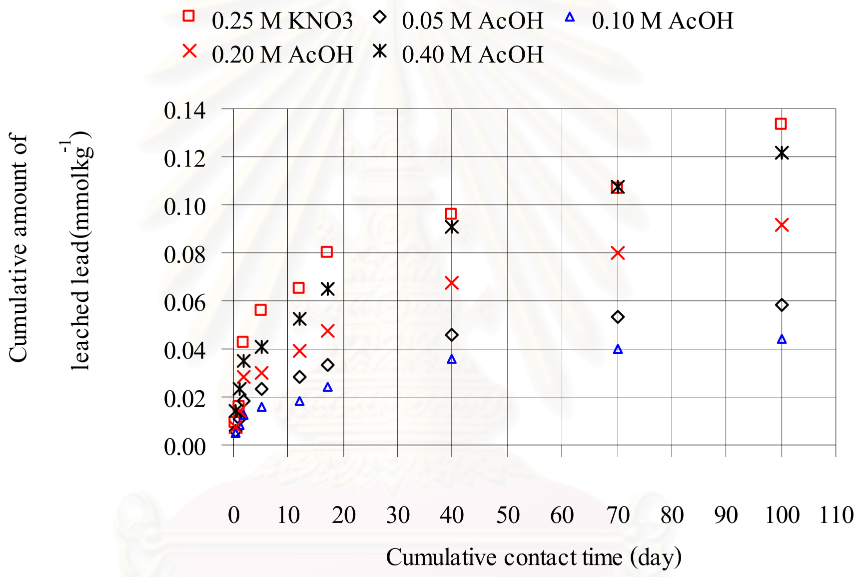
(b)

Figure 4.32 Relationship between cumulative contact time (day) and cumulative amount of leached nickel (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of (a) potassium nitrate and acetic acid solutions and, (b) humic acid in leachants.

While the cumulative amounts of nickel in humic leachants were similar to cadmium, nevertheless little higher concentration could be determined.

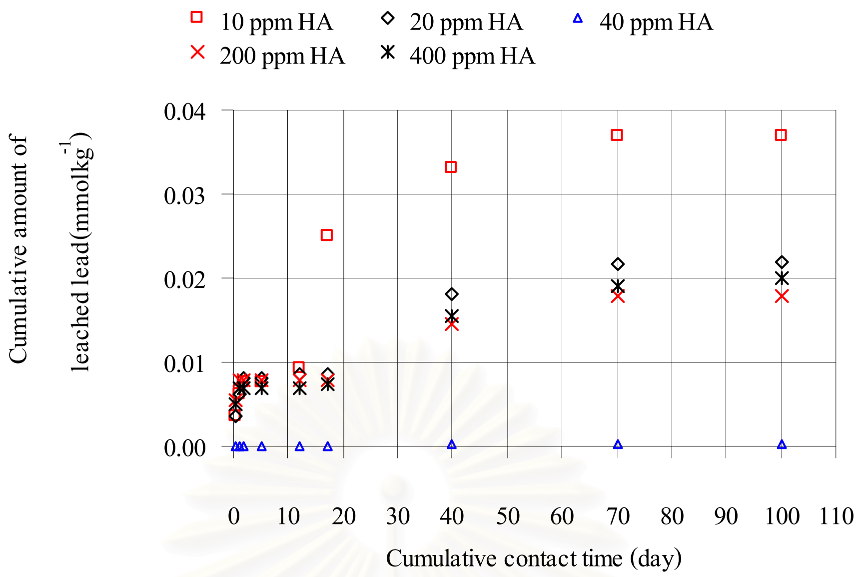
(i) Lead in leachates

The cumulative amounts of leached lead depend on type of leaching medium. As showed in **Fig. 4.33**. The amounts of lead released in acetic acid were lower than of potassium nitrate. Their amounts did not increase proportionally to acetic cid concentration in leachants, which the leached amount of lead under 0.05 mol L^{-1} acetic acid was higher than 0.10 mol L^{-1} acetic acid conditions.



(a)

Figure 4.33 (a) Relationship between cumulative contact time (day) and cumulative amount of leached lead (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of potassium nitrate and acetic acid solutions.



(b)

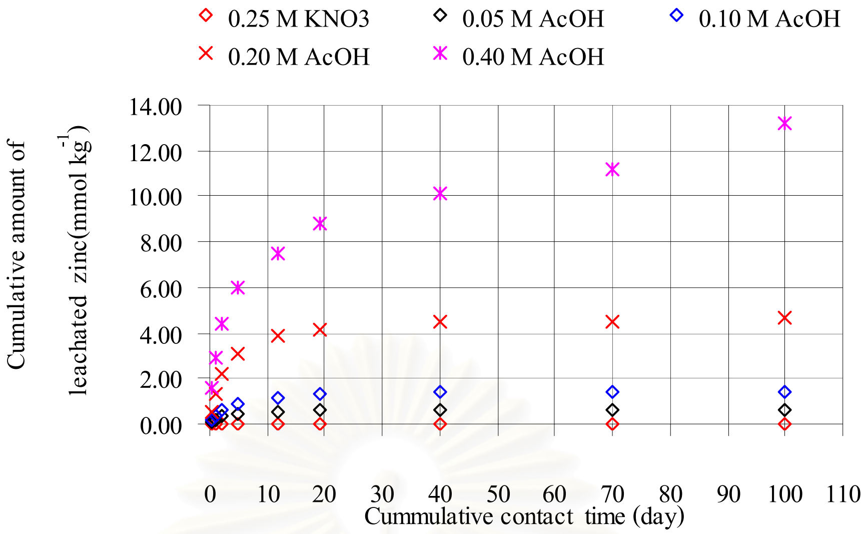
Figure 4.33 (b) Relationship between cumulative contact time (day) and cumulative amount of leached lead (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of humic acid in leachants.

The increase of cumulative amount of lead was independent to their humic concentration, similar to those of nickel and chromium.

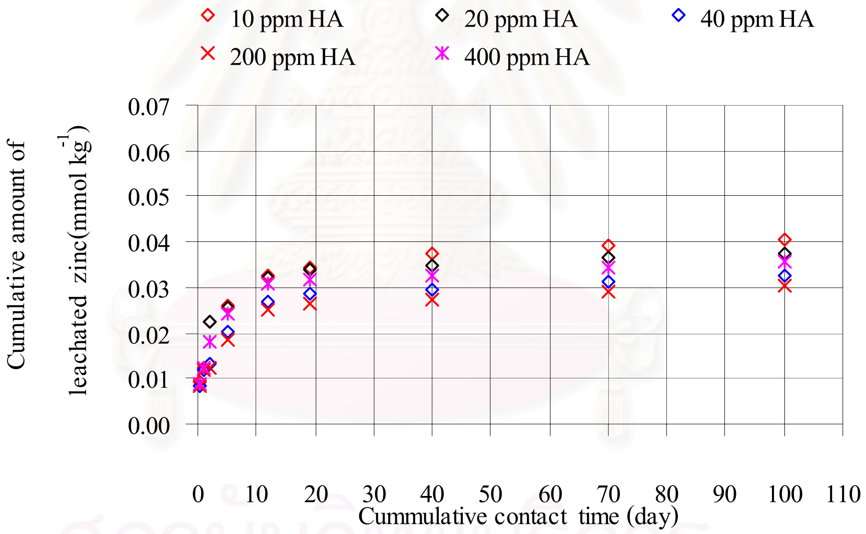
(j) Zinc in leachates

The cumulative amounts of leached zinc were proportional to the increasing of acetic acid concentrations. The highest cumulative amounts were observed under 0.40 mol L^{-1} acetic acid medium (**Fig. 4.34**-a). This was because the zinc releasing was significantly pH- dependent, like the copper. For humic acid in leachants (**Fig. 4.34**-b), the cumulative amount of zinc ranged from 0.03 to 0.04 mmol kg^{-1}.

In conclusion, the data from the ML test indicated that each ion species had a different leaching rate, depended on various factors (e.g. pH, type of leachant medium, counter ions, ionic strength and especially its leaching nature.



