

## CHAPTER 3



## METHODOLOGY

As mentioned before, this research consists of six sub-parts, but part six has no experiment. Therefore, the materials and experiment programs of each part except part VI will be separately discussed as follow.

### Part I

#### 3.1 Materials

##### 3.1.1 Reagents and Glassware

All chemicals were reagent grade and were used without further purification. All solutions were prepared with water purified by reverse osmosis and deionized using ELGA Purelab system. All glassware was cleaned by soaking in 10% HNO<sub>3</sub> and rinsed four times with deionized (DI) water. The arsenite stock solution was prepared from the sodium arsenite, NaAsO<sub>2</sub>, (UNIVAR) dissolved in 1% (v/v) trace metal grade HCl (Scharlau). The Fe(III) stock solution was prepared from ferric chloride hexahydrate, FeCl<sub>3</sub>·6H<sub>2</sub>O (Riedel-deHaën) dissolved in 1% (v/v) trace metal grade HCl.

##### 3.1.2 Arsenic-Iron Hydroxide Sludge

In this study, five different recipes of raw arsenic containing sludge-S1, S2, S3, S4, and S5- varying in the ratio of ferric to arsenic (mole:mole) were synthesized at pH 7 by simulating the chemical reaction between ferric chloride and arsenite in the arsenic removal process by coagulation/co-precipitation. According to the recent

study (Vandecasteele et al., 2002), it was found that between two oxidation states of arsenic, arsenite (+3) and arsenate (+5), when subjected to leaching tests, leachability of arsenite was the more critical. To be conservative, the speciation of arsenic used in synthesizing the sludge for the present study was arsenite.

All five different recipes of raw arsenic containing sludge were subjected to two different preparations. The first set of the sludge was dewatered by a vacuum pump until no free water could be extracted anymore. This preparation was to simulate the condition of the dewatered sludge before disposed in a landfill. This set of sludge was codified into SW series, so S1, S2, S3, S4, and S5 became SW1, SW2, SW3, SW4, and SW5, respectively. The second set of the sludge was not only dewatered by a vacuum pump like the first set but also dried by an oven until no water could be evaporated anymore. Then, the sludge was ground in a ceramic to achieve a homogeneous size of below 9 mm. This set of sludge was codified into SD series, so S1, S2, S3, S4, and S5 became SD1, SD2, SD3, SD4, and SD5, respectively.

## **3.2 Experimental Programs**

### **3.2.1 Characterization of the Raw Arsenic-Iron Hydroxide Sludge**

#### **3.2.1.1 Chemical Compositions of the Raw Sludge**

To identify the percent of two most important chemical compositions, arsenic and iron, in each kind of sludge, three replicates of each were sampled, destructed according to EPA method 3051, microwave assisted acid digestion of sludge (USEPA, 1994), and analyzed by Inductive Couple Plasma-Optical Emission Spectroscopy (ICP-OES), a multi-element analytical technique of which typical 3 sigma detection limits are 3 µg/L for arsenic at the wavelength of 188.98 nm (Varian, 2001).

### 3.2.1.2 Particle Size Analysis of the Raw Sludge

Both SW and SD sludge were subjected to particle size analysis by Malvern Particle Size Analyzer Model Mastersizer S that can measure particle size ranging from 0.05 to 880 microns. In this study, water was used as a medium with dispersing refractive index of 2.44.

### 3.2.1.3. Vibrational Characterization of the Raw Sludge

The five different recipes, S1 to S5, were subjected to Fourier Transform Infrared Spectroscopy (FT-IR) for further characterization through vibrational aspects providing insight into molecular structure. All FT-IR spectra in the present study were recorded by BIO-RAD Fourier Transform Infrared Spectroscopy using potassium bromide pellets at sample: KBr ratio of 1:50. The spectra were recorded under the wavelength of 4000-400  $\text{cm}^{-1}$  with 8  $\text{cm}^{-1}$  resolution and 200 scans each time.

### 3.2.1.4 Microstructures of the Raw Sludge

The same sets of the sludge subjected to FT-IR were coated with gold and observed their microstructures by JSM 6400 Scanning Electron Microscopy (SEM). Moreover, Energy Dispersive Analysis of X-ray (EDS) Link<sup>1818</sup> Series was used to examine surface phenomena of these sludge specimens by examining the arrangement of their element compositions.

