

# CHAPTER 1



## INTRODUCTION

### 1.1 General

Named “the largest mass poisoning of a population in history” (Khundkar, 2003), the contamination of groundwater by arsenic in Bangladesh has been a point of attention and become a global issue. In reality, not only Bangladesh but also many countries throughout the world such as Argentina, Chile, China, Hungary, India (West Bengal), Mexico, Pakistan, Thailand, USA, and Viet Nam have been facing the same problem (Adeel and Ali, 2003: 1). It was estimated that around 41 million of the world’s population are potentially exposed to this fatal contaminant (Smedley and Kinniburgh, n.d : 30-34)

True to its nickname, ‘the silent killer’ (Adeel and Ali, 2003: 1), arsenic hides behind the consumable appearance of groundwater in contaminated shallow aquifers. Due to the fact that arsenic dissolved in water has no color, smell, and taste, it is not surprising that the poor villagers in the affected areas have drunk this poison for decades without awareness of being at risk of diseases ranging from melanosis to skin cancer and gangrene (Harun-ur-Rashid and Abdul Karim Mridha, 1998: 162-163).

In order to decrease the severity of this problem, several arsenic removal technologies such as ion exchange, activated alumina, membrane, coagulation with ferric salts, and iron-oxide-coated sand (Amy et al., 2000: 1-10) have been applied in those regions. Each technology has its own advantages and disadvantages; however, one of the economical technologies (Meng, Korfiatis, Christodoulatos et al., 2001: 2805) usually used in Asian countries is coagulation with ferric chloride because it is suitable for poor villagers’ situation in this region.

In addition to removing arsenic from contaminated groundwater to produce safe drinking water, coagulation with ferric chloride can be used to deal with liquid residuals of other arsenic removal technologies such as a waste brine solution from an ion exchange process. The concentration of arsenic in such solution is generally too concentrated to discharge to a sanitary sewer without violating regulations. Therefore, ferric chloride precipitation is required to reduce arsenic concentration in the brine solution prior discharging to a sanitary sewer (Amy et al., 2000: 199).

Added into water in the form of  $\text{FeCl}_3$ , the coagulant dissociates and is rapidly dispersed through the reactor. As a result, the solid precipitate  $\text{Fe}(\text{OH})_{3(s)}$  and complexes are formed. These amorphous products play a crucial role in the success of removing both arsenite and arsenate from the contaminated water. Generally, surface complexation reactions are believed to be the removal mechanisms of arsenic by these amorphous products (Goldberg and Johnston, 2000: 204).

Consequently, arsenic in water transfers to amorphous ferric hydroxide, and therefore the by-product of this arsenic removal process is arsenic containing sludge. The amount of arsenic in the sludge may vary widely, depending on initial arsenic concentration, finished water target, and background coagulant demand (Frey et al., n.d.). Owing to the fact that initial arsenic concentrations and finished water targets in the contaminated areas may vary from place to place, background coagulant demands to remove arsenic in each contaminated site undoubtedly vary widely as well. Consequently, some relevant properties of arsenic containing sludge from the coagulation process in one region may be greatly different from that in another region. As the sludge can be either non-hazardous or hazardous waste, the most proper, cost-effective management strategy for this kind of waste may differ from case to case. One of the global concerns is the fact that hazardous waste can present a threat to the environment and public health if improperly managed. For example, if the hazardous sludge is managed as non-hazardous waste such as dumping it together with municipal solid waste in sanitary landfills, large amount of arsenic in the sludge may leach out and ultimately contaminate the groundwater. For this reason, classifying whether the sludge as a result of removing arsenic from an initial arsenic

concentration to one final target is hazardous or not is very important. However, nowadays, the tool to do this task is unavailable.

Placing a special concern on safe disposal and long-term stability of hazardous waste, each country established the regulatory limit for maximum allowable arsenic concentration leaching out of the residual. The worst case of leaching is generally simulated by a laboratory extraction procedure such as Toxicity Characteristic Leaching Procedure (TCLP) used in the United States and the leaching procedure under the Notification of the Ministry of Industry No. 6 used in Thailand (LP-NO.6). The important link between these regulatory limits and a drinking water standard, known as maximum contaminant level (MCL), is that the allowable concentration of arsenic in leachate of the residual classified as non-hazardous waste must not exceed 100 times the MCL of arsenic in drinking water standard (Amy et al., 2000: 192). For example, like the United States' regulatory limit before October 31, 2001, Thailand's regulatory limit of maximum arsenic concentration in drink water is fifty  $\mu\text{g/L}$ , so the maximum allowable concentration of arsenic in leachate is five  $\text{mg/L}$ . On the other hand, the present regulatory limit of arsenic in drinking water in the United States is ten  $\mu\text{g/L}$ , so the maximum allowable concentration of arsenic in leachate should be one  $\text{mg/L}$ .