(a)



(b)

Figure 4.34 Relationship between cumulative contact time (day) and cumulative amount of leached zinc (mmol kg^{-1}) in pore water of a monolithic concrete varied in the concentration of (a) potassium nitrate and acetic acid solutions and, (b) humic acid in leachants.

4.3.4.6 Pore water (PW) and Maximum mobile fraction (MMF) Test

The initial equilibrium composition of the pore solution was defined by Maximum mobile fraction (MMF) obtained from the pore water study. The results were shown by the plotting of pH vs. L/S ratio.

Fig. 4.35 showed that two different pH features vs. L/S ratio were observed. For S-OS, the pH in the pore solution increased with increasing the L/S ratios. All pH in the pore solution of S-OS were lower than 8.4 associated to the less amount of 31 % cement using for treating contaminated soil. On the contrary, the pH in the pore solutions increased with increasing the L/S ratio for S-HS. The reasons were from the rising of the dissociation of humic acids increased with L/S ratio. The changes of pH were small due to the buffer capacity of humic materials in S-HS.

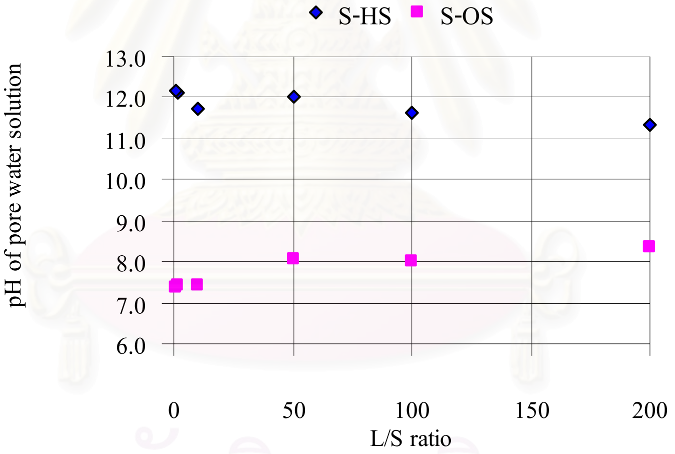


Figure 4.35 pH of pore water solution vs. L/S ratio.

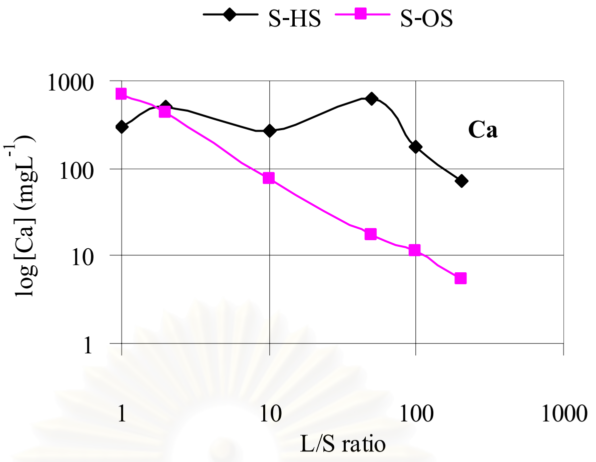


Figure 4.36 Concentration of calcium in the pore water solution of the stabilized – soils

The higher L/S ratio the lower calcium concentration was detected (**Fig. 4.36**). For S-OS, concentration of calcium in the pore water decreased proportionally to the increase of L/S ratios. However, for S-HS its concentration decreased disproportionally to the increase of L/S ratios. The concentrations of calcium from S-HS were higher than the ones from S-OS. This may be mainly resulted from the effect of humic acids.

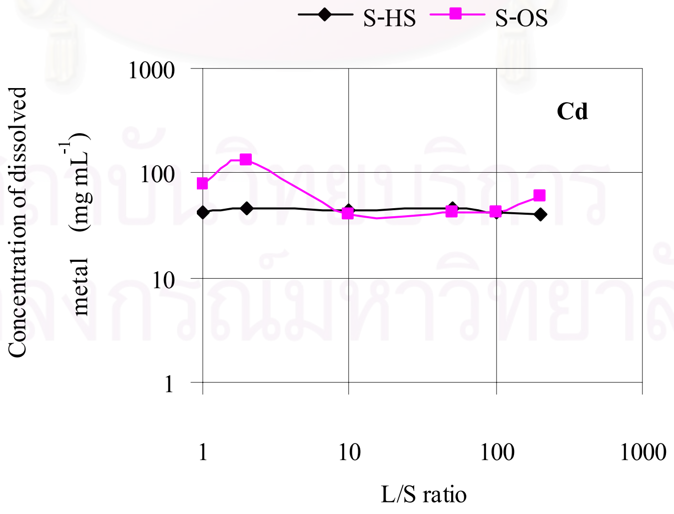


Figure 4.37 Concentration of cadmium in the pore water solution of the stabilized – soils

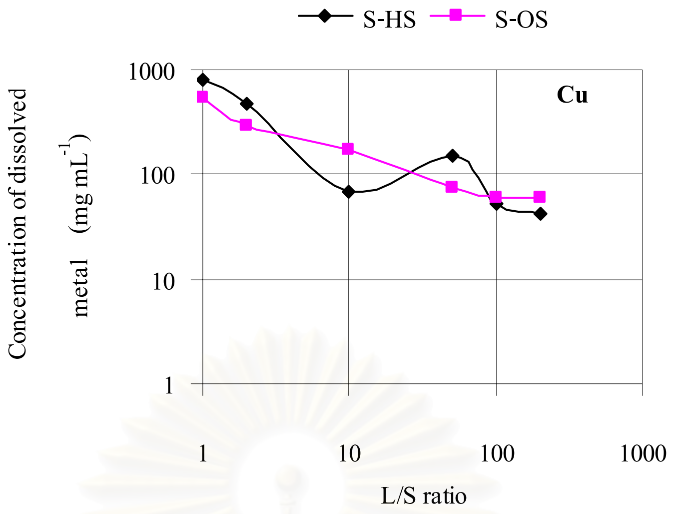


Figure 4.38 Concentration of copper in the pore water solution of the stabilized – soils

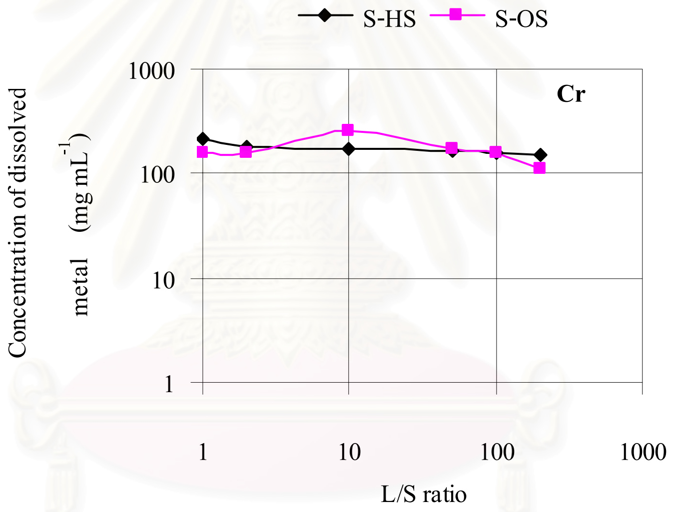


Figure 4.39 Concentration of chromium in the pore water solution of the stabilized –soils

The dissolution behavior of cadmium, copper, and chromium species for both S-OS, and S-HS were similar. The concentration of these species decreased with increasing the L/S ratio. The amounts of these metals can be estimated from the L/S dependent of the test solutions at the L/S ratio corresponding to the saturated open porosity [18].