## **3.2.2 Characterization of the Leached Arsenic-Iron Hydroxide Sludge**

After 48 hours of the TCLP test, SD samples obviously turned to two different groups of leached sludge. One was dispersed among the aqueous phase of the extraction fluid while another settled at the bottom of an extraction vessel. The dispersed sludge samples were sampled, filtrated through a 0.6 to 0.8  $\mu\text{m}$  glass fiber filter, dried in open air, and codified as SD-SUSPENDED group. In the same way, the sludge samples settling at the bottom of an extraction vessel were also sampled.

dried in open air, and codified as SD\_BOTTOM group. In contrast, all the leached sludge of SW was dispersed among the aqueous phase of the extraction fluid. Like SD\_SUSPENDED, it was sampled, filtrated through a 0.6 to 0.8  $\mu\text{m}$  glass fiber filter, dried in open air, and codified as Leached SW group.

Both SD\_SUSPENDED and SD\_BOTTOM as well as Leached SW were subjected to Malvern Particle Size Analyzer Model Mastersizer S, BIO-RAD Fourier Transform Infrared Spectroscopy (FT-IR), and JSM 6400 Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Analysis of X-ray (EDS) Link<sup>™</sup> Series. All of these experiments were conducted to obtain particle size, vibrational and morphological information of the sludge after the leaching test in order to compare to those of the raw sludge.

### 3.2.3 Leachate Characteristics of the Arsenic-Containing Sludge

To examine which recipes of the sludge is classified as hazardous waste and to conduct the comparative study of the sludge leachability under differently simulated condition, in this study, both SW and SD samples were subjected to not only the TCLP but also LP-NO 6.

Under the TCLP, one of the most universal extraction procedures, issued by the U.S. EPA under the Hazardous and Solid Waste Amendments of 1984 (HSWA), the tested materials were crushed to a particle size smaller than 9.5 mm. The extraction fluid was made with water and acetic acid to a pH of  $4.93 \pm 0.05$ , which was selected to mimic conditions in a municipal landfill. The crushed materials were mixed with a weak acetic acid extraction liquid, in a liquid-to-solid weight ratio of 20:1, and agitated in a rotary extraction for 18 hours at 30 rpm and 22 °C. After 18 hours of agitation, the samples were filtered through a 0.6 to 0.8  $\mu\text{m}$  glass fiber filter, and the filtrates were defined as the TCLP extract (Method 1311, 1992). In this study, the filtrates were analyzed by ICP-OES for arsenic and iron concentration. In addition, pH of leachate samples were measured by HACH Sension 3.

On the other hand, Thailand has developed its own leaching procedure under the Notification of Ministry of Industry No. 6, B.E. 2540 since 1997. This leaching procedure is almost identical to TCLP except that the extraction fluid made with 80% of sulfuric acid and 20% of nitric acid in deionized (DI) water to a pH of 5.00 ( Podjane, 2002). In addition, this extraction fluid somewhat likes the leachant prepared from the Synthetic Precipitation Leaching Procedure (SPLP) regulatory test (U.S. EPA SW-846 Method 1312) in that the SPLP extraction fluid is made with 60% of sulfuric acid and 40% of nitric acid in deionized (DI) water to a pH of  $4.20 \pm 0.05$  for the east side of the Mississippi river or  $5.00 \pm 0.05$  for the west side to simulate acid rain condition ( Podjane, 2002).

## **Part II**

### **3.3 Materials**

#### **3.3.1 Reagents and Glassware**

All chemicals used in this part and the procedures of stock solution preparation as well as glassware preparation are the same as discussed in 3.1.1.

### **3.4 Experimental Programs**

#### **3.4.1 Batch Coagulation/Co-precipitation Tests of Arsenic Removal by Ferric Chloride.**

Batch coagulation/co-precipitation tests were conducted with the five different synthesized water of which initial arsenite concentrations were 140, 480, 1,465, 4370, and 12,790  $\mu\text{g/L}$ . Seven different coagulant doses of which  $\text{FeCl}_3$ -to-initial As ratios were 0, 5, 10, 20, 40, 80, and 160 were added to each synthesized water. The mixtures of which initial hardness was 50 mg/L of  $\text{CaCO}_3$  were adjusted to pH 7. Next, the mixtures were rapidly mixed with 100 rpm for 1 minute, followed by slow mixing with 40 rpm for 30 minutes. The samples were then allowed to stand for 1 hour for

settlement and filtered with No 4 filter papers (Whatman) The filtered water samples were acidified with nitric acid and then analyzed for the residual arsenic and iron concentrations using ICP-OES

### **3.4.2 Linear Regression Analysis**

The results from the previous step were subjected to linear regression analysis by SPSS for Windows Release 11.0.0, a statistical program, to correlate removal efficiency (%) of arsenic with coagulant doses ( FeCl<sub>3</sub>-to-initial As ratios) and initial arsenic concentrations and to correlate sludge property ( As-to-Fe ratios) with coagulant doses ( FeCl<sub>3</sub>-to-initial As ratios) and initial arsenic concentrations

