CHAPTER 2

LITERATURE REVIEW

2.1 Some Historical, Chemical, and Physical Aspects of Arsenic

Arsenic, which has been called the "King of Poisons" since the time of the Roman Empire (MacRae, n.d.), has probably influenced human history more than any other element or toxic compound (Nriagu, 2002: 1). This fatal toxic began its long association with human culture by poisoning the god, Hephaestus, who first endeavored to find some beneficial use for it. In addition, it was a popular way to get rid of unwanted relatives or rivals. The death of Napoleon Bonaparte, French emperor from 1804 – 1814, is one of the most infamous cases where it is believed he was murdered by arsenic poisoning. The use of arsenic to knock off inconvenient people was finally slowed down by advances in chemistry and forensic science. Once a test was developed to measure arsenic in tissue or body fluids in 1836, it was possible to prove the cause of death, making it much harder to get away with the crime (MacRae, n.d.).

Chemically, arsenic is classified as a metalloid element, identified by the symbol **As**. Some of its physical and chemical properties are summarized in Table 2.1. Arsenic may occur as a semi metallic element (As^{0}), arsenate (As^{5+}), arsenite (As^{3+}), or arsine (As^{3-}). Owning to the fact that arsenic has several oxidation states, the chemistry of arsenic is undoubtedly complex; witness the fact that, there are many different compounds of both inorganic and organic arsenic as shown in Table 2.2.

Despite the fact that arsenic can form many different compounds, the two most important forms of arsenic existing in groundwater are arsenate, As(V), and arsenite, As (III). Figure 2.1 illustrates the important difference in molecular structure between arsenate and arsenite. The double bond oxygen in the arsenate molecule influences its ability to become ionized through the loss of hydrogen ions, the process is termed *dissociation*. A negative charge develops on the molecule when dissociation occurs. The double bond oxygen increases the capacity to delocalize that charge, easing the loss of hydrogen ions. The propensity for ionization is expressed by pK_a the constant of dissociation (which is a negative log, a smaller number shows a greater degree of dissociation).For arsenate and arsenite pK_a values are as follows (Vance. 2001):

Arsenate-H_3AsO_4	pK1=2.19	pK2=6.94	pK3=11.5
Arsenite- H_3AsO_3	pK1=9.20	pK2=14.22(a)	pK3=19.22(a)

(a)These values are extrapolated from the strength of oxygen acid rules (Pauling,1970 cited in Vance, 2001).

Table 2.1 Physical and chemical properties of arsenic (Budavari et al., 1989 cited in USEPA. 2000:6)

CAS Number	7440-38-2
Atomic Number	33
Atomic Weight	74.92
Melting Point at 28 atm	817 °C
Boiling Point	613 °C
Critical Temperature	1,400 °C
Heat of Vaporization	11.2 kcal/g-atom
Critical Pressure	22.3 MPa
Density (at 14 °C)	5.727 g/cm3
Most Stable Isotope	75As
Covalent Radius	1.19 angstroms
Atomic Radius	1.39 angstroms
Ionic Radius	2.22 angstroms
Vapor Pressure	1 mm (375 °C)
	10 mm (437 °C)
	100 mm (518 °C)

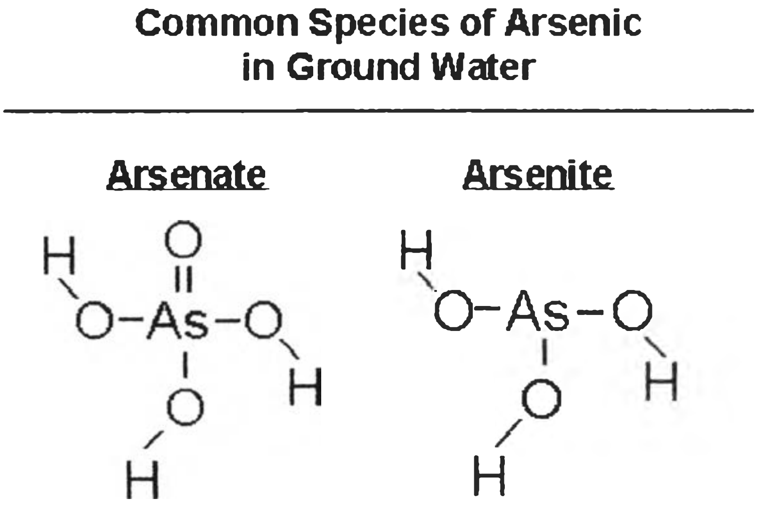

Figure 2.1 Molecular structure of arsenate and arsenite (Vance, 2001)

The chemical character of arsenic is dominated by the fact that it is labile, readily changing oxidation state or chemical form through chemical or biological reactions that are common in the environment. Therefore, rather than solubility equilibrium controlling the mobility of arsenic, it is usually controlled by redox conditions, pH, biological activity, and adsorption/desorption reactions. For example, Figure 2.2 not only illustrates the pH at which these ionization steps occur is significantly different between arsenate and arsenite, but also also shows the control of redox potential (Eh) on the arsenate/arsenite transition. This Eh/pH relationship is a key to understand arsenic mobility in groundwater and the effectiveness of arsenic water treatment systems (Vance, 2001).

Besides geochemical factors, microbial agents can influence the oxidation state of arsenic in water, and can mediate the methylation of inorganic arsenic to form organic arsenic compounds. Microorganisms can oxidize arsenite to arsenate, reduce arsenate to arsenite, or reduce arsenate to arsine (Cullen and Reimer, 1989 cited in USEPA, 2000: 8). Bacterial action also oxidizes minerals such as orpiment (As_2S_3), arsenopyrite (FeAsS), and enargite (Cu_3AsS4) to release arsenate. Under aerobic conditions, the common aquatic bacterium Pseudomonas fluorescens reduces arsenate to arsenite. In a river in New Zealand, investigators found the predominant oxidation state of arsenic varied seasonally, because of (at least in part) the bacterium Anabaena oscillaroides which reduces arsenate to arsenite. Arsenite was found to predominate in spring and summer months, while arsenate was prevalent at other times of the year (USEPA, 2000: 8).

Table 2.2 Some important arsenic compounds in the environment (USEPA, 2000)

Name	Synonyms	Formula
Inorganic arsenic		
- Arsenic	Metallic arsenic	As_4
- Arsenic (III) oxide	Arsenic trioxide Arsenous oxide White arsenic	As_2O_3 (or As_4O_6)
- Arsenous acid	-	H_3AsO_3
- Arsenenous acid.arsenites, salts of arsenous acid	Arsenious acid	$HAsO_2$, $H_2AsO_3^-$, $HAsO_3^{-2}$ or AsO_3^{-3}
- Arsenic (III) chloride	Arsenic trichloride Arsenous trichloride	$AsCl_3$
- Arsenic (III) sulfide	Arsenic trisulfide Orpiment, Auripigment	As_2S_3
- Arsenic (V) oxide	Arsenic pentoxide	As_2O_5
- Arsenic acid	Orthoarsenic acid	H_3AsO_4
- Arsenenic acid arsenates, salts of arsenic acid (ortho)	Metaarsenic acid	$HAsO_3$, $H_2AsO_4^-$, $HAsO_4^{-2}$ or AsO_4^{-3}
Organic arsenic		
- Methylarsonic acid	Methanearsonic	$CH_3AsO(OH)_2$
- Dimethylarsinic acid	Cacodylic acid	$(CH_3)_2AsO(OH)$
- Trimethylarsine oxide	-	$(CH_3)_3AsO$
- Methylarsine	-	CH_3AsH_2
- Dimethylarsine	-	$(CH_3)_2AsH$
- Trimethylarsine		$(CH_3)_3As$

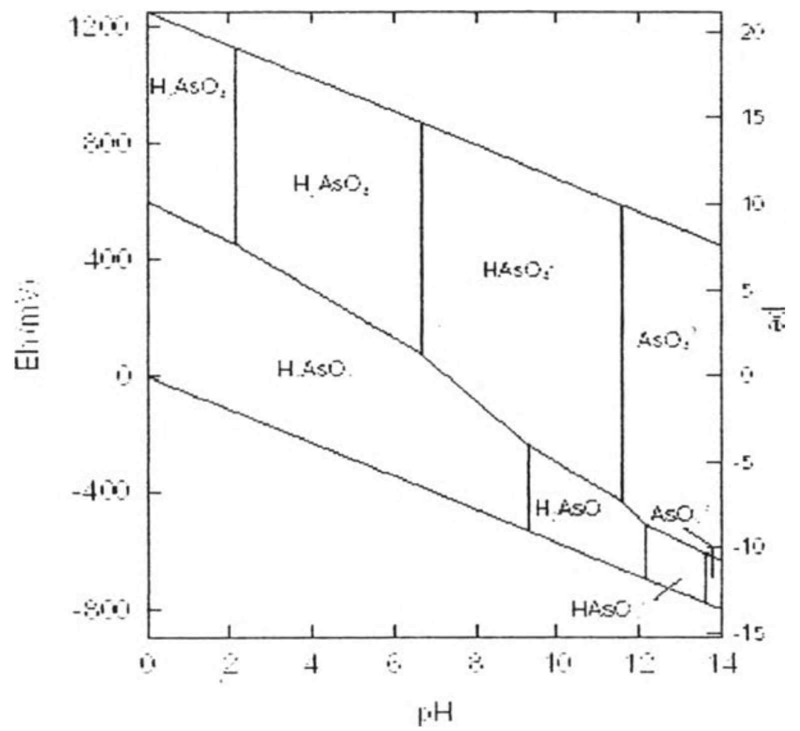

Figure 2.2 Eh-pH diagram of aqueous arsenic species in the system As–O_2–H_2O at 25°C 1 bar total pressure (Smedley and Kinniburgh, n.d.: 4)

2.2 Source of Arsenic

In fact, there are a great variety of sources of arsenic. However, these sources can be categorized into two broad categories: natural sources and anthropogenic sources.