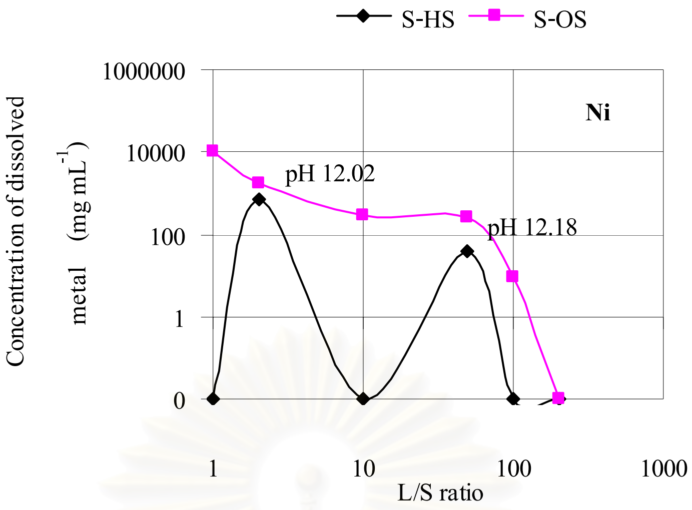


Figure 4.40 Concentration of nickel in the pore water solution of the stabilized – soils

The concentration of leached zinc decreased with increasing L/S ratio. No significant differences were found between the concentrations of zinc in pore water on the S-OS and S-HS (**Fig. 4.41**).

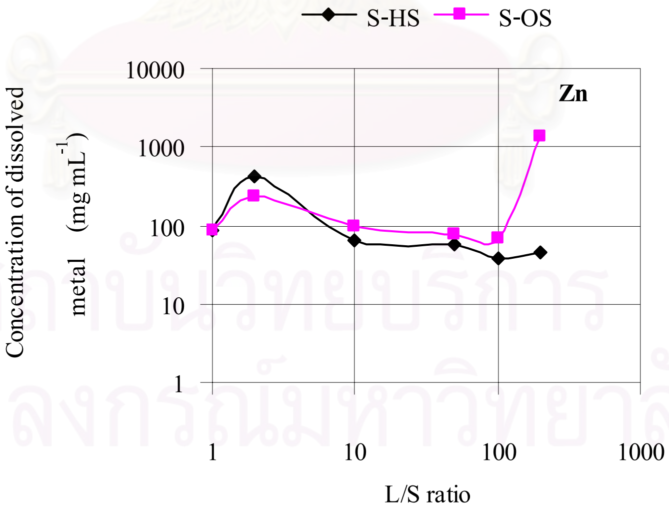


Figure 4.41 Concentration of zinc in the pore water solution of the stabilized – soils

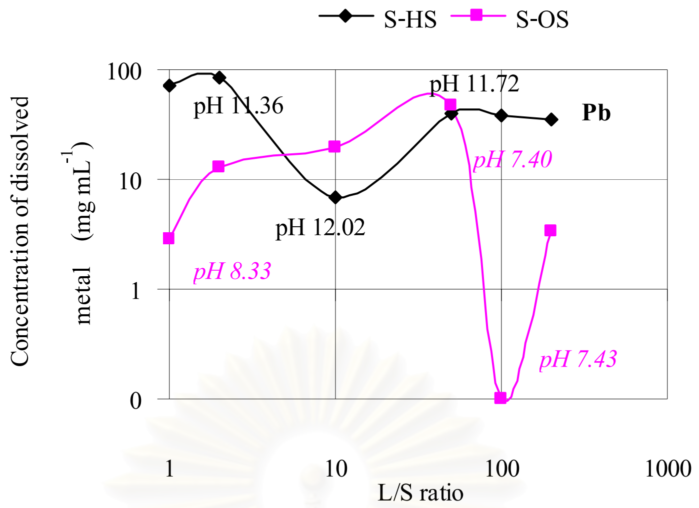


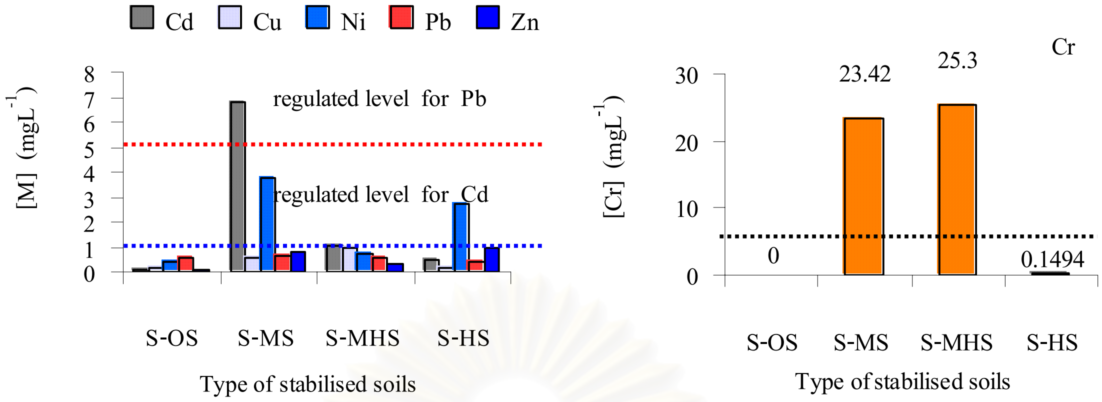
Figure 4.42 Concentration lead in the pore water solution of the stabilized – soils

The concentration of lead fluctuated with L/S ratio, and leachant pH. These indicated that solubility of lead species as well as nickel species in pore water depended seriously upon the variables such as soil minerals, humic acid reactions, pH, and L/S ratio etc.

In addition, the MMF of all metal species (exclude nickel) for both S-OS and S-HS could be estimated at the indicated L/S ratio, most of the cases L/S were equal to 200 (**Table 4.16**). Comparing to the total content the MMF was much smaller. This indicated that most fractions of metal species were converted to the less mobile forms in the solidified matrix.

4.3.4.7 TCLP test

In almost all stabilized soils, concentration of metals leached were below the TCLP regulatory levels [7], except for cadmium and chromium in S-MS; and chromium in S-MS and S-MHS (**Figs. 4.43**- a and b). The concentrations of leached cadmium and nickel significantly decreased in S-MHS. Humic acids in soils apparently affected the retention of metals studied based on TCLP testing especially for cadmium and nickel.



(a) (b)

Figure 4.43 TCLP testing for (a) Cd, Cu, Ni, Pb, and Zn; and (b) Cr

Although chromium was the primary retained target on soil in the sorption experiment, it was the highest released metal in stabilized soil comparing to other metals for S-MS and S-MHS. In the presence of humic acids in soils, the increase of leached amount of chromium was observed (**Fig. 4.43**-b). The concentration of leached chromium from S-MS and S-MHS were higher than TCLP regulatory level requirement (5 mgL^{-1}) as shown in **Fig. 4.43**-b. On the contrary, the concentration of leached cadmium decreased in the presence of humic riches- soil (**Fig. 4.43**-a). In addition, the concentrations of copper, nickel, lead, and zinc were below the regulated concentrations.

4.3.5 Total chemical analysis of stailized soils

Total of metal (Na, Ca, Cd, Cr, Cu, Ni, Pb, and Zn) in the stabilized concrete (**Table 3.13**) was determined after digestion by aqua regia using ICP-AES shown in **Table 4.16**.

4.4 Leaching flux of ion species

Metal leaching form the stabilized soil (S-OS) was assessed using the ML test with contact time over 100 days. The mean of each point represented the experimental flux (mg/m^{2}s) are plotted vs. Ti, which is defined for each leaching sequence by:

$$Ti = \left[\frac{\sqrt{t_i} + \sqrt{t_{i+1}}}{2}\right]^2$$

After 100 days of leaching, a residual flux can be detected; however, it was quantitatively low comparing to the former one. The flux depends on porosity.

The results from the ML test as illustrated in **Figs. 4.44- 4.52**, three cases of leaching behavior –ion types could be distinguished:

Case I: Soluble species whose solubilities unvarying with the pH, types of leachants, humic acids.