## **Part III**

### **3.5 Materials**

#### **3.5.1 Arsenic-Iron Hydroxide Sludge for the Solidification/Stabilization**

The purpose of this part is to study the management strategy for the sludge in case of it being classified as hazardous waste. According to the results in Part I, all five recipes of arsenic containing sludge in Part I were classified as hazardous waste on the basis of the United States regulatory limit while only the sludge of which As-to-Fe ratio was around 0.153 was classified as hazardous waste on the basis of both Thai and the United States regulatory limit. Therefore, to be conservative, the worst case scenario was used as a criterion. For this reason, the sludge with As-to-Fe ratio of 0.153 was subjected to solidification/stabilized process in this part Some physical properties of the sludge are shown in Table 3.1

#### **3.5.2 Portland Cement**

The Elephant brand ASTM Type-I Portland cement according to ASTM C150-95 manufactured by the Siam Cement Company Ltd., Bangkok, Thailand is

used throughout the experiments. The chemical compositions and physical properties of the Portland cement are shown in Table 3.1.

**Table 3.1** Some Chemical and Physical Characteristics of the Binders and the Sludge used in Part III

Chemical composition of binder materials(wt%)					
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Ca(OH) <sub>2</sub>
Portland Cement	22	6	3	65	-
Hydrated lime	-	-	-	-	96.0
Physical properties of binders, sludge, and sand					
	Cement	Lime	Dried sludge	Sand	
Specific gravity	3.15	2.24	2.49 <sup>a</sup>	2.46 <sup>b</sup>	
Absorption (%)	-	-	54.34 <sup>c</sup>	-1.2 <sup>d</sup>	

<sup>a</sup> specific gravity of the sludge was tested under saturated surface dry condition (SSD) simulated by pouring water through the sludge lying on filter and allowing water to freely flow through the sludge until the sludge was in SSD condition in which no water could be sorbed or desorbed anymore. <sup>b</sup> specific gravity of sand was tested under saturated surface dry condition by following ASTM C 128-79. <sup>c</sup> adsorption of the sludge was tested in the same manner as <sup>a</sup>. <sup>d</sup> the moisture content of as-collected sand was 2.43% while moisture content of the same sample under SSD condition according to ASTM C 128-79 was only 1.23%, so as-collected sand would desorb 1.2% of water during mixing.

### 3.5.3 Hydrated Lime

Hydrated lime, calcium hydroxide, (analytical reagent grade, UNIVAR), was also used as a stabilization binder throughout the experiments. The chemical compositions and physical properties of the hydrated lime are shown in Table 3.1

### 3.5.4 Sand

River sand used for making specimens was natural silica sand that conformed to the requirements for graded sand as specified by ASTM C 778-92.

### 3.5.5 Water

Ordinary tap water was used for all mixed.

## 3.6 Experiment Programs

### 3.6.1 Physical Properties and Phase Analyses of the Solidified/Stabilized Arsenic-Iron Hydroxide Sludge

#### 3.6.1.1 Compressive Strength of the Solidified/Stabilized Sludge

Ten solidification/stabilization recipes shown in Table 3.2, which include two formulas of control matrices, were used in this study. Each recipe differed from one another in waste-to-binder, Portland cement-to-lime, and water-to-binder ratio. For each recipe, three replicates were cast with the weight of cement to sand ratio of 1.00:2.75 according to ASTM C109-95, for 2x2x2-inch mortar. All 30 matrices were tested for their unconfined compressive strength at 28 days age in order to examine each one's potential of utilization as construction materials.

#### 3.6.1.2 SEM-EDS Application for Examining Macroencapsulation of the Solidified /Stabilized Sludge

The eight out of ten samples of cement paste at the same components as Table 3.2, except SW4-S15-L00 and SW9-S15-L04 were cast into 5 mm-diameter plastic tubes. After 28 days, the samples were cross-sectionally cracked, coated with gold, and their macroencapsulation as well as microencapsulation were observed by JSM 6400 Scanning Electron Microscopy. Moreover, EDS, Link<sup>TM</sup> Series, was used to identify various microstructures in these solidified waste forms by determining their elemental composition.