Although arsenic is the twentieth most abundant element in the earth's crust (NAS, 1977 cited in USEPA, 2000: 14), there are more than 200 kinds of major arsenic minerals, available in the environment. Some of them are listed in Table 2.3. The greatest concentrations of these minerals occur in mineralized areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. Of all these minerals, the most abundant arsenic mineral is arsenopyrite, FeAsS (Smedley and Kinniburgh, n.d.: 17). However, these minerals are relatively rare in the natural environment (Smedley and Kinniburgh, n.d.: 17). In addition, it should be noted that most of these minerals are only formed under high temperature conditions in the earth's crust such as hydrothermal veins and hot springs. Furthermore, according to a number of studies summarized in Tables 2.4 and 2.5 by Smedley and Kinniburgh (n.d.: 16-19), it is found that arsenic is also often present in varying concentrations in other common rock-forming minerals as well as in rock, sediment, and soil. However, it should be recognized that arsenic concentrations in soils and sediments depend not only on the parent materials from which they were derived but also on anthropogenic sources in that region.

In addition to the minerals, rocks, and soils discussed above, volcanic activity surprisingly releases large amounts of arsenic into the environment every year. It is estimated that about one third of the total annual amount of arsenic released into the atmosphere is from volcanoes (MacRae, n.d.). Some studies regarding the estimated amount of arsenic released into the atmosphere by natural activities such as, volcanic activity and forest and grass fires are summarized in Table 2.6. Similarly, in the oceans, some animals and plants produce and accumulate organic arsenic compounds. Although these can become quite concentrated in an organism, they are generally of low toxicity (MacRae, n.d.).

Like natural sources, anthropogenic sources release arsenic into terrestrial and aquatic environments as well as into the atmosphere owning to the fact that arsenic is used in a number of specific economic sectors as summarized in Table 2.7. Of these anthropogenic sources, it is estimated that arsenic used in wood preservation is responsible for about 70% of global arsenic use, and may be a large source of arsenic released into the environment. Similarly, agricultural uses account for about 22% of global arsenic use. Unlike wood preservation and agricultural activity, none of arsenic is used in the mining/smelting of copper, gold, lead or zinc ores, but a great deal of this fatal poison is a by-product of these two industrial activities since most of these ores are relatively rich in arsenic. While some of the arsenic is purified for other uses, some remains in the waste rock (MacRae, n.d.). Arsenic in waste rock is not a problem on its own, but bacteria can produce acid and start wearing away the rock to be released into the water. Similarly, smelting, which is metal purification at very high temperatures, can also release a large amount of arsenic into the atmosphere.

This and burning of fuels that contain arsenic are the largest industrial contributors of arsenic into air, water and soil (MacRae, n.d.).

Table 2.3 Some of major arsenic minerals occurring in nature (Smedley and Kinniburgh, n.d.: 15)

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	$NiAs$	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	$CoAsS$	High-temperature deposits, metamorphic rocks
Arsenopyrite	$FeAsS$	The most abundant As mineral, dominantly mineral veins
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	Hydrothermal veins
Enargite	Cu_3AsS_4	Hydrothermal veins
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As_2O_3	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	$FeAsO_4 \cdot 2H_2O$	Secondary mineral
Annabergite	$(Ni,Co)_3(AsO_4)_2 \cdot 8H_2O$	Secondary mineral
Hoernesite	$Mg_3(AsO_4)_2 \cdot 8H_2O$	Secondary mineral, smelter wastes
Haematolite	$(Mn,Mg)_4Al(AsO_4)(OH)_8$	
Conichalcite	$CaCu(AsO_4)(OH)$	Secondary mineral
Pharmacosiderite	$Fe_3(AsO_4)_2(OH)_3 \cdot 5H_2O$	Oxidation product of arsenopyrite and other As minerals

Table 2.4 Typical arsenic concentration in common rock-forming minerals (Smedley and Kinniburgh, n.d.: 16-17)

Mineral	As concentration range (mg kg–1)	References
Sulfide Minerals:		
Pyrite	100–77,000	Baur and Onishi (1969); Arehart et al. (1993); Fleet and Mumin (1997)
Pyrrhotite	5–100	Boyle and Jonasson (1973); Dudas (1984); Fleet and Mumin (1997)
Marcasite	20–126,000	
Galena	5–10,000	
Sphalerite	5–17,000	
Chalcopyrite	10–5000	
Oxide minerals:		
Haematite	up to 160	
Fe oxide (undifferentiated)	up to 2000	
Fe(III) oxyhydroxide	up to 76,000	Pichler et al. (1999)
Magnetite	2.7–41	
Ilmenite	<1	
Silicate minerals:		
Quartz	0.4–1.3	
Feldspar	<0.1–2.1	
Biotite	1.4	
Amphibole	1.1–2.3	
Olivine	0.08–0.17	
Pyroxene	0.05–0.8	
Carbonates minerals:		
Calcite	1–8	
Dolomite	<3	

Table 2.4 (Cont.)

Mineral	As concentration range (mg kg–1)	References
Sulphate minerals:		
Gypsum/anhydrite	<1–6	
Barite	<1–12	
Jarosite	34–1000	
Other minerals:		
Apatite	<1–1000	
Halite	<3–30	Stewart (1963)

Table 2.5 Typical arsenic concentrations in rocks, sediments, soils and other surficial deposits (Smedley and Kinniburgh, n.d.: 18-19)

Rock/sediment type	As concentration average and/or range (mg kg–1)	No of analyses	Reference
Igneous rocks:			
Ultrabasic rocks (peridotite, dunite, kimberlite etc)	1.5 (0.03–15.8)	40	Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Ure and Berrow (1982); Riedel and Eikmann (1986)
Basic rocks (basalt)	2.3 (0.18–113)	78	
Basic rocks (gabbro, dolerite)	1.5 (0.06–28)	112	
Intermediate (andesite, trachyte, latite)	2.7 (0.5–5.8)	30	
Intermediate (diorite, granodiorite, syenite)	1.0 (0.09–13.4)	39	
Acidic rocks (rhyolite)	4.3 (3.2–5.4)	2	
Acidic rocks (granite, aplite)	1.3 (0.2–15)	116	
Acidic rocks (pitchstone)	1.7 (0.5–3.3)		
Volcanic glasses	5.9 (2.2–12.2)	12	

Table 2.5 (Cont.)

Rock/sediment type	As concentration average and/or range (mg kg–1)	No of analyses	Reference
Metamorphic rocks:			
Quartzite	5.5 (2.2–7.6)	4	
Hornfels	5.5 (0.7–11)	2	
Phyllite/slate	18 (0.5–143)	75	
Schist/gneiss	1.1 (<0.1–18.5)	16	
Amphibolite and greenstone	6.3 (0.4–45)	45	
Sedimentary rocks:			Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Cronan (1972); Riedel and Eikmann (1986); Welch et al. (1988); Belkin et al. (2000)
Marine shale/mudstone	3–15 (up to 490)		
Shale (Mid-Atlantic Ridge)	174 (48–361)		
Non-marine shale/mudstone	3.0–12		
Sandstone	4.1 (0.6–120)	15	
Limestone/dolomite	2.6 (0.1–20.1)	40	
Phosphorite	21 (0.4–188)	205	
Iron formations and Fe-rich sediment	1–2900	45	
Evaporites (gypsum/anhydrite)	3.5 (0.1–10)	5	
Coals	0.3–35,000		

Table 2.5 (Cont.)

Rock/sediment type	As concentration average and/or range (mg kg–1)	No of analyses	Reference
Unconsolidated sediments:			
Various	3 (0.6–50)		Azcue and Nriagu (1995)
Alluvial sand (Bangladesh)	2.9 (1.0–6.2)	13	BGS and DPHE (2001)
Alluvial mud/clay (Bangladesh)	6.5 (2.7–14.7)	23	BGS and DPHE (2001)
River bed sediments (Bangladesh)	1.2–5.9		Datta and Subramanian (1997)
Lake sediments, Lake Superior	2.0 (0.5–8.0)		Allan and Ball (1990)
Lake sediments, British Colombia	5.5 (0.9–44)	119	Cook et al. (1995)
Loess silts, Argentina	5.4–18		Legeleux et al. (1994)
Continental margin sediments (argillaceous, some anoxic)	2.3–8.2		Boyle and Jonasson (1973) Gustafsson and Tin (1994)

Table 2.6 Estimated amount of arsenic released to the atmosphere by natural activities such as volcanic activity and forest and grass fires (USEPA, 2000: 14)

Estimated annual natural releases (metric tons)	Reference
44,100	Tamaki and Frankenburger, 1992
1,100 - 23,500	Pacyna et al., 1995
2,800 - 8,000	Loebenstein, 1994

Table 2.7 Summary of current and past uses of arsenic (USEPA, 2000: 15)

Sector	Uses
Lumber	Wood preservatives
Agriculture	Pesticides, insecticides, defoliants, debarking agents, soil sterilant
Livestock	Feed additives, disease preventatives, animal dips, algaecides
Medicine	Antisyphilitic drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dye and soaps, ceramics, pharmaceutical substances, alloys (automotive solder and radiators), battery plates, solar cells, optoelectronic devices, semiconductor applications, light emitting diodes in digital watches

2.3 World Distribution of Groundwater Arsenic Problems

In some conditions such as, a strongly oxidising or reducing environment, high alkalinity, or arid conditions, arsenic in the natural sources discussed above may leach out and contaminate groundwater. In the same way, if the waste from mining activities is not managed properly, arsenic may leach out and contaminate groundwater as well. For this reason, a number of large aquifers in various parts of the world have been identified with arsenic contamination problems as shown in Figure 2.3. Some of the documented cases are summarized in Table 2.9. Making a comparison between the concentration of arsenic in contaminated groundwater in the regions shown below and the allowable concentration of arsenic in the drinking water of each region in Table 2.8 may accentuate how serious the problem is.