In case of sodium, leaching flux showed in **Fig. 4.44**, chemical conditions did not directly affected the flux. This was because the dissolution and carbonation reactions in a heterogeneous porous material throughout the pH gradient within the material were generated while leaching scenario. Although the previous studied showed that the slope of -0.5 of leaching flux; (the experiment performed in the closed vessel), these features were represented the initial semi-infinite diffusional release flux [4]. The lower slope of sodium –experimental leaching flux was observed. The increase in atmospheric CO_2 uptake by carbonation in the ML test -solution resulted in decreasing of pH of leachants (**Fig. 4.25**). This phenomenon resulted in the increase of calcium carbonate/hydrate silicates solubility that counters the adverse effects of sodium leaching flux. Emprise here that in case I, humic acids in leachant do not affected to the relevant ions releasing.

Table 4.16 Amounts of metal in the monolithic stabilized soils

Total content (mg kg^{-1})	S-OS	S-MS	S-MHS	S-HS
Na	2,053	9,540	5,483	-
Ca	545,094	513,912	389,428	531,214
Cd	68.9	2362.6	2126.6	72.6
Cr	247.7	2226.3	2115.3	255.0
Cu	103.7	1693.6	1488.7	98.5
Ni	108.3	4716.3	925.0	100.1
Pb	132.3	1914.42	2208.1	125.4
Zn	105.0	1761.0	1044.0	100.0

The MMF of metal species in the monolithic stabilized soils (mg kg^{-1}) and L/S ratio

	S-OS	L/S	S-HS	L/S
Ca	1,060.46	200	3,0457.78	50
Cd	11.83	200	8.11	200
Cr	21.88	200	29.73	200
Cu	11.88	200	8.42	200
Ni	10.57	1	1.86	50
Pb	0.66	200	6.96	200
Zn	258.97	200	8.98	200

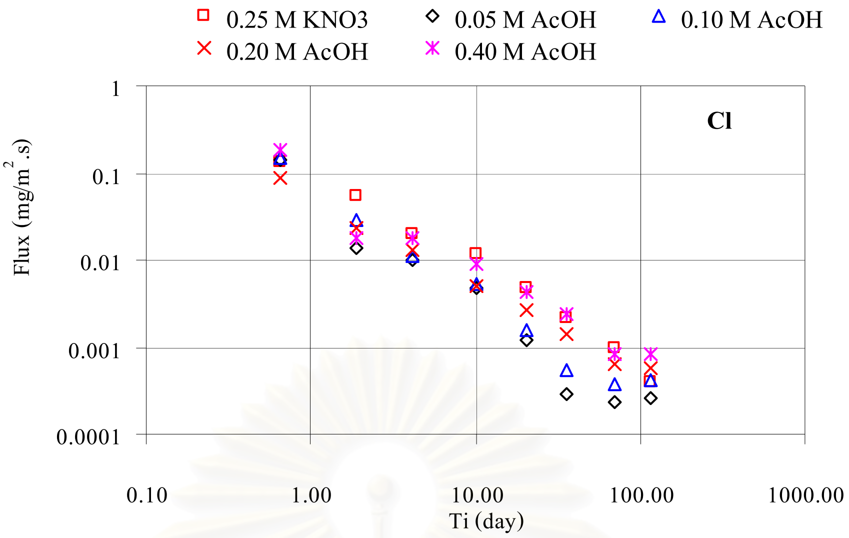
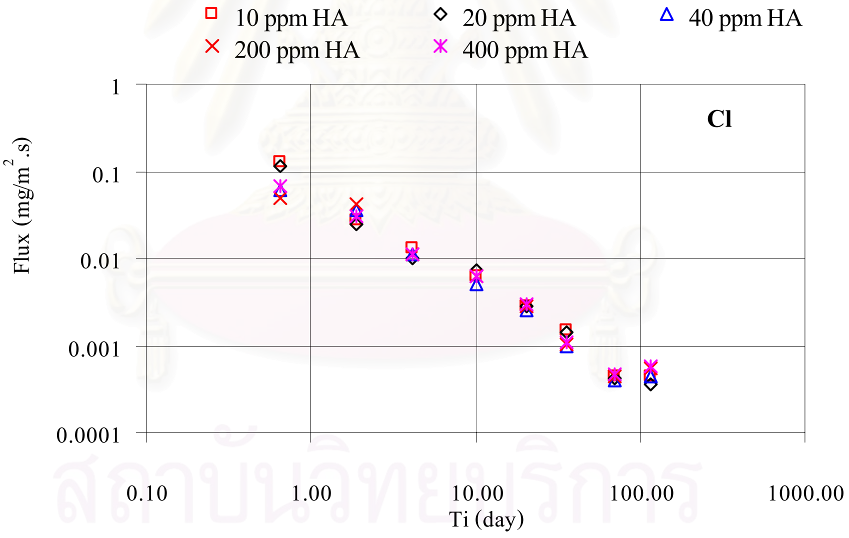


Figure 4.44 (a) Relation between average contact time (Ti) and flux of chloride ion for 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH



(b)

Figure 4.44 (b) Relation between average contact time (Ti) and flux of chloride ion for 10, 20, 40,200, and 400 ppm HA

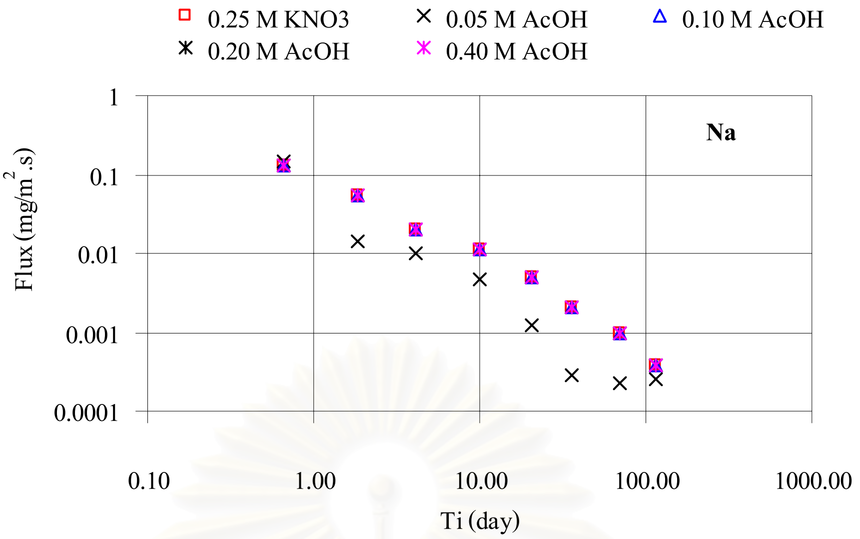


Figure 4.45 (a) Relation between average contact time (Ti) and flux of sodium for 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH

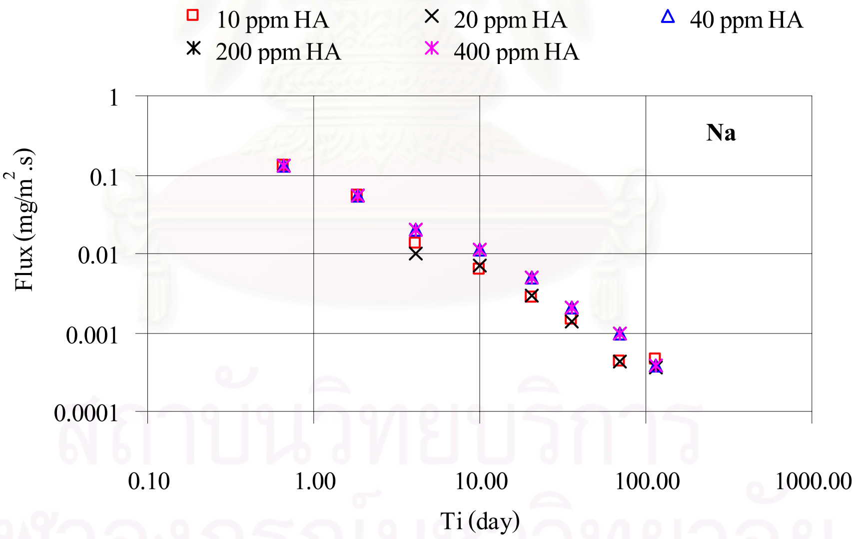
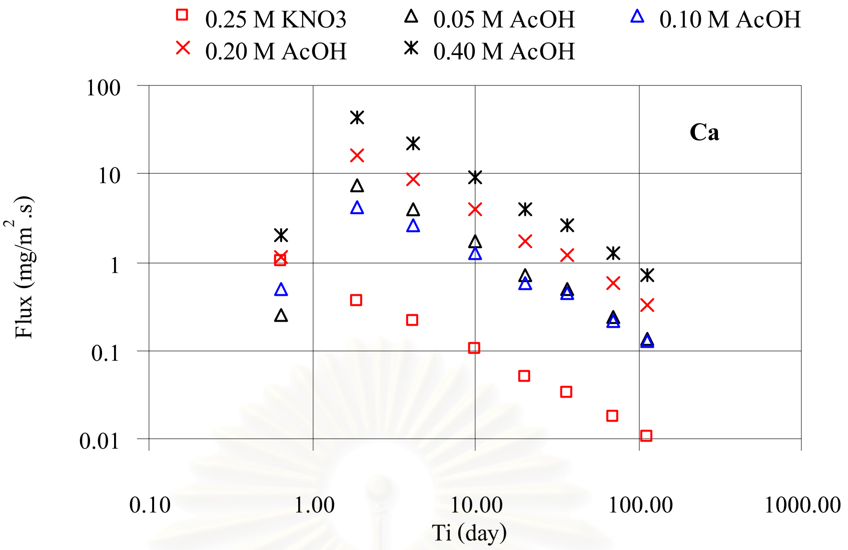


Figure 4.45 (b) Relation between average contact time (Ti) and flux of sodium for 10, 20, 40,200, and 400 ppm HA

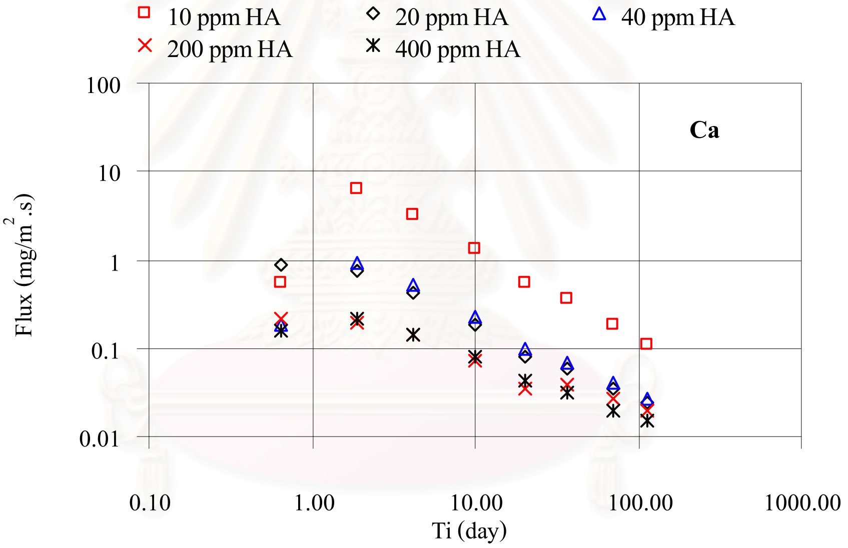
Case II: Species whose solubilities significantly depend on the physico-chemical leaching conditions; such as primarily pH of leachant, and type of leachants (e.g. Ca, Cd, and Cu). The pollutants released were controlled by the solubility of the species in the pore water at the local chemical properties.

In the beginning of leaching period, calcium flux was low because the equilibrium was not reached. It was observed that acetic acids (**Fig. 4.46-**a) promoted the released flux of calcium more than humic acid ones (**Fig. 4.46-**b). While the concentrations of humic acid increased, the released flux of calcium decreased apparently.

The released flux of cadmium and copper was also categorized to this case, due to the difference in flux when humic acid solutions were used as leachant (**Fig. 4.47**/b – **48**/b). It was found that released flux rate of cadmium under acetic acid/potassium nitrate was not constant, but the flux intensity was pH- dependent. Likewise, the rate of cadmium released under humic acid, the highest released flux rate was observed in the least amount of humic acid existing. The flux of copper under acetic acid was constant, and the flux intensity was pH- dependent, nevertheless, the flux under potassium nitrate was particular different from all mentioned cases.



(a)

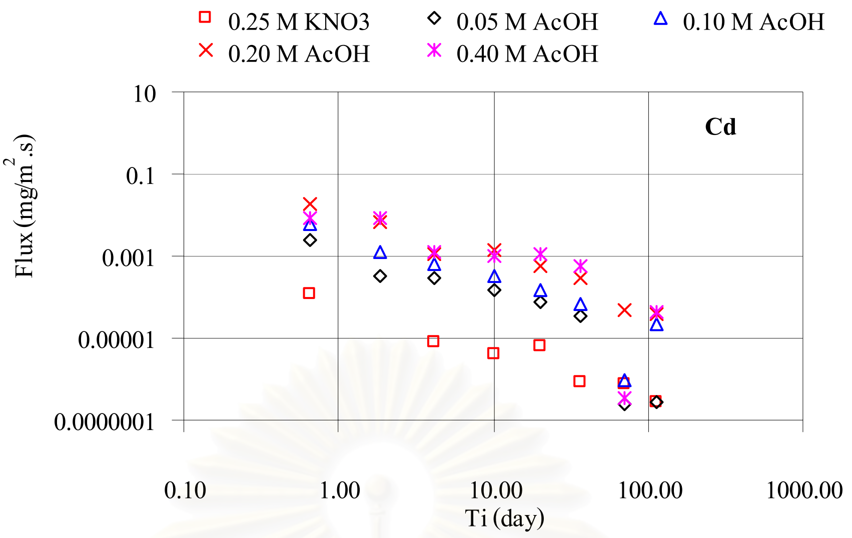


(b)

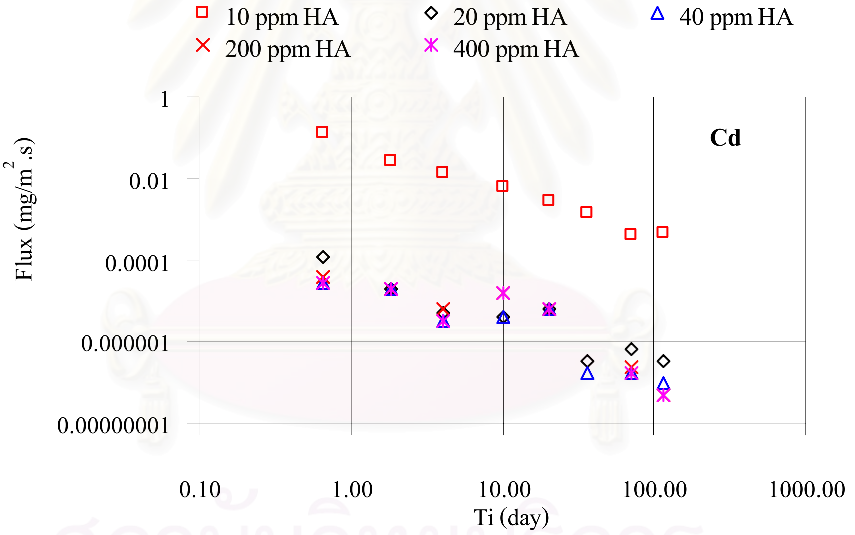
Figure 4.46 Relation between average contact time (Ti) and flux of calcium

(a) 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH

(b) 10, 20, 40,200, and 400 ppm HA



(a)