To be in line with health evidence, the World Health Organization (WHO) guideline for arsenic in drinking water was provisionally reduced in 1993 from fifty  $\mu\text{g/L}$  to ten  $\mu\text{g/L}$  (Smith et al., 2002: 2145). Consequently, some countries such as the United States, Japan, and Australian have reduced their MCL of arsenic in drinking water; while many other countries, especially all affected developing countries, still operate at the present fifty  $\mu\text{g/L}$  standard (Yamamura, n.d.: 12). According to the relationship between residual management and the MCL of arsenic in drinking water described in the previous paragraph, it is possible that those countries having lowered or planning to lower their MCL of arsenic in the future may face the problem of residual management. Reducing their MCL can increase the possibility of the sludge to become hazardous by the regulatory definition due to not only lessening the regulatory limit but also raising the amount of arsenic in sludge.

From a management perspective, if the sludge turns to be hazardous waste, it may present the responsible parties with economic difficulty due to the fact that the cost of hazardous waste disposal is relatively high. Moreover, incineration of arsenic containing waste is limited because of the volatilization of arsenic containing compounds (Leist, Casey, and Caridi, 2000: 126). For this reason, to reach a compromise between reasonable operation costs of waste management and sufficient long-term stability of the waste, this study focuses on the solidification/ stabilization (S/S) technique because not only is the solidified waste form considered stable and safe for public and environmental health but also its physical property is suitable for some applications in the field of civil engineering. As an added value, the reutilization of solidified-waste products may help to relieve the economic impact of sludge disposal.

From a research and development standpoint, although several kinds of arsenic containing wastes, ranging from simple arsenic salt (Bothe and Brown, 1999a, 1999b; Leist and Caridi, 2003; Mollah, Lu, and Cocke, 1998) to arsenic waste that originates from a metallurgical process (Dutr e and Vandecasteele, 1995a, 1995b, 1996, 1998; Vandecasteele et al., 2002), have been subjected to S/S to study its performance, limited research has been conducted on the S/S treatment of iron hydroxide sludge containing arsenic, which can be found in drinking water treatment residual and mine tailings (Jing, Korfiatis, and Meng, 2003). Moreover, no research concerning the utilization potential of the solidification/stabilization matrices of arsenic sludge has been conducted yet.

In conclusion, this study is not only the first attempt to build the tool for sludge classification but also the first attempt to evaluate utilization potential of the solidified/stabilized product of arsenic-iron hydroxide sludge. The experimental program was divided into six sub-parts to obtain a great deal of information for better understanding for both management and development standpoint.

## 1.2 Objectives

The main objectives of this study are to investigate the physical, chemical, and leaching characteristics of arsenic-iron hydroxide sludge and to examine properties and utilization potential of the solidified and stabilized matrices as a result of the solidification and stabilization process of the arsenic containing sludge with Portland Cement and lime. The specific objectives are as follows:

1. To determine the physical and chemical characteristics of dewatered and dried arsenic-iron hydroxide sludge before and after the leaching tests.
2. To investigate the leaching mechanism of arsenic from the the dewatered and the dried arsenic-iron hydroxide sludge subjected to the two leaching tests.
3. To examine and compare the arsenic leachability of the dewatered and the dried sludge subjected to the TCLP and LP-No.6.
4. To establish the relationship among the leachability of arsenic from the dewatered and the dried arsenic-iron hydroxide sludge, an initial arsenic concentration of the contaminated water, a finished water target.
5. To determine the compressive strength of the solidified/stabilized matrices with varying amount of sludge added.
6. To investigate the physical and chemical interferences in the strength of the solidified/stabilized matrices due to the addition of the sludge.

7. To examine and compare leachability of the solidified and stabilized arsenic-iron hydroxide sludge under TCLP and LP-No.6.
8. To examine the utilization potential of the solidified/stabilized sludge form as a construction material.
9. To examine the immobilization potential and the interaction between arsenic and each kind of hydration by-product in the cementitious environment.
10. To determine the compressive strength of the solidified/stabilized with matrices with varying water-to-binder ratios and lime-to-binder ratios at the curing ages of 3, 7, 14, and 28 days.
11. To characterize the physical and chemical interferences in strength of the solidified/stabilized matrices due to addition of sludge.
12. To examine the influence of water-to-binder ratios and lime-to-binder ratios on leachability of arsenic from the solidified/stabilized sludge.
13. To evaluate the three management strategies of arsenic-iron hydroxide sludge, which are disposal of the dewatered sludge, disposal of the dried sludge, and utilization of the solidified and stabilized waste form as a construction material.