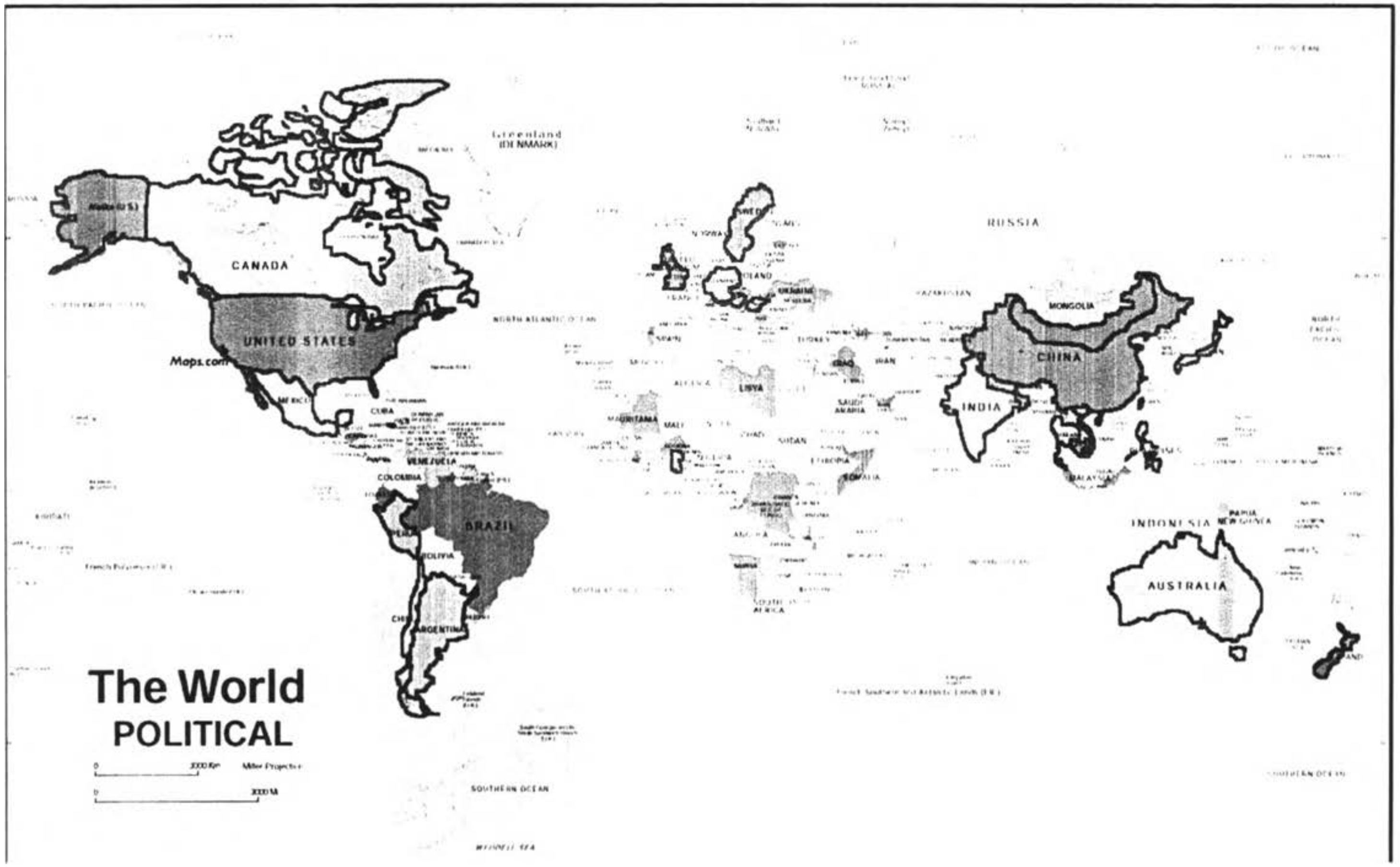

Figure 2.3 Map of documented world arsenic problem (Smedley and Kinniburgh, n.d.: 30)

Table 2.8 The currently accepted national standards for arsenic in drinking water (Yamamura, n.d.: 12)

Countries/ Organizations	Standard (the year standard was established)
Australia	0.007 mg/L (1996)
Jordan	0.01 mg/L (1991)
Laos	0.01 mg/L (1999)
Mongolia	0.01 mg/L (1998)
Namibia	0.01 mg/L
Syria	0.01 mg/L (1994)
European Union	0.01 mg/L (1998)
Japan	0.01 mg/L (1993)
the United States	0.01 mg/L(2001)
World Health Organization (WHO)	0.01 mg/L (1993)
Canada	0.025 mg/l (1999)
Thailand	0.05 mg/L
Bahrain	0.05 mg/L
Bangladesh	0.05 mg/L
Bolivia	0.05 mg/L (1997)
China	0.05 mg/L
Egypt	0.05 mg/L (1995)
India	0.05 mg/L
Indonesia	0.05 mg/L (1990)
Oman	0.05 mg/L
Philippines	0.05 mg/L (1978)
Saudi Arabia	0.05 mg/L
Sri Lanka	0.05 mg/L (1983)
Viet Nam	0.05 mg/L (1989)
Zimbabwe	0.05 mg/L

Table 2.9 Summary of documented cases of naturally-occurring As problems in world groundwaters (Smedley and Kinniburgh, n.d.: 33-34)

Country/Region	Area (km^2)	Population exposed	Concentration ranges (µg l–1)	Aquifer type	Groundwater conditions	Reference
Bangladesh	150,000	ca. 3x10^7	<0.5 to 2500	Holocene alluvial/ deltaic sediments. Abundance of solid organic matter	Strongly reducing, neutral pH, high alkalinity,slow groundwater flow rates	DPHE/BGS/MML (1999)
West Bengal	23,000	6x10^6	<10 to 3200	As Bangladesh	As Bangladesh	CGWB (1999); POA(1999)
China:		5.6x10^6				Sun et al. (2000)
Taiwan	4000	10^5 (formerly)	10 to 1820	Sediments, including black shale	Strongly reducing, artesian conditions, some groundwaters contain humic acid	Kuo (1968), Tseng et al.(1968)
Inner Mongolia (Huhhot Basin (HB), Bayingao, Hexi, Ba Meng, Tumet Plain)	4300 (HB) 30,000 total	ca. 10^5 in HB	<1 to 2400	Holocene alluvial and lacustrine sediments	Strongly reducing conditions, neutral pH,high alkalinity. Deep groundwaters often artesian, some have high concentrations of humic acid	Luo et al. (1997), Zhai et (1998), Ma et al. (1999), Sun et al. (1999), Smedley et al. (2000b, 2001b)

Table 2.9 (Cont.)

Country/ Region	Area (km^2)	Population exposed	Concentration ranges (μg l–1)	Aquifer type	Groundwater conditions	Reference
Xinjiang (Tianshan Plain)	38,000	(500 diagnosed)	40 to 750	Holocene alluvial plain	Reducing, deep wells (up to 660 m) are artesian	Wang and Huang (1994)
Hungary, Romania (Danube Basin)	110,000	29,000	<2 to 17^{6}	Quaternary alluvial plain	Reducing groundwater, some artesian. Some high in humic acid	Varsányi et al. (1991); Gurzau (2000)
Argentina (Chaco-Pampean Plain	10^{6}	$2x10^{6}$	<1 to 5300 (7800 in some porewaters)	Holocene and earlier loess with rhyolitic volcanic ash	Oxidising, neutral to high pH, high alkalinity. Groundwaters often saline. As(V), accompanied by high B, V, Mo, U. Also high As concentrations in some river waters	Nicolli et al., 1989; Nicolli and Merino (2001); Smedley et al. (2001a); Sancha and Castro (2000)
Northern Chile (Antofagasta)	125,000	500,000	100 to 1000	?Quaternary volcanogenic sediment	Generally oxidising. Arid conditions, high salinity, high B. Also high-As river waters	Cáceres et al. (1992), Karcher et al. (1999); Sancha and Castro (2000)

Table 2.9 (Cont.)