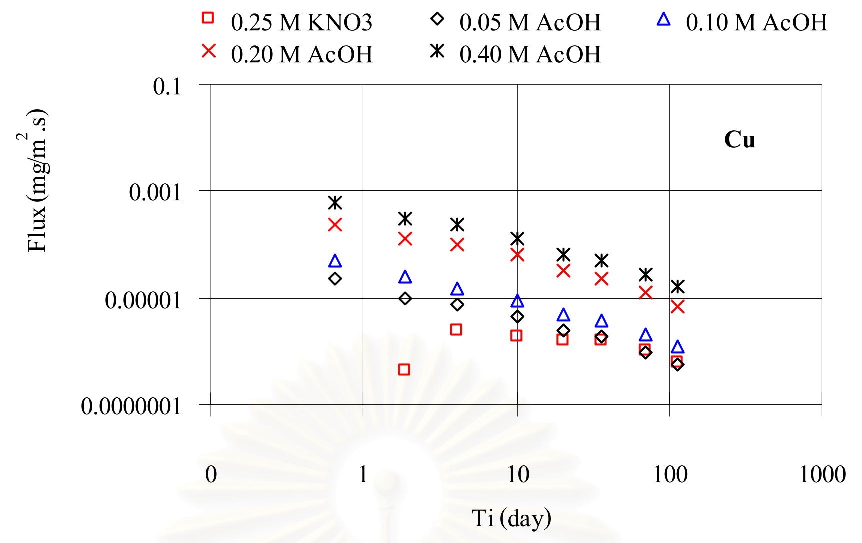


(b)

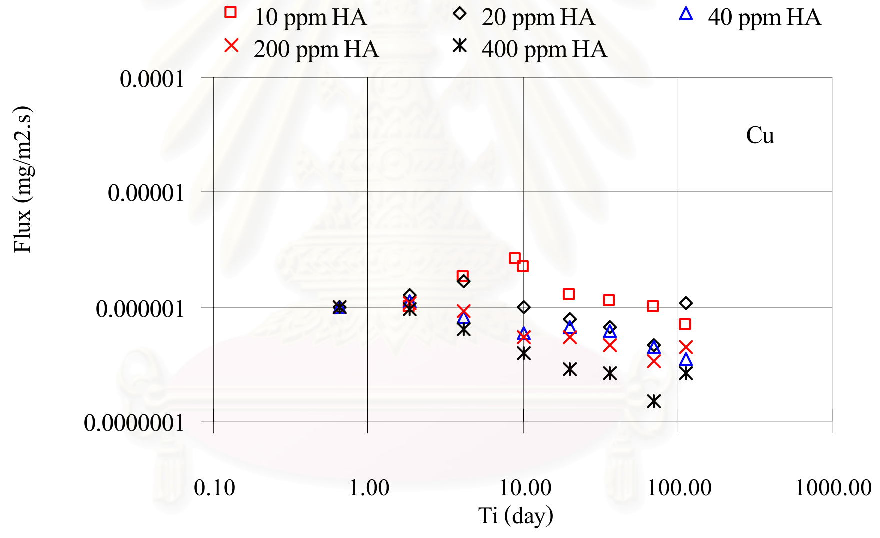
Figure 4.47 Relation between average contact time (Ti) and flux of cadmium

(a) 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH

(b) 10, 20, 40,200, and 400 ppm HA



(a)



(b)

Figure 4.48 Relation between average contact time (Ti) and flux of copper

(a) 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH

(b) 10, 20, 40,200, and 400 ppm HA

The two rationalizations could be proposed for the observation why humic acids influenced the released flux of calcium, cadmium and copper were in following:

(1) The high content of humic acid in leachant resulted in the increasing of

ionic strength (humate ions) of leachant. This diminished ions concentration gradient of copper and cadmium species between pore water/ matrix and surrounding solution.

(2) The released flux was restricted by the enveloping of humate (occurring of humic-metal salts) onto the solid/liquid interface of monolithic concrete, especially in the high concentration of humic acid in leachant. Accordingly, the diffusional transport rate of these metal species might be slower. However, the explanation of this phenomenon should be further elucidated.

Case III: Species whose solubilities were sensitive to potassium nitrate and acetic acid, but insensitive to humic acids in leachant (e.g. Ni, Zn, Cr, and Pb). The released flux of nickel, zinc, chromium, and lead cadmium under acetic acid/potassium nitrate was pH-dependent (**Figs. 4.49-4.52**) like calcium, cadmium, and copper. The flux increased with increasing of acetic acid concentration and potassium nitrate as well. However, the flux under humic acid as leachant was particular different in which no significant effects were found.

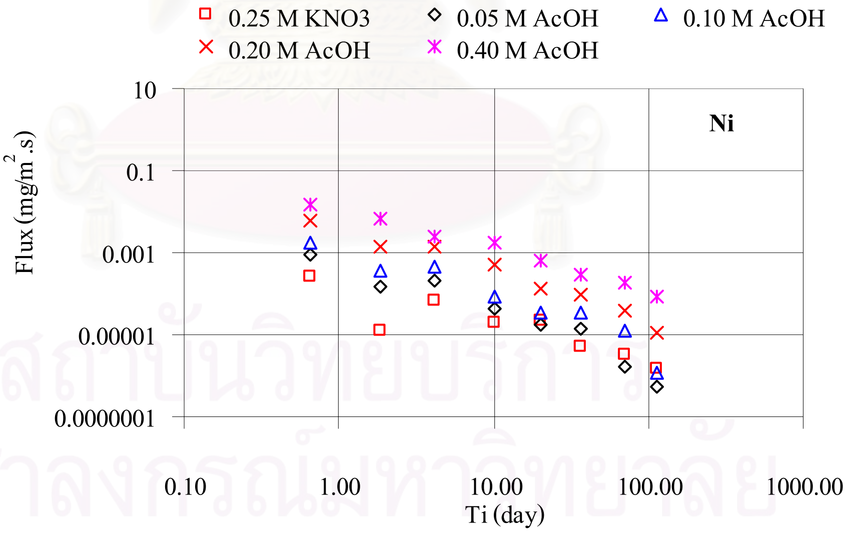
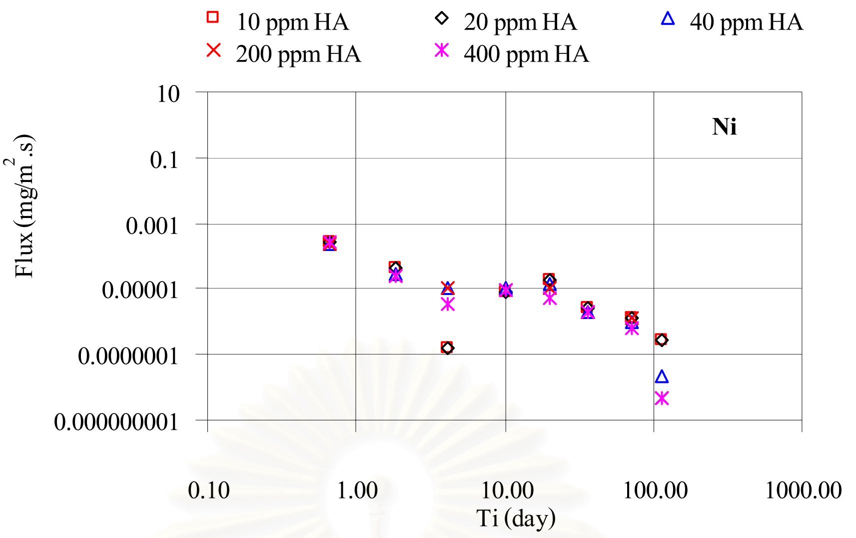


Figure 4.49-a Relation between average contact time (Ti) and flux of nickel for 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH



(b)

Figure 4.49-b Relation between average contact time (Ti) and flux of nickel for 10, 20, 40,200, and 400 ppm HA