**Table 3.2** Mixture Proportion of the Solidified/Stabilized Samples in Part III

Notation	Mixture proportion ( lb/ ft <sup>3</sup> )					Ratio		
	Water (w)	Cement (c)	Lime (l)	SSD Sludge <sup>c</sup> (s)	SSD Sand	w (l c)	s (l c)	l (l c)
CW4-S00-L00	13.58	33.96	0.00	0.00	93.38	0.40	0.00	0.00
SW4-S15-L00	13.15	32.88	0.00	4.93	90.41	0.40	0.15	0.00
SW4-S25-L00	12.88	32.20	0.00	8.05	88.54	0.40	0.25	0.00
SW4-S50-L00	12.24	30.61	0.00	15.30	84.17	0.40	0.50	0.00
SW4-S100-L00	11.11	27.86	0.00	27.86	76.62	0.40	1.00	0.00
CW9-S00-L04	23.51	15.67	10.45	0.00	71.82	0.90	0.00	0.40
SW9-S15-L04	22.93	15.28	10.19	3.82	70.05	0.90	0.15	0.40
SW9-S25-L04	22.56	15.04	10.03	6.27	68.92	0.90	0.25	0.40
SW9-S50-L04	21.68	14.45	9.64	12.05	66.25	0.90	0.50	0.40
SW9-S100-L04	20.12	13.41	8.94	22.36	61.48	0.90	1.00	0.40

<sup>c</sup>SSD sludge was composed of dried sludge(45.66% by weight) and sorbed water(54.34% by weight)

### 3.6.1.3 XRD Application for Phase Analysis of the Solidified Stabilized Waste

To obtain a better understanding of the physical and chemical influence of the sludge on the mineralogical and mechanical properties of hydrated cement, another set of cement paste, eight samples, at the same mixtures as those of 3.6.1.2 was pulverized by grinding it with acetone to stop hydration by dewatering and to obtain a homogeneous mixture at the age of 28 days and analyzed by the JEOL JDX-3530 X-ray Diffraction Spectroscopy using Cu K<sub>α</sub> radiation at 35 KV and 25 mA at 0.04 steps and 1-s counting time

### 3.6.1.4 FT-IR Application for Examination of Hydration Inhibition

The same set of cement paste, analyzed by XRD, was subjected to FT-IR for structure. All FT-IR spectra in the present study were recorded by BIO-RAD Fourier Transform Infrared Spectroscopy using potassium bromide pellets at sample: KBr ratio of 1:50. The spectra were recorded under the wavelength of 4000-400  $\text{cm}^{-1}$  with 8  $\text{cm}^{-1}$  resolution and 200 scans each time.

### 3.6.2 Leachate Characteristics of the Solidified/Stabilized Waste

After 28 days of curing and the unconfined compressive strength tests, all 30 samples cast in 3.6.1 were crushed to a particle size smaller than 9.5 mm and subjected to both the TCLP and LP-NO 6 as described in 3.2.2 to examine influence of waste-to-binder ratios on leachability of arsenic.

## Part IV

### 3.7 Materials

#### 3.7.1 The Arsenic-Iron Hydroxide Sludge, Portland Cement, Hydrated Lime, and Water

The arsenic-iron hydroxide sludge, Portland cement, hydrated lime, and water used in this part was the same as those in 3.5.1 to 3.5.5.

### 3.8 Experimental Programs

#### 3.8.1 Morphologies of the Solidified/Stabilized Sludge

Six sets of cement paste of which mixtures are shown in Table 3.3 were cast into 7 mm-diameter plastic tubes. By the age of 3, 7, 14, and 28 days, respectively, the samples were cross-sectionally cracked, coated with gold, and their microstructures

were observed by JSM 6400 Scanning Electron Microscopy. Moreover, EDS, Link<sup>ISIS</sup> Series, was used to identify various microstructures in these solidified waste forms by determining their elemental composition.

## Part V

### 3.9 Materials

#### 3.9.1 The Arsenic-Iron Hydroxide Sludge, Portland Cement, Hydrated Lime, and Water

The arsenic-iron hydroxide sludge, Portland cement, hydrated lime, and water used in this part was the same as those in 3.5.1 to 3.5.5.

**Table 3.3** Mixture Proportion of the Solidified Stabilized Sample in Part IV

Notation	Mixture proportion (lb/ft <sup>3</sup> )				Ratio		
	Water (w)	Cement (c)	Lime (l)	SSD Sludge (s)	w (l-c)	s (l-c)	l (l-c)
SW4-S25-L00	30.51	76.28	0.00	19.07	0.40	0.25	0.00
SW4-S25-L04	28.70	43.06	28.70	17.95	0.40	0.25	0.40
SW6-S25-L00	36.77	61.29	0.00	15.32	0.60	0.25	0.00
SW6-S25-L04	35.01	35.01	23.35	14.59	0.60	0.25	0.40
SW9-S25-L00	42.55	47.40	0.00	11.90	0.90	0.25	0.00
SW9-S25-L04	41.01	27.34	18.30	11.46	0.90	0.25	0.40