Country/Region	Area (km^2)	Population exposed*	Concentration ranges (µg l–1)	Aquifer type	Groundwater conditions	Reference
South-west USA:		$3.5x10^5$ (tot)				Smith et al. (1992)
Basin & Range, Arizona	200,000		up to 1300	Alluvial basins, some evaporites	Oxidising, high pH. As (mainly As (V)) correlates positively with Mo, Se, V, F	Robertson (1989)
Tulare Basin, San Joaquin Valley, California	5000		<1 to 2600	Holocene and older basinfill sediments	Internally-drained basin. Mixed redox conditions. Proportion of As(III) increases with well depth. High salinity in some shallow groundwaters. High Se, U, B, Mo	Fujii and Swain (1995)
Southern Carson Desert, Nevada	1300		up to 2600	Holocene mixed aeolian, alluvial, lacustrine sediments, some thin volcanic ash bands	Largely reducing, some high pH. Some with high salinity due to evaporation. Associated high U, P, Mn, DOC (Fe to a lesser extent) Some saline groundwaters, with high U	Welch and Lico (1998)
Mexico (Lagunera)	32,000	$4x10^5$	8 to 620	Volcanic sediments	Oxidising, neutral to high pH, As mainly as As(V)	Del Razo et al. (1990)

Table 2.9 (Conts)

Country/ Region	Area (km^2)	Population exposed*	Concentration Ranges (μg l–1)	Aquifer type	Groundwater conditions	Reference
Some problem areas related to mining activity and mineralized areas:						
Thailand (RonPhibun)	100	15,000	1 to 5000	Dredged Quaternary alluvium (some problems in limestone), tailings	Oxidation of disseminated arsenopyrite due to former tin mining, subsequent groundwater rebound	Williams et al. (1996), Williams (1997)
Fairbanks, Alaska, USA			up to 10,000	Schist, alluvium, mine tailings	Gold mining, arsenopyite, possibly scorodite	Wilson and Hawkins (1978); Welch et al. (1988) and Wai (1990)
Moira Lake, Ontario, Canada	100		50–3000	Mine tailings	Ore mining (gold, haematite, magnetite, lead, cobalt)	
Coeur d'Alene, Idaho, USA			up to 1400	Valley-fill deposits	River water and groundwater affected by leadzinc-silver mining	

2.4 Arsenic and Human Health

By making a comparison between arsenic concentration in the contaminated groundwater reported in Table 2.9 and the current accepted national standards for arsenic in drinking water shown in Table 2.8, it is clearly seen how seriously the contamination levels in such contaminated water violate the acceptable levels regulated by each country. To emphasize the hazard of drinking arsenic contaminated water, Table 2.10 shows lifetime risks of dying of cancer from arsenic in water. It should be noted that although arsenic concentration in drinking water is as low as those required by the current accepted national standards for arsenic in drinking water shown in Table 2.8, which are 50 and 10 μg/L in most of the countries in the world, the lifetime risks of dying of cancer from arsenic in water is still several times higher than the acceptable risk. Now let us roughly extrapolate the lifetime risk of dying of cancer from drinking arsenic contaminated water in some contaminated regions reported in Table 2.9. This may give a clearer picture of the serious health problems that may occur in the consumers of such high level arsenic-contaminated water.

Table 2.10 Lifetime risks of dying of cancer from arsenic in water (Natural Research Defense Council, n.d.)

Arsenic Level in Water (in parts per billion, or ppb)	Approximate Total Cancer Risk (assuming 2 liters consumed/day)
0.5 ppb	1 in 10,000 (highest cancer risk EPA usually allows in water)
1 ppb	1 in 5,000
3 ppb	1 in 1,667
4 ppb	1 in 1,250
5 ppb	1 in 1,000
10 ppb	1 in 500
20 ppb	1 in 250
25 ppb	1 in 200
50 ppb	1 in 100

In reality, there are several studies regarding health problems from arsenic in drinking water. Generally, such health problems can be categorized into two groups: cancer effects and non-cancer effects.

Published in 1968 in the *Journal of the National Cancer Institute*, the Tseng's study indicated a correlation in the oral intake of arsenic and the prevalence of nonmelanoma skin cancers in a rural southwestern part of Taiwan. It was also found that blackfoot disease—a severe disease of blood vessels—was relatively common in that region, where there was an association of this disease and a combination of excessive arsenic intakes and nutritional deficiencies. According to the researchers, the arsenic concentrations in water from most of the wells in that area ranged from 400–600 µg/L. The arsenic concentration of the water in some of the wells, however, was more than 1,500 µg/L, while that of the water in other wells was only 10 µg/L. In the same way, the Tseng's study published in 1977 in *Environment Health Perspectives* found that cancer of various internal organs was the leading cause of death among patients in the study area who had either blackfoot disease or skin cancer (Brown, 2002: 10-12). Moreover, in the 1980s, Chen's study found that—for cancers of the colon, kidney, bladder, liver, lung, and skin— the incidence of death from cancer in the same area significantly exceeded that of Taiwan's population (Brown, 2002: 10-12)

For noncancer effects, chronic arsenic poisoning affects the skin, hair, and nails, and together such symptoms are among its more characteristic early manifestations. This syndrome includes unusual darkening of the skin and subsequent abnormal thickening of part of the skin at the palm and sole. These effects had occurred at a concentration of arsenic in water of at least 200 µg/L. There was no reliable evidence that the incidence of this syndrome in the U.S. was at all significant to the nation, or that arsenic at concentrations less than 200 µg/L was a causal factor for any skin condition . Moreover, findings from a Taiwanese study published in 2000 suggest a causal relationship of type 2 diabetes (non-insulin-dependent diabetes) and arsenic in water at concentrations of 700–930 µg/L. Findings from other recent Asian studies further those of previous studies linking noncancerous lung disorders such as bronchitis and arsenic in water at concentrations of 500–600 µg/L (Brown, 2002: 10).

2.5 Technologies for Arsenic Removal

As reported in the previous section, the serious health problems may occur in consumers of the arsenic-contaminated water. Therefore, the best way to protect the public in the contaminated areas from such adverse affects is to provide them with new sources of arsenic-free drinking water. However, in some areas, arsenic-contaminated water may be abundant while arsenic-free sources are scarce or may be polluted with other compounds. For this reason, in such areas, removing arsenic from the contaminated water may become the most efficient option, at least as a short-term measure. There are a number of technologies for arsenic removal available. Some of them are summarized in Table 2.11 together with their removal efficiency and some issues regarding the technologies.

Table 2.11 Summary of technologies for arsenic removal (Johnston, Heijnen and Wurzel, 2001: 54)

Technology	Removal Efficiency As (III)	Removal Efficiency As (V)	Institutional experience and issues
Coagulation with iron salts	++	+++	Well proven at central level, piloted at community and household levels. Phosphate and silicate may reduce arsenic removal rates. Generates arsenic rich sludge. Relatively inexpensive.
Coagulation with alum	-	+++	Proven at central level, piloted at household levels. Phosphate and silicate may reduce arsenic removal rates. Optimal over a relatively narrow pH range. Generates arsenic-rich sludge. Relatively inexpensive
Lime softening	+	+++	Proven effective in laboratories and at pilot scale. Efficiency of this chemical process should be largely independent of scale. Chiefly seen in central systems in conjunction with water softening. Disadvantages include extreme pH and a large volume of waste generated. Relatively inexpensive, but more expensive than coagulation with iron salts or alum because of larger doses required, and waste handling.

Table 2.11(Cont.)

Technology	Removal Efficiency		Institutional experience and issues
	As (III)	As (V)	
Ion exchange resins	-	+++	Pilot scale in central and household systems, mostly in industrialized countries. Interference from sulfate and TDS. High adsorption capacity, but long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive. Regeneration produces arsenic-rich brine.
Activated alumina	+/++	+++	Pilot scale in community and household systems, in industrialized and developing countries. Arsenite removal is poorly understood, but capacity is much less than for arsenate. Regeneration requires strong acid and base, and produces arsenic-rich waste. Long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pretreatment to prevent media clogging. Moderately expensive.
Membrane methods	-/+++	+++	Shown effective in laboratory studies in industrialized countries. Research needed on removal of arsenite. and efficiency at high recovery rates, especially with low-pressure membranes. Pretreatment usually required. Relatively expensive, especially if operated at high pressures.
Fe-Mn oxidation	?	+/++ /+++	Small-scale application in central systems, limited studies in community and household levels. More research needed on which hydrochemical conditions are conducive for good arsenic removal. Inexpensive.
Porous media sorbents (iron oxide coated sand, greensand, etc.)	+/ ++	++/ +++	Shown effective in laboratory studies in industrialized and developing countries. Need to be evaluated under different environmental conditions, and in field settings. Simple media are inexpensive, advanced media can be relatively expensive.
In situ immobilization	++	+++	Very limited experience. Long-term sustainability and other effects of chemical injection are not well documented. Major advantage is no arsenic-rich wastes are generated at the surface, major disadvantage is the possibility of aquifer clogging. Should be relatively inexpensive.

Notation: +++ Consistently > 90% removal, ++ Generally 60 – 90% removal

+ Generally 30 – 60% removal, - < 30% removal

? Insufficient information

As shown in Table 2.11, each technology has its own advantages and disadvantages. However, in the view of economic consideration, one of the economical technologies (Meng, Korfiatis, Jing et al, 2001: 2805) usually used in Asian countries is coagulation with ferric chloride because it is suitable for the poor villagers' situation in this region. In addition, as mentioned in Chapter 1, coagulation with ferric chloride can be used to deal with liquid residuals from other removal technologies such as the waste brine solution from the ion exchange process. The next topic will emphasize some studies regarding arsenic removal by coagulation with ferric chloride.

2.6 Arsenic Removal by Coagulation/Co-Precipitation with Ferric Chloride

The removal of arsenic by coagulation with metal salts has been around since at least 1934 (Buswell, 1943 cited in Johnston et al., 2001: 28). The most commonly used metal salts are ferric salts such as ferric chloride or ferric sulfate. Ferrous sulfate has also been used, but is less effective (Jekel, 1994; Hering et al., 1996; Hering et al., 1997 cited in Johnston et al., 2001: 28). Under optimal conditions in laboratories, it has been reported that the efficiency of arsenic removal by ferric chloride can be higher than 99% removal with residual arsenic concentrations of less than 1 µg/L (Cheng et al., 1994 cited in Johnston et al., 2001: 28). However, full-scale plants typically report a somewhat lower efficiency, from 50% to over 90% removal (Johnston et al., 2001: 28).