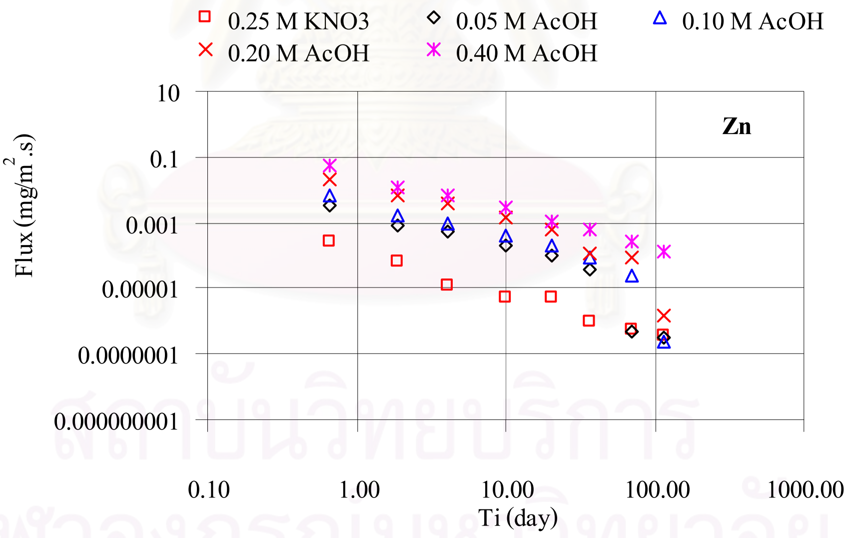


Figure 4.50-a Relation between average contact time (Ti) and flux of zinc for 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH

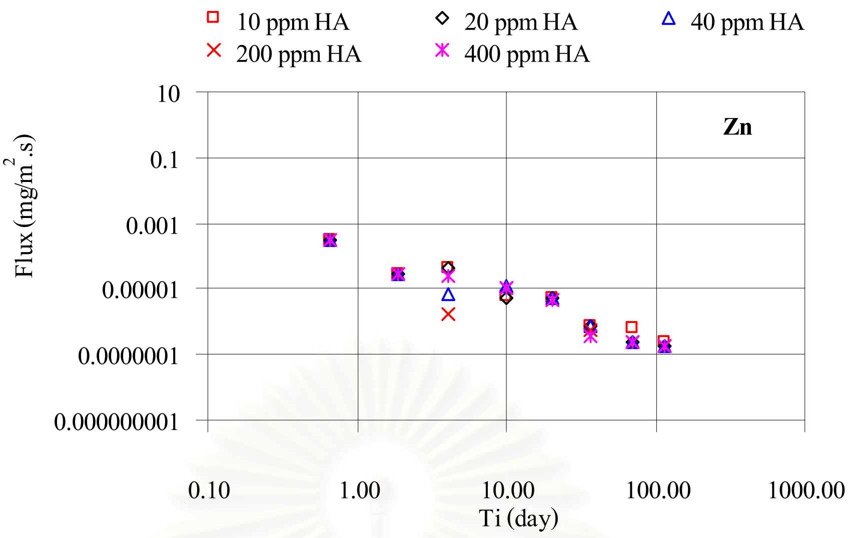


Figure 4.50-b Relation between average contact time (Ti) and flux of zinc for 10, 20, 40,200, and 400 ppm HA

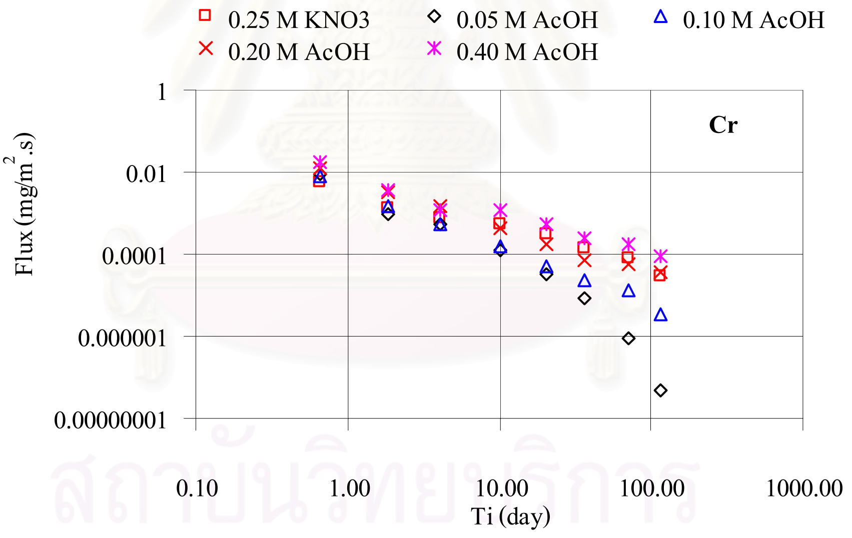
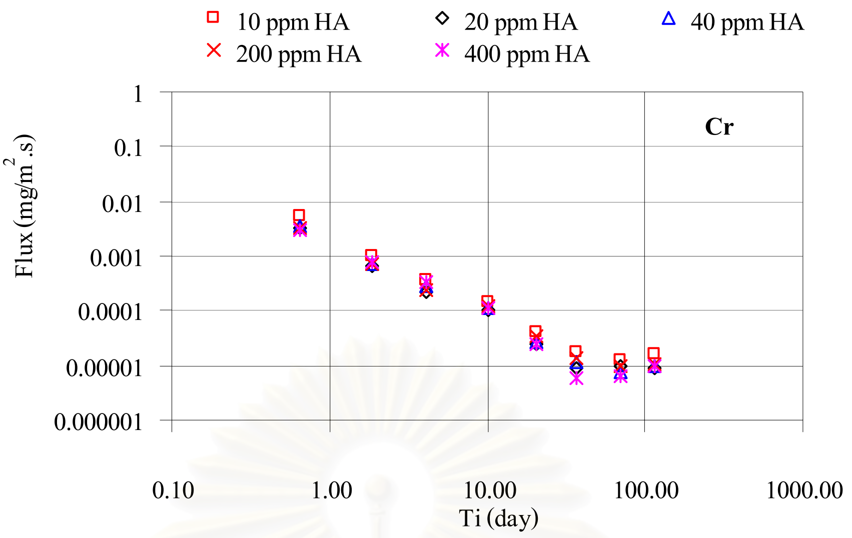


Figure 4.51-a Relation between average contact time (Ti) and flux of chromium for 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH



(b)

Figure 4.51-b Relation between average contact time (Ti) and flux of chromium for 10, 20, 40,200, and 400 ppm HA

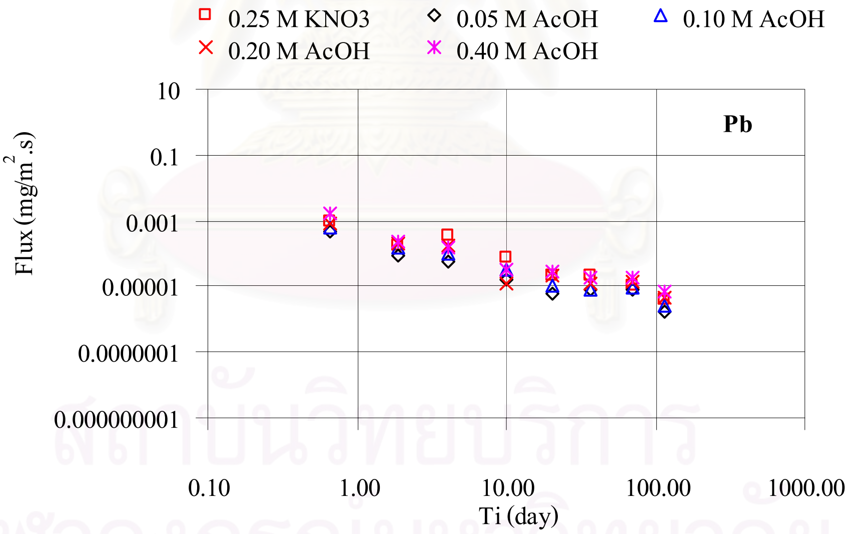


Figure 4.52-a Relation between average contact time (Ti) and flux of lead for 0.25 M KNO_3 and 0.05, 0.10, 0.20, and 0.40 M AcOH