### 1.3 Scopes of the Study

The research was conducted to examine the physical and chemical properties of arsenic-iron hydroxide sludge in the two conditions, dewatered and dried by heat, both before and after the leaching tests as well as their leachate characteristics together with their suitable management regarding potential environmental impact and economic consideration. Moreover, this research was conducted to evaluate the utilization potential of the solidified/ stabilized arsenic containing sludge concerning the suitability in application, potential environmental impact, and economic feasibility. The arsenic-iron hydroxide sludge used in this study was synthesized by simulating chemical reaction between arsenite ( $\text{As}^{3+}$ ) and ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ). The following scopes of the research were studied in each part.

#### Part I

1. The five recipes of the arsenic-iron hydroxide sludge, both dewatered and dried by heat, of which arsenic-to-iron ratios were 0.069, 0.101, 0.105, 0.132, and 0.153, respectively, were studied for their chemical composition, particle size distribution, surface phenomena, and microstructures both before and after the leaching tests.
2. The two standard regulatory methods to determine leaching metals for Thailand and the United States, an extraction test according to the Notification of the Ministry of Industrial No.6 (LP-No.6) and the Toxicity Characteristic Leaching Procedure (TCLP) test, were chosen to predict environmental impacts from leachate of the dewatered and dried sludge without solidification/stabilization.

## Part II

3. The batch experiments to simulate arsenic removal process by coagulation with ferric chloride were conducted with five initial arsenite concentration: 140, 480, 1,465, 4,370, and 12,790  $\mu\text{g/l}$  and seven ferric chloride-to-arsenite ratios: 0, 5, 10, 20, 40, 80, and 160, respectively.
4. The data from the previous step were analyzed and processed by SPSS, a statistical program, to build two empirical models predicting the leaching of the characteristics of the dewatered and dried sludge produced from different arsenic removal conditions.

## Part III

5. The solidification/stabilization recipes differing in amount and combination of the binding materials – between Portland Cement and lime - set by variation of water to binders ratio of 0.4 and 0.9 and lime-to-binder ratios of 0 and 0.4 were used in this part with the saturated surface dried sludge-to-binder ratios of 0.15, 0.25, 0.5, and 1, respectively. The dried sludge used in this part had arsenite-to-iron ratio of 0.153 mg/mg. The weight of cement to sand ratio of 1.00:2.75 according to ASTM C109-95 for 2x2x2-inch mortar was used in this part.
6. The physical and chemical properties of the solidified/ stabilized arsenic-iron hydroxide such as compressive strength, chemical and mineralogical compositions, and microstructures were studied.



7. The two standard regulatory methods to determine leaching metals for Thailand and the United States, an extraction test according to the Notification of the Ministry of Industrial No.6 (LP-No.6) and the Toxicity Characteristic Leaching Procedure (TCLP) test, were chosen to predict environmental impacts from leachate of the solidified and stabilized arsenic-iron hydroxide sludge.

#### Part IV

8. The solidification/stabilization recipes differing in amount and combination of the binding materials – between Portland Cement and lime- set by variation of water to binders ratio of 0.4, 0.6 , and 0.9, and lime-to-binder ratios of 0, 0.2, and 0.4 were used in this part with the saturated surface dried sludge-to-binder ratios of 0.25 and without addition of sand. The dried sludge used in this part had arsenite-to-iron ratio of 0.153 mg/mg .
9. The microstructures and interaction between arsenic from the sludge and hydration by-products of cement and lime were studied.

#### Part V

10. The same solidification/stabilization recipes in Part IV but with addition of sand according to ASTM C109-95 were used in this part to examine the influence of water-to-binder and lime-to-binder ratios on UCS and leachability of arsenic.
11. The physical and chemical properties of the solidified/ stabilized sludge such as compressive strength as well as chemical and mineralogical compositions were also studied.

12. The two standard regulatory methods to determine leaching of metals for Thailand and the United States, an extraction test according to the Notification of the Ministry of Industrial No.6 (LP-No.6) and the Toxicity Characteristic Leaching Procedure (TCLP) test, were chosen to predict environmental impacts from leachate of these solidified and stabilized arsenic-iron hydroxide recipes.

#### Part VI

13. The spreadsheet to evaluate three management strategies of arsenic-iron hydroxide sludge, which are disposal of the dewatered sludge, disposal of the dried sludge, and utilization of the solidified and stabilized waste form as a construction material, in term of the economic consideration and environmental impacts from leachate was created.