Added into water in the form of $FeCl_3$, the coagulant will dissociate according to the following equation (Sincero and Sincero, 2003: 561-562):

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^- \qquad (2\text{-}1)$$

To achieve the complete coagulation process, these ions must be rapidly dispersed thoughtout the reactor. As a result, the solid precipitate $Fe(OH)_{3(s)}$ and complexes are formed with the respective equilibrium constants at 25°C as follows (Sincero and Sincero, 2003: 561-562):

$$\mathrm{Fe(OH)_{3(s)}} \longleftrightarrow \mathrm{Fe^{3+} + 3OH^-} \qquad K_{sp,\ \mathrm{Fe(OH)3}} = 10^{-38} \qquad (2\text{-}2)$$

$$\mathrm{Fe(OH)_{3(s)}} \longleftrightarrow \mathrm{FeOH^{2+} + 2OH^-} \qquad K_{sp,\ \mathrm{FeOH\ c}} = 10^{-26.16} \qquad (2\text{-}3)$$

$$\mathrm{Fe(OH)_{3(s)}} \longleftrightarrow \mathrm{Fe(OH)_2^{+} + OH^-} \qquad K_{sp,\ \mathrm{Fe(OH)2\ c}} = 10^{-16.74} \qquad (2\text{-}4)$$

$$\mathrm{Fe(OH)_{3(s)} + OH^-} \longleftrightarrow \mathrm{Fe(OH)_4^-} \qquad K_{sp,\ \mathrm{Fe(OH)4\ c}} = 10^{-5} \qquad (2\text{-}5)$$

$$\mathrm{2Fe(OH)_{3(s)}} \longleftrightarrow \mathrm{Fe_2(OH)_2^{4+} + 4OH^-} \qquad K_{sp,\ \mathrm{Fe2(OH)2\ c}} = 10^{-50.8} \qquad (2\text{-}6)$$

The solids formed initially are amorphous with a high specific surface area. Dixit and Hering (2003: 4183) measured the specific surface area ($m^2\ g^{-1}$) of such hydrous ferric oxide by N_2BET coupled with an assumed value based on the study by Dzombak and Morel (1990 cited in Wilkie and Hering, 1996: 102) regarding the surface complexation modeling hydrous ferric oxide and reported that the specific surface area could be as high as 600 $m^2\ g^{-1}$. In contrast, Goldberg and Johnston, who investigated the specific surface area of the same type of iron oxide, concluded that its specific surface area was only 290 $m^2\ g^{-1}$. However, overtime, the amorphous products can be transformed to more crystalline forms such as, goethite and hematite of which the specific surface areas are only 54 and 90 $m^2\ g^{-1}$, respectively, according to the same study by Dixit and Hering (2003: 4183).

These amorphous products play a crucial role in the success of removing both arsenite and arsenate from the contaminated water. There are three possible mechanisms of arsenic removal, which can occur during coagulation: (1) precipitation: the formation of the insoluble compounds such as Fe(AsO4), (2) coprecipitation: the incorporation of soluble arsenic species into a growing metal hydroxide phase, and (3) adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide (Edwards, 1994 cited in Johnston et al., 2001: 29).

All of these three mechanisms can independently contribute towards arsenic removal. However, direct precipitation of arsenic has not been shown to play an important role (Johnston et al., 2001: 29). In contrast, coprecipitation and adsorption are both active arsenic removal mechanisms. Some studies suggest that coprecipitation is the more important removal mechanism, by showing that hydrous ferric oxide (HFO) formed in situ can remove approximately five times as much arsenic from contaminated water as preformed HFO (Edwards, 1994 cited in Johnston et al., 2001: 29). In contrast, others believed that adsorption is the dominant mechanism for arsenic removal, at least at high coagulant doses (Hering et al., 1996 cited in Johnston et al., 2001: 29). However, the details of adsorption and the surface complexation mechanism of arsenic removal will be discussed under the next topic. Focused here is the review of studies concerning arsenic removal by ferric chloride.

Between the two forms of inorganic arsenic, usually found in contaminated groundwater, arsenate is relatively easy to remove from water, since it bears a negative charge in natural waters above pH 2.2, and is electrostatically attracted to the positive charge on metal hydroxide surfaces (Johnston et al., 2001: 30). It was reported that the maximum arsenic adsorption capacities were in the range of 0.1 M As(V)/M Fe for fresh, performed hydrous ferric oxide. When the sorbents are formed in situ, capacities are much higher, in the vicinity of 0.5 to 0.6 M As(V)/M Fe. This difference accentuates the effects of coprecipitation. Preformed hydroxides only remove arsenic through adsorption, while in situ formation leads to coprecipitation as well (Edwards. 1994 cited in Johnston et al., 2001: 30).

In general, the removal efficiency of arsenate by coagulation is mainly controlled by the pH and coagulant dose, and is largely independent of the initial arsenic concentration. Theoretically, adsorption is favored at a pH below a sorbent's point of zero charge, since the positively charged surface can attract the arsenate anion. Laboratory tests have shown that arsenate adsorption onto HFO is optimal below a pH of 8. Adjustment of the pH will often result in greater improvements in efficiency, rather than increasing the coagulant dose (Sorg and Logsdon, 1978; Edwards. 1994; Hering et al., 1996 cited in Johnston et al., 2001: 30). Optimal dosing will depend on the specific water chemistry and the required removal efficiency, but typical doses range from 5 to 30 mg/L $FeCl_3$.

Another form of inorganic arsenic is arsenite which is uncharged in most natural waters (below pH 9.2). It is more difficult to remove in comparison to arsenate. since there is no electrostatic attraction to charged solids. The reported maximum surface density on preformed HFO is 0.4 M As/M Fe. It should be noticed that this value is significantly higher than the comparable density for arsenate. Edwards(1994 cited in Johnston et al., 2001: 30) offered several explanations for this anomalous phenomenon, and the most convincing explanation is that ferric solids oxidize the arsenite, forming arsenate and ferrous ions, which are subsequently reoxidized to ferric iron by oxygen, causing co-precipitation of arsenate. However, some researchers have reported arsenite removal with HFO to be somewhat less effective than arsenate removal.

Adsorption of arsenite onto HFO is relatively insensitive to the pH within most natural waters, and is theoretically favored from about a pH 5 to 8 (Sorg and Logsdon, 1978 cited in in Johnston et al., 2001: 32). However, one laboratory study examining arsenite removal found that it would be best at extreme pH values (4 and 9), and lowest at a pH of 6. The explanation for this unexpected result is due to the formation of smaller flocs at extreme pH values, which would have a larger surface area for adsorption. A second possible explanation is that even over the short period between formation and application, the surface of the HFO may undergo significant structural evolution, altering its sorption capacity (Hering et al., 1996 cited in Johnston et al., 2001: 32).

Practically, both arsenate and arsenite removal through coagulation will be either negatively or positively affected by the presence of other anions and cations. Some anions will lower removal efficiency, by competing with arsenic for sorption sites and lowering the surface charge. In contrast, some cations can increase the positive surface charge, and enhance arsenic adsorption. However, from those limited studies, there are three conclusions generally accepted: first, effects of co-occurring solutes will be most pronounced when adsorption density is nearing saturation; second, arsenite makes a weaker bond than arsenate with metal oxides, and is thus more likely to be displaced by competing anions; and, third, surface complexation chemistry is complex, particularly when multiple anions are present (Johnston et al., 2001: 34).

At a near-neutral pH, Manning and Goldberg (1996 cited in Johnston et al., 2001: 34) provided the theoretical affinity for anion sorption on metal oxides as follows:

$$PO_4 > SeO_3 > AsO_4 > AsO_3 >> SiO_4 > SO_2 > F > B(OH)_3$$

Phosphate is the anion considered most likely to compete with arsenic for adsorption sites, because of its strong affinity for metal oxides, and its similarity to the arsenate ion. Phosphate has been shown to mobilize arsenic in soils contaminated with lead pesticides (Davenport and Peryea, 1991; Peryea, 1991; Peryea and Creger, 1994; Peryea and Kammereck, 1997 cited in Johnston et al., 2001: 34).

Dissolved silicate is usually found in much higher concentrations than phosphate, and can interfere with removal of both arsenate and arsenite. Ghurye et al. (1999 cited in Johnston et al., 2001: 34) reported that in slightly basic waters (pH > 7) silicate levels above 15-30 mg Si/L reduced the arsenate removal efficiency. Meng et al.(2000 cited in Johnston et al., 2001: 34) reported that arsenite removal rates declined from 95% to under 50% with the addition of 18 mg/L Si. Thus, arsenate removal decreased by 13%. They suggested that the silicate reduced the arsenic removal efficiency in two ways: by competing directly for adsorption sites, and by changing the electrostatic properties of the HFO surface.

In the same way, elevated levels of sulfate and carbonate can slightly reduce arsenite removal rates, but have little effect on arsenate removal (Wilkie and Hering, 1996; Meng et al., 1999; Meng et al., 2000 cited in Johnston et al., 2001: 34).

Ammonium can also interfere with floc formation, and thus indirectly reduce arsenic removal rates (Csanady, 1999 cited in Johnston et al., 2001: 34). Natural organic matter also somewhat reduces the efficiency of arsenite removal at a pH of 4 through 9. In contrast, the presence of calcium and magnesium can enhance arsenic removal, by increasing the positive charge on the HFO surface. (Hering et al., 1996; Wilkie and Hering, 1996; Hering et al., 1997 cited in Johnston et al., 2001: 34).

2.7 Interfacial Chemistry of Arsenic Removal by Iron Hydroxide sludge

In this section, the arsenic removal mechanism by hydrous ferric oxide will be reviewed. This interfacial mechanism influences not only chemical property but also the stability of the sludge, and two crucial factors controlling applicability of available disposal alternatives which will also be discussed later in this chapter.