### **3.10 Experimental Programs**

#### **3.10.1 XRD Application for Examining Hydration Development and the Formation of Calcium-Arsenic Compounds**

To obtain a better understanding of the interference of hydration development in the presence of the sludge as well as progress of calcium-arsenic compound formation, the six out of nine of the solidified/stabilized recipes which are SW4-S25-L00, SW4-S25-L04, SW6-S25-L00, SW6-S25-L04, SW9-S25-L00, and SW9-S25-L04 as well as the six out of nine of the control samples which are CW4-S00-L00, CW4-S00-L04, CW6-S00-L00, CW6-S00-L04, CW9-S00-L00, and CW9-S00-L04 in Table 3.4 but without addition of sand were pulverized by grinding them with acetone to stop hydration by dewatering and to obtain a homogeneous mixture at the age of 3, 7, 14, and 28 days. All samples were analyzed at each age by the JEOL JDX-3530 X-ray Diffraction Spectroscopy using Cu K<sub>α</sub> radiation at 35 kV and 25 mA at 0.04 steps and 1-s counting time.

#### **3.10.2 Application of compressive Strength tests for Characterizing Physically and Chemically Interfering in Mechanical Property of Solidified Matrices due to Addition of Arsenic Sludge**

The eighteen solidification/stabilization recipes shown in Table 3.4, which include nine formula of control matrices, were used in this study. Each recipe differed from one another in waste-to-binder, Portland cement-to-lime, and water-to-binder ratio. For each recipe, three replicates were cast with the weight of cement to sand ratio of 1:00:2.75 according to ASTM C109-95, for 2x2x2-inch mortar. All 216 matrices were tested for their unconfined compressive strength at the age of 3, 7, 14, 28 days in order to examine compressive strength development of the solidified waste form and to compare the compressive strength development of the solidified/stabilized samples with that of the control samples.

### 3.10.3 Leaching Characteristics of the Solidified/Stabilized Sludge as a Function of Water-to Binder Ratio and Lime-to Binder Ratio

To exam influence of water-to-binder ratios and lime-to binder ratios on leachability of the solidified/stabilized products, after 28 days of curing and the unconfined compressive strength tests, all solidified/stabilized control samples cast according to Table 3.4 were crushed to a particle size smaller than 9.5 mm and subjected to both the TCLP and LP-NO.6 as described in 3.2.2

**Table 3.4** Mixture proportion of the solidified/stabilized sample in Part V

Notation	Mixture proportion (lb/ft <sup>3</sup> )					Ratio		
	Water (w)	Cement (c)	Lime (l)	SSD Sludge (s)	SSD Sand	w/(l+c)	s/(l+c)	l/(l+c)
SW4-S25-L00	12.86	32.22	0.00	8.04	88.56	0.40	0.25	0.00
SW4-S25-L02	12.73	25.39	6.34	7.93	87.39	0.40	0.25	0.20
SW4-S25-L04	12.53	18.81	12.53	7.85	86.24	0.40	0.25	0.40
SW6-S25-L00	17.53	29.15	0.00	7.30	80.25	0.60	0.25	0.00
SW6-S25-L02	17.29	23.05	5.75	7.22	79.30	0.60	0.25	0.20
SW6-S25-L04	17.09	17.07	11.38	7.14	78.35	0.60	0.25	0.40
SW9-S25-L00	23.04	25.55	0.00	6.38	70.38	0.90	0.25	0.00
SW9-S25-L02	22.80	20.24	5.08	6.34	69.63	0.90	0.25	0.20
SW9-S25-L04	22.54	15.03	10.00	6.24	68.94	0.90	0.25	0.40
CW4-S00-L00	13.60	33.97	0.00	0.00	93.38	0.40	0.00	0.00
CW4-S00-L02	13.40	26.78	6.70	0.00	92.07	0.40	0.00	0.20
CW4-S00-L04	13.20	19.80	13.20	0.00	90.84	0.40	0.00	0.40
CW6-S00-L00	18.36	30.58	0.00	0.00	84.22	0.60	0.00	0.00
CW6-S00-L02	18.16	24.16	6.07	0.00	83.15	0.60	0.00	0.20
CW6-S00-L04	17.92	17.90	11.93	0.00	82.12	0.60	0.00	0.40
CW9-S00-L00	24.03	26.66	0.00	0.00	73.39	0.90	0.00	0.00
CW9-S00-L02	23.75	21.11	5.27	0.00	72.60	0.90	0.00	0.20
CW9-S00-L04	23.51	15.65	10.43	0.00	71.81	0.90	0.00	0.40