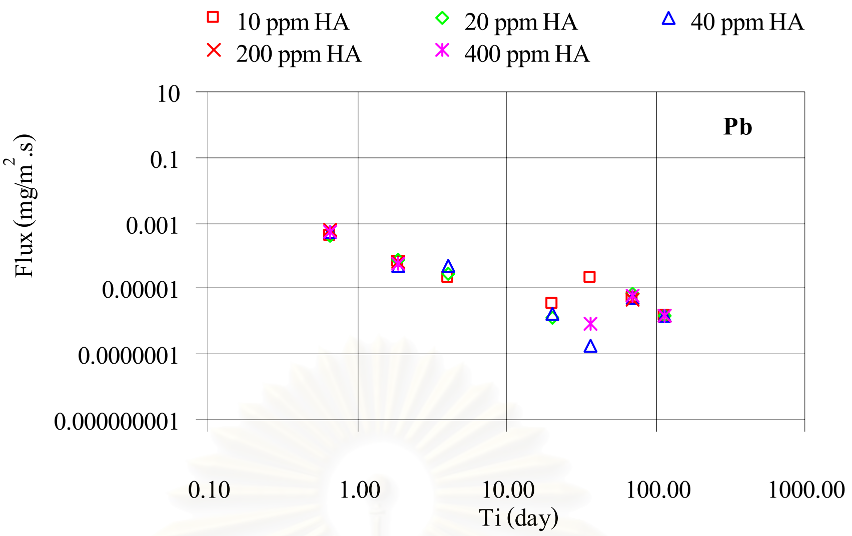


Figure 4.52-b Relation between average contact time (Ti) and flux of lead for 10, 20, 40,200, and 400 ppm HA

4.5 Conclusion on leaching behavior

In conclusion, the long-term leaching behaviors of meal/heavy metals in the stabilized humic -soil had been elucidated in followings:

Calcium: The leaching behavior was pH-dependent; the amount of releasing of S-HS was lower than that of S-OS. The decrease of leaching was disproportional to the increase of L/S ratios, which contrasted to the S-OS one. The MMF was determined at the highest L/S ratio of 200 but this fraction was very low comparing to its total content. Calcium was defined as species in case no. 2. The great cumulative amount of leached calcium was observed in the highest acetic acid concentration, but the least amount in the highest in humic acid concentration.

Cadmium: The solubilization of cadmium was pH-dependent. The result form pH on solubilization test showed that the amount of leached cadmium in the S-HS was lower than of the S-OS. Humic acids also affected the cumulative amount on cadmium, which the lower amount was observed in the S-OS with a hundred days of the dynamic leaching.

However, this amount was lower than the leached amount under acetic acid conditions. The curves of cumulative amount were continuously constant after undergoing for 20 days-leaching for all leachants. This indicated that cadmium species go on releasing. The MMF of cadmium in the S-HS was lower than of the S-OS (with L/S ratio =200). In addition, the flux of leached cadmium was affected by the concentration of humic acids in leachant, thus the long - term leaching behavior of cadmium was defined as species in case No.2, like calcium.

Copper: The long - term leaching behavior of copper was defined as species in case No.2, similar to the first of two metals. Because, the results showed that percentage of leached copper was highest under 0.5 molL^{-1} AcOH solution, L/S equal to 3. The solubilization of leached copper was pH-dependent. The lower pH of acetic acid the higher amount of copper released. The L/S ratio of copper in pore water did not significant affected the copper retention. The MMF in the S-OS was greater than the S-HS. In addition, the increase of flux of copper was affected by increasing of concentration of acetic acid. On the contrary, the lowest of copper flux were observed at the highest humic acids concentration.

Chromium: Chromium was a species with the maximum of affinity to soil adsorption, nevertheless, the concentration of chromium performed by TCLP test was the highest among the metals studied and this concentration was greater than a required value. This was one of the problems of the S/S treatment especially for the high chromium contaminated enriches humic –soil. The long-term leaching behavior of chromium species were defined as species in case No.3. The results showed that the L/S ratios and humic acids content in the stabilized soil as well as the leachants containing humic acids did not affect the flux and concentration in pore water. The MMF in the S-OS was less than the S-HS.

Nickel: Approximate 2 % of nickel species, the S-OS were leached compared with its total content under 0.5 mol L^{-1} AcOH as leachant (L/S =3). This indicated that most fractions of nickel species were retained in the concrete matrix. The solubilization of nickel species was pH-dependent. The lower pH of leachant the higher amount of nickel released. Acetic acid affected the leached nickel much more than humic acids. Its amount in pore water was fluctuated with the L/S ratios. The concentration of nickel in pore water for the S-HS was lower than of the S-OS. The results showed that the L/S ratio of 1 and 50 obtained the MMF for S-OS, and S-HS, respectively. These ratios differed from the previous ones. Humic acid in soil/ leachant did not affect the leached flux of nickel. Thus, the long - term leaching behavior of nickel was defined as species in case No.3.

Lead: The low affinity of lead adsorption onto soil had been observed. However, it was enable to retain in the concrete matrix such other metal. The solubilization of lead species was affected by the low and high excessive pH of leachant. The result from the ML test showed that amount of lead releasing was highest in potassium nitrate leachant and lowest in 40 mg L^{-1} humic acid. The L/S ratios affected the concentration in pore water both S-OS and S-HS.

Zinc: The retention of zinc species in the S-OS and S/HS were similar. The low MMF indicated that the most fractions of zinc species retained in the concrete matrix. The solubilizations of zinc species were pH-dependent, similar to those of nickel species. The lower pH of leachant the higher amount of zinc released. Acetic acid affected the leached nickel much more than humic acids. The concentration of zinc in pore water for the S-HS was significant lower than of the S-OS. Humic acid in soil/ leachant did not affect the leached flux of zinc. Thus, the long - term leaching behavior of zinc was defined as species in case No.3.

CHAPTER V

CONCLUSION

A significant relationship between the presence of HA in soil and the metal-adsorption ability was explored and was an important evidence for the effectiveness of metal retention in the stabilized soil. This resulted partly from soluble-metal complexation.

1. Humic acids was defined as a factor limited the effectiveness of the S/S in long term by reduced the CS of concrete mortars and increased the leaching rate of some heavy metals contaminated soils. These clarified the understanding the mobilization of metal species in solidified wastes the humic phase.

2. The influences on the metal retention had been considered, that each metal species had been observed in differently leaching behaviors. Laboratory leaching tests showed that calcium, sodium, and chloride ions were the major constituents in leachate for all leaching medium because they were very soluble. While the heavy metal retention in stabilized soil depend on the pH associated with chemical of leaching medium and environmental conditions.

3. Consequently, the retention of ion species in the stabilized soil was categorized into three groups by their long-term behaviors leaching tests:

(a) Soluble species whose leachability is significantly independent of leaching conditions (i.e. sodium, and chloride ions)

(b) Species that the leachability is significantly dependent on the physico-chemical leaching conditions (e.g. calcium, cadmium, and copper). The influences were including:

1. Influences of pH on metal leaching
2. Influences of type of leaching medium

3. Influence of contact time, and

4. Influences of leaching environment e.g. under closed/open systems, dynamic/static leaching.

(c) Species whose solubilities are sensitive to humic acids in leachant (e.g. chromium, nickel, lead, and zinc)

4. The evaluation of cement-based S/S technologies as the effective means for safe disposal landfill of HM contaminated soil containing humic acids was considered a satisfaction approach to the S-OS (contaminated no-enriches humic soil). For the cases of S-MS, and S-MHS, these S/S technologies should be improved and realized particularly for highly -chromium and cadmium contaminated soils.

Suggestions for the future research

Future researchers might wish to modify a simulation model, which provide the better understanding of saturated landfill scenarios. The additive binder should be investigated further those aspects of the cement - S/S process based on improving of compressive strength of stabilized soil. In addition, the future development of model revealed with harmonization of the approaches across different fields should attempt more vigorously.

Likewise, suggestions were made to examine the effect of other ions; e.g. radioactive nuclides, cyanide ion; particularly the addition of humic substances (fulvic acids/humic acids) by implementing a similar leaching test as used in this study. The use of the novel developed model was also suggested.

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