Nowadays, there are two models used to describe the arsenic removal mechanism by iron hydrous oxides: the constant capacitance model and the triple-layer model. In the constant capacitance model, it is assumed that all surface complexes are inner-sphere of which the surface complexation reactions for the functional group XOH (where X can be both Al and Fe) are defined below (Goldberg and Johnston, 2001: 207):

$$XOH_{(s)} + H^{+}_{(aq)} \longleftrightarrow XOH^{+}_{2(s)} \qquad (2\text{-}7)$$

$$XOH_{(s)} \longleftrightarrow XO^{-}_{(s)} + H^{+}_{(aq)} \qquad (2\text{-}8)$$

$$XOH_{(s)} + H_3AsO_{4(aq)} \longleftrightarrow XH_2AsO_4(s) + H_2O \qquad (2\text{-}9)$$

$$XOH_{(s)} + H_3AsO_{4(aq)} \longleftrightarrow XHAsO_4^{-}(s) + H^{+}_{(aq)} + H_2O \qquad (2\text{-}10)$$

$$XOH_{(s)} + H_3AsO_{4(aq)} \longleftrightarrow XAsO_4^{2-}(s) + 2H^{+}_{(aq)} + H_2O \qquad (2\text{-}11)$$

$$XOH_{(s)} + H_3AsO_{3(aq)} \longleftrightarrow XH_2AsO_3(s) + H_2O \qquad (2\text{-}12)$$

$$XOH_{(s)} + H_3AsO_{3(aq)} \longleftrightarrow XHAsO_3^{-}(s) + H^{+}_{(aq)} + H_2O \qquad (2\text{-}13)$$

The intrinsic equilibrium constants of such inner-sphere surface complexaion reactions are described in the following equations (Goldberg and Johnston, 2001: 207):

$$K_{+}(int) = \frac{[XOH_2^{+}]}{[XOH][H^{+}]} \exp(F\psi_o/RT) \qquad (2\text{-}14)$$

$$K_{-}(int) = \frac{[XO^{-}][H^{+}]}{[XOH]} \exp(-F\psi_o/RT) \qquad (2\text{-}15)$$

$$K^{1IS}_{As(v)}(int) = \frac{[XH_2AsO_4]}{[XOH]\,[H_3AsO_4]} \qquad (2\text{-}16)$$

$$K^{2IS}_{As(v)}(int) = \frac{[XHAsO_4^{-}]\,[H^{+}]}{[XOH]\,[H_3AsO_4]} \exp(-F\psi_o/RT) \qquad (2\text{-}17)$$

$$K^{3IS}_{As(v)}(int) = \underline{[XAsO_4^{-2}]\,[H^{+}]^2} \exp(-2F\psi_o/RT) \qquad (2\text{-}18)$$

$$[XOH]\,[H_3AsO_4]$$

$$K^{1is}_{As(III)}(int) = \frac{[XH_2AsO_3]}{[XOH]\,[H_3AsO_3]} \qquad (2\text{-}19)$$

$$K^{2is}_{As(III)}(int) = \frac{[XHAsO_3^-]\,[H^+]\exp(-F\psi_o/RT)}{[XOH]\,[H_3AsO_3]} \qquad (2\text{-}20)$$

When F is the Faraday constant (c mol_c^{-1}); ψ_o is the surface potential (V); *o* refers to the surface plane of adsorption; R is the molar gas constant (J mol^{-1} K^{-1}); and T is the absolute temperature (K).

On the other hand, the triple layer model allows ion adsorption as either inner-sphere as described in constant capacitance model or outer-sphere surface complexes. For this reason, besides the inner-sphere surface complexation reactions described above, the triple layer model considers outer-sphere surface complexation reactions for the background electrolyte as shown below (Goldberg and Johnston, 2001: 207):

$$XOH_{(s)} + Na^+_{(aq)} \longleftrightarrow XO^- - Na^+_{(s)} + H^+_{(aq)} \qquad (2\text{-}21)$$

$$XOH_{(s)} + H^+_{(aq)} + Cl^-_{(aq)} \longleftrightarrow XOH^+_2\text{-}Cl^-_{(s)} \qquad (2\text{-}22)$$

$$XOH_{(s)} + H_3AsO_{4(aq)} \longleftrightarrow XOH^+_2\text{-}H_2AsO^-_{4(s)} \qquad (2\text{-}23)$$

$$XOH_{(s)} + H_3AsO_{4(aq)} \longleftrightarrow XOH^+_2\text{-}HAsO^{2-}_{4(s)} + H^+_{(aq)} \qquad (2\text{-}24)$$

$$XOH_{(s)} + H_3AsO_{4(aq)} \longleftrightarrow XOH^+_2\text{-}AsO^{3-}_{4(s)} + 2H^+_{(aq)} \qquad (2\text{-}25)$$

$$XOH_{(s)} + H_3AsO_{3(aq)} \longleftrightarrow XOH^+_2\text{-}H_2AsO^-_{3(s)} \qquad (2\text{-}26)$$

$$XOH_{(s)} + H_3AsO_{3(aq)} \longleftrightarrow XOH^+_2\text{-}HAsO^{2-}_{3(s)} + H^+_{(aq)} \qquad (2\text{-}27)$$

$$2XOH_{(s)} + H_3AsO_{3(aq)} \longleftrightarrow (XOH^+_2)_2\text{-}HAsO^{2-}_{3(s)} \qquad (2\text{-}28)$$

$$2XOH_{(s)} + H_3AsO_{3(aq)} \longleftrightarrow (XOH^+_2)_2\text{-}AsO^{3-}_{3(s)} + H^+_{(aq)} \qquad (2\text{-}29)$$

The intrinsic equilibrium constants of these outer-sphere surface complexaion reactions are also described in the following equations (Goldberg and Johnston, 2001: 207):

$$K_{Na+}(int) = \frac{[XO^- - Na^+][H^+]\exp[F(\psi_{\beta}-\psi_{o}) / RT]}{[XOH][Na^+]} \qquad (2\text{-}30)$$

$$K_{Cl^-}(int) = \frac{[XSOH_2^+ - Cl^-]}{[XOH][H^+][Cl^-]} \exp[F(\psi_o - \psi_\beta) / RT] \quad (2\text{-}31)$$

$$K^{1os}_{As(V)}(int) = \frac{[XOH_2^+ - H_2AsO_4^-]}{[XOH][H_3AsO_4]} \exp[F(\psi_o - \psi_\beta) / RT] \quad (2\text{-}32)$$

$$K^{2os}_{As(V)}(int) = \frac{[XOH_2^+ - HAsO_4^{2-}][H^+]}{[XOH][H_2AsO_4]} \exp[F(\psi_o - 2\psi_\beta) / RT] \quad (2\text{-}33)$$

$$K^{3os}_{As(V)}(int) = \frac{[XOH_2^+ - AsO_4^{3-}][H^+]^2}{[XOH][H_2AsO_4]} \exp[F(\psi_o - 3\psi_\beta) / RT] \quad (2\text{-}34)$$

$$K^{1os}_{As(III)}(int) = \frac{[XOH_2^+ - H_2AsO_3^-]}{[XOH][H_3AsO_3]} \exp[F(\psi_o - \psi_\beta) / RT] \quad (2\text{-}35)$$

$$K^{2os}_{As(III)}(int) = \frac{[XOH_2^+ - HAsO_3^{2-}][H^+]}{[XOH][H_2AsO_3]} \exp[F(\psi_o - 2\psi_\beta) / RT] \quad (2\text{-}36)$$

$$K^{1os}_{As(III)}(int) = \frac{[(XOH_2^+) - HAsO_3^{2-}]}{[XOH]^2[H_3AsO_3]} \exp[F(2\psi_o - 2\psi_\beta) / RT] \quad (2\text{-}37)$$

$$K^{2os}_{As(III)}(int) = \frac{[(XOH_2^+) - AsO_3^{3-}][H^+]}{[XOH]^2[H_3AsO_3]} \exp[F(2\psi_o - 3\psi_\beta) / RT] \quad (2\text{-}38)$$

As mentioned above, the major difference between these two theories is that the constant capacitance model assumes that the surface complexation reactions for the surface functional group XOH (where X can be both Al and Fe) is only inner-sphere while the triple-layer model allows ion adsorption as either inner-sphere or outer-sphere surface complexation. Generally, inner-sphere surface complexes contain no water molecules between the adsorbing ion and the surface functional group while outer-sphere surface complexes contain one or more water molecules between the adsorbing ion and the surface functional group. It is important to distinguish between inner-sphere and outer-sphere surface complexes because in inner-sphere complexes the surface oxide ions act as σ-donor ligans, which increase the electron density of the coordinated metal ion. Therefore, arsenic ion bound inner-spherically is a different chemical entity than if it is bound outer-spherically or present in the diffuse part of the double layer. This distinction influences the leachability and stability of the sludge.

Consequently, according to recent studies, a variety of macroscopic and microscopic methods of inferring sorption behavior were used to classifies types of surface complexes of both arsenite and arsenate sorbing on several kinds of iron oxides.

One of the macroscopic experiments usually applied to infer the mode of the bonding of arsenic anions on a mineral surface is the investigating of the relationship among the shifting in the point of zero charge, electrophoretic, and ion concentration. Electrophoretic, EM, is a measure of the movement of charged particles in response to an applied electric field. Zero EM indicates the condition of zero surface charge called the point of zero charge, PZC. Shifts in PZC of minerals and reversals of EM with increasing ion concentration can be used as evidence of strong specific ion adsorption and inner-sphere surface complex formation. By this relationship, Goldberg and Johnston (2001: 209) concluded that both arsenite and arsenate were supposed to inner-spherically bind onto amorphous ferric oxide.

Another macroscopic method for inferring adsorption mechanism is the evaluation of the effect of changes in ionic strength on adsorption behavior. McBride (1997, cited in Goldberg and Johnston, 2001: 205) indicated that ions forming outer-sphere surface complexes showed a decreasing adsorption with an increasing solution ionic strength, while ions forming inner-sphere surface complexes showed little ionic strength dependence or showed an increasing adsorption with an increasing solution ionic strength. Hsia, Lo, Lin, and Lee (1994 cited in Goldberg and Johnston, 2001: 205) found that arsenic sorption on amorphous iron oxide had very little ionic dependence as a function of the solution pH which suggested an inner-sphere adsorption mechanism.

In the same way, several spectroscopic techniques such as, to extend the X-ray absorption fine structure (EXAFS), X-ray adsorption spectra (XAS), Fourier transform infrared (FI-IR), and Raman spectroscopy helpfully characterized the mode of bonding. Fendorf, Eick, Grossl, and Sparks (1997 cited in Goldberg and Johnston, 2001: 205) used EXAFS to examine the As(III)/As(V)-goethite system and revealed the three different inner-sphere As(V)- goethite complexations characterized by As-Fe distance of 0.285, 0.323, and 0.360 nm respectively. Similarly, Manning, Fendorf, and Goldberg (1998 cited in Goldberg and Johnston, 2001: 205) studied As(III)- goethite complex by means of XAS and revealed a binuclear inner-sphere complex identified by a well-resolved As-Fe distance of 0.338 nm.

Table 2.12 Raman and IR band positions and assignments of As(III) and As(V) species in aqueous solution (Goldberg and Johnston , 2001)

Oxidation state	Species	IR (cm^{-1})	Raman	Description
As(III) at pH5	$As(OH)_3$	-	655^b, 669^b	As-OH stretch
		-	709^b, 710^b	Symm As-OH stretch
		795^a	-	As-O stretch
As(III) at pH10.5	$AsO(OH_2)^-$	-	570^b	Symm stretch As-(OH)
		-	606^a . 610^b	Asymm stretch As(OH)
		-	790^b, 796^a	As-O stretch
As(V) at pH5	$AsO_2(OH)_2^-$	-	742^a, 745^c	Symm strech As-OH
		-	765^c	Asymm strech As-OH
		-	843^c	Polymeric vibration
		875^c, 878^a	874^a, 875^c	Symm stretch As-O
		907^a, 908^c	915^c	Asymm stretch As-O
As(V) at pH 9	$AsO_3(OH)^{2-}$	-	700^a, 707^c	Symm strech As-OH
		-	811^c	Polymeric vibration
		-	834^a, 838^c	Symm stretch As-O
		858^a, 860^c	866^c	Asymm strech As-O

Reference: [a] is from Goldberg and Johnston (2001: 208); [b] is from Sprycha (1984 cited in Goldberg and Johnston, 2001: 208); and [c] is from Tossell (1997 cited in Goldberg and Johnston, 2001: 208).

Table 2.13 Raman and IR band positions and assignments of As(III) and As(V) species sorbing onto amorphous ferric hydroxide (Goldberg and Johnston , 2001)

Oxidation state	Species	IR (cm^{-1})	Description
As(III) at pH5	$As(OH)_3$	783[d]	As-O vibration of As-O-Fe group
		794[e]	As-O vibration of As-O-Fe group
As(III) at pH10.5	$AsO(OH_2)^-$	-	-
As(V) at pH5	$AsO_2(OH)_2^-$	824[d]	As-OH vibration of As-O-Fe group
		861[d]	Non surface complex As-O bond
As(V) at pH 9	$AsO_3(OH)^{2-}$	817[d]	As-OH vibration of As-O-Fe group
		854[d]	Non surface complex As-O bond

Reference: [d] is from Goldberg and Johnston (2001: 214 - 215) and [e] is from Suarez, Goldberg, and Su (1998 cited cited in Goldberg and Johnston, 2001: 215).

In comparison to the two spectroscopic techniques discussed in the previous paragraph, FT-IR and Raman spectroscopy seemed likely to be more frequently used. So abundantly were the two approaches used for this purpose that Goldberg and Johnston (2001, 211) summarized all in the form of a table in their study. Table 3.1 and 3.2 adapted from that study show Raman and IR band positions and the assignments of As(III) and As(V) species in aqueous solution as well as As(III) and As(V) species sorbing to amorphous iron oxide, respectively.

In conclusion, according to the data summarized in these two tables, Goldberg and Johnston (2001: 204) concluded that arsenate forms inner-sphere surface complexes on Fe oxide, while arsenite forms both inner- and outer-sphere surface complexes on Fe oxide.

2.8 Source, Characteristic, and Factors Controlling Properties of Arsenic-Iron Hydroxide Sludge

It is well known that the by-product of arsenic removal by coagulation is arsenic containing sludge. In fact, as mentioned before, not only through the coagulation process by ferric ions but also by many other kinds of arsenic removal technologies, such as ion exchange (Ion Ex), reverse osmosis (RO), nanofiltration (NF), activated alumina (AA), and iron removal processes can produce iron hydroxide sludge containing large amounts of arsenic. Moreover, characteristics of the sludge may vary from one type of process to another. For this reason, in this section, sources of arsenic sludge are divided into two types: conventional coagulation processes and other kinds of arsenic removal technologies including Ion Ex, RO, NF, AA, and iron removal processes.

2.8.1 Characteristics and Factors Controlling Properties of Arsenic-Iron Hydroxide Sludge from the Conventional Coagulation Process

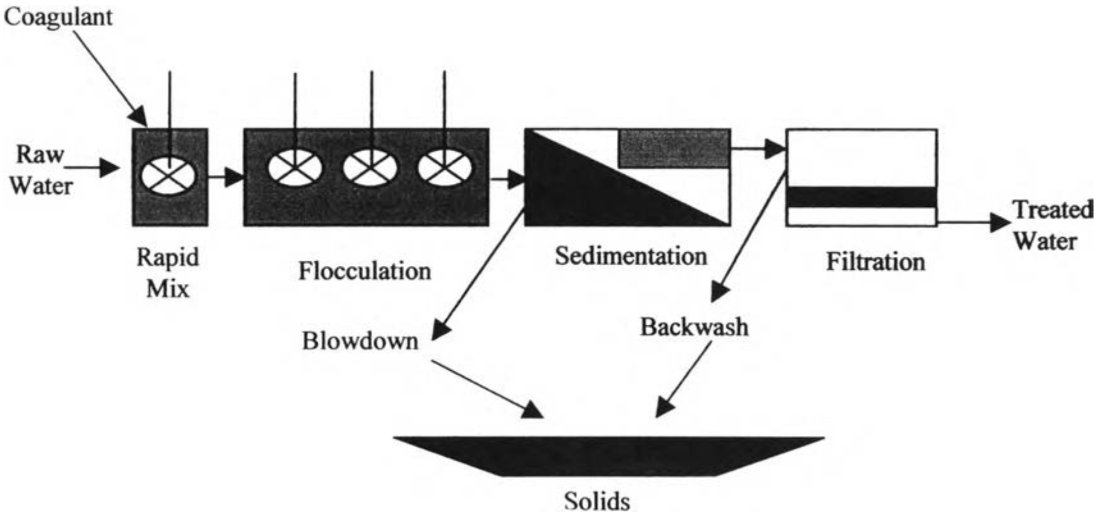

Figure 2.4 Conventional Coagulation Process (adapted from Amy et al., 2000: 196)

A schematic diagram in Figure 2.4 illustrates a conventional coagulation process. It is shown that the residual is generated from a sedimentation basin and the backwash of the filters. However, property of the residual is site-specified despite most of the coagulation facilities having the same type of operational schematic as shown above. Witness the fact that the estimated range of total arsenic in residual from coagulation facilities in California was from 700-15,000 mg/kg (Frey et al., n.d.). On the other hand, Chwirka (1999 cited in Macphee, Charles, and Cornwell, 2001: 1-2) investigated a conventional coagulation facility and reported that the volume of the residual produced was 4300 gal/MG; arsenic concentration in the residual volume was 9.25 mg/L; the quantity of sludge produced was 180 lbs/MG; and arsenic concentration in solids was 1850 mg/kg (dry weight). In the same way, Bartley *et al.* (1991 cited in Macphee et al., 2001: 1-2) characterized residuals produced at eight water treatment plants, including one arsenic removal plant and concluded that averaged arsenic levels in composite contact basin solid samples collected over a period of six months was 5,880 mg/kg.

The sharp distinction of these three studies might be under the influence three important factors: geological variation of initial arsenic concentration, finished water target depending on drinking water regulation, and background coagulant demand.

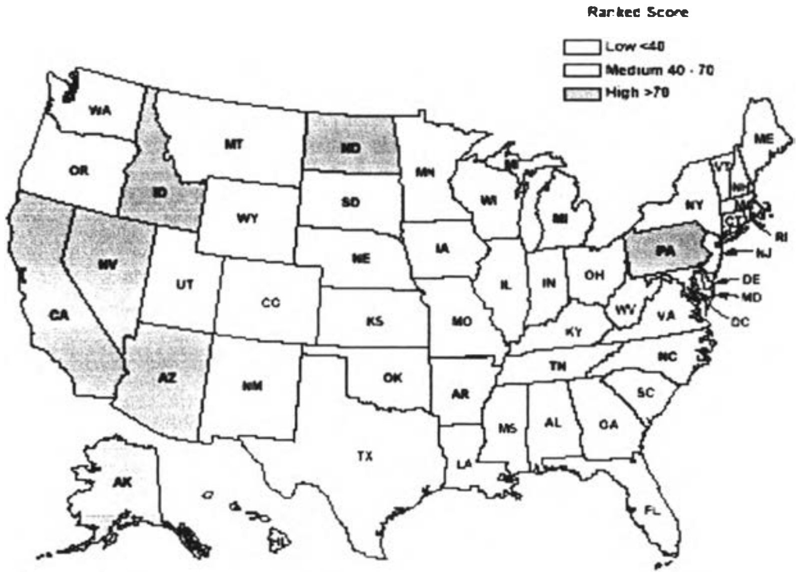

Figure 2.5 Natural Occurrence Factors for Arsenic in Groundwater Systems (Frey and Edwards, 1997 cited in Macphee, Charles, and Cornwell, 2001: 1-2)

Although produced from the same technologies, characteristics of the sludge varies geologically because the initial arsenic concentration in raw water is different from place to place. For example, Frey and Edwards (1997 cited in Macphee et al., 2001: 1-2) surveyed locations in the U.S. that were likely to have high raw water arsenic levels and used the natural occurrence factor, a descriptive variable, to differentiate arsenic occurrence patterns geographically as presented in Figure 2.5.

This implies that despite in only the United States itself, amounts of arsenic in sludge may vary across the states. To emphasize this issue, the arsenic concentration in contaminated water throughout the world shown in Table 2.9 ranks from <1 to 100,000 μg/L. For this reason, the properties of the sludge from conventional coagulation process undoubtedly varies from country to country.

In addition. another factor contributing to the great variation in the properties of sludge from one country to another is their maximum contaminant level (MCL), The amounts of arsenic in drinking water according to the primary drinking water regulations of each country is shown in Table 2.8. MCL refers to the finished water target that influences coagulant demand. Therefore, when comparing between two countries of which the initial arsenic concentrations are the same. but finished water targets are different, the coagulant dose required to achieve the target of each country is different. Thus, the amount of arsenic per one unit of the sludge of these two situations are automatically different.

2.8.2 Characteristics and Factors Controlling Properties of Arsenic-Iron Hydroxide Sludge from Other Removal Processes

Schematics of several arsenic removal processes besides coagulation are depicted in Figure 2.6. It is clearly seen that each technology generates either liquid or semi-liquid residuals such as AA reagent. NF concentrate, RO concentrate, spent filter backwash water from a Fe removal plant, the blend of spent filter backwash water, and the adsorption clarifier flush from Fe removal plant (Macphee et al.,2001: 10). Usually. these residuals are so concentrated that they require further treatment such as coagulation with ferric chloride before being released into the environment.

Therefore, arsenic-iron hydroxide sludge may be generated from such processes. In the same way, those are produced through the conventional coagulation process, the sludge produced from AA processes, Ion Ex processes, membrane processes, or iron manganese removal filtration processes are site-specified, and three major factors controlling characteristics of the residuals are initial arsenic concentration, finished water target depending on waste water regulations, and background coagulant demand.

Some examples are in Table 2.14, which shows residual characteristics of several removal processes calculated by Chwirka (1999 cited in Macphee et al., 2001: 1-2). Note that the arsenic concentration of these technologies can be almost 8 times higher than that of conventional coagulation estimated by the same author mentioned before.

Table 2.14 Summary of example residuals characteristic (Chwirka, 1999 cited in Macphee et al., 2001: 1-2)

Treatment Technology	Volume of residuals produce (gal/MG)	Arsenic concentration in Residuals volume (mg/L)	Quantity of solids produced (lbs/ MG)	As concentration in solids (mg/kg dry weight)
Ion Exchange	4000	10	23.4	14.250
Activited alumina	4200	9.52	23.4[f]	14,250 [f]
Iron oxide coated sand	21,000	1.9	23.4[f]	14,250[f]
Nanofiltration/ Reverse osmosis	664,000	0.098	NA	NA

Note: [f] is calculated value

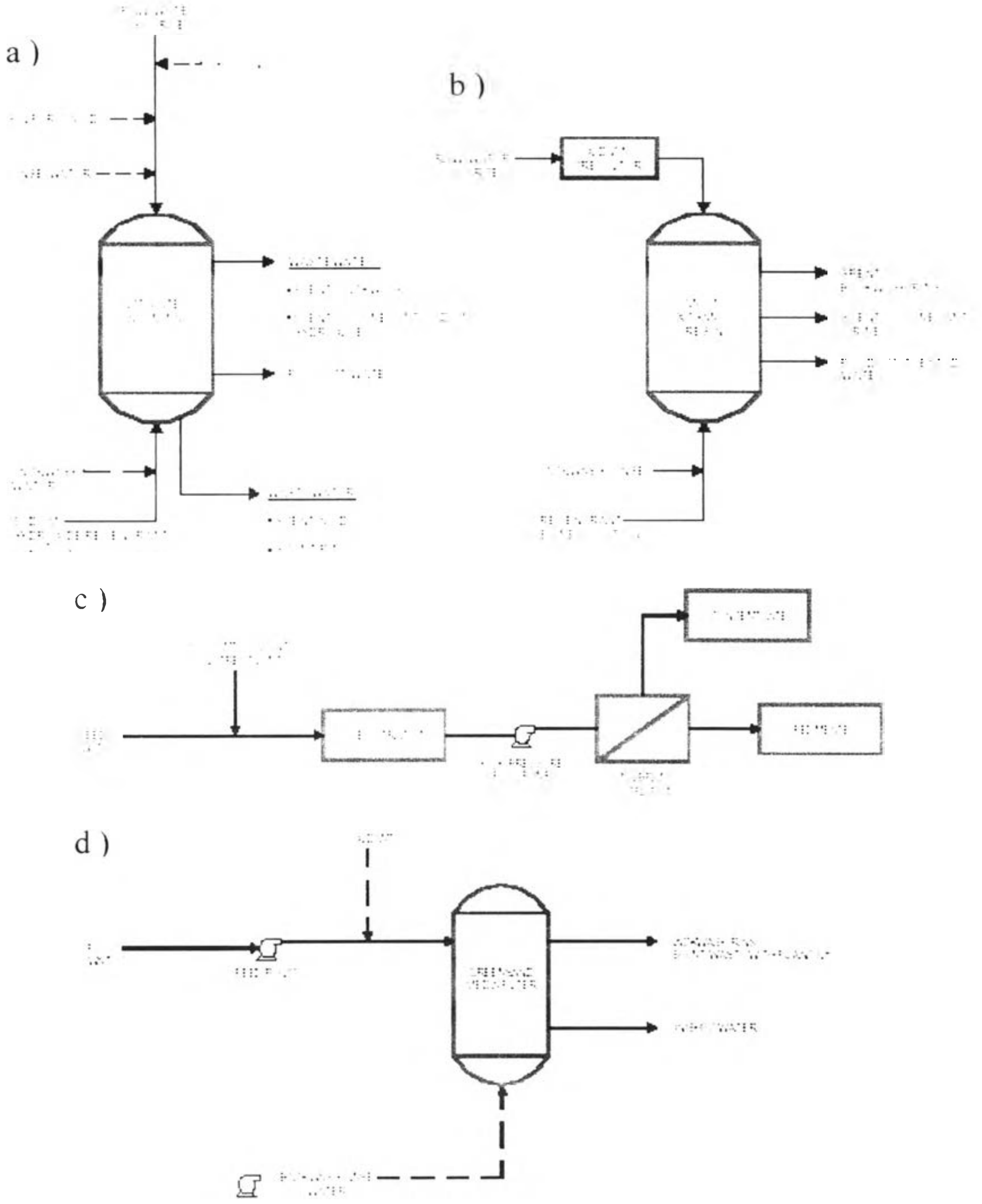

Figure 2.6 Schematics of (a) activated alumina sorption process, (b) Ion Exchange process, (c) membrane process, and (d) iron manganese removal filtration process.(Macphee et al., 2001: 7-9)

2.9 Arsenic Residual Management

This section consists of two sub-topics regarding the residual management issue. Firstly, the present federal disposal regulations of the United States and Thailand are reviewed; thus, in the second part, arsenic residual management alternatives in the United States that comply with its regulations are summarized

2.9.1 Federal Disposal Regulations

Both the United States and Thailand currently do not have existing comprehensive federal regulations that specifically apply to water treatment plant (WTP) residuals, and in particular for arsenic removal plants. However, there are existing federal regulations that were developed for biosolids and solid waste disposal.

Macphee et al. (2001: 46-48) summarized the federal regulations that are currently adopted to deal with WTP residuals in the United States. The five most relevant regulations are discussed below:

- 40 CFR 257: Classification of Solid Waste Disposal Facilities and Practices:

This regulation includes provisions that deal with a land application of a solid waste, including WTP residuals. In order to comply with Section 405(d) of the Clean Water Act, the owner or generator of a publicly owned treatment facility must comply with the guidelines for sludge applications outlined in 40 CFR 257.

- 40 CFR 258: Criteria for Municipal Solid Waste Landfills (MSWLF):

The 40 CFR 258 regulation establishes minimum national criteria for all MSWLF units and for MSWLF that are used to dispose of biosolids. Biosolids, solid wastes, and WTP residuals that are placed in a MSWLF must be nonhazardous as determined by 40 CFR 261, and must not contain free liquids as determined by the Paint Filter Liquid Tests.

- 40 CFR 261: Toxicity Characteristic Leaching Procedure (TCLP) Test:

The 40 CFR 261 identifies the solid waste materials which are subject to regulation as hazardous waste. A solid is considered a hazardous waste if it exhibits any of the characteristics of ignitability, corrosivity, reactivity, or toxicity as defined in Subpart C of CFR 261 or if it is listed in Subpart D of CFR 261. This regulation is pertinent since the final use options considered for WTP residuals application require a nonhazardous designation. Since WTP residuals are not ignitable, corrosive, reactive, or considered hazardous wastes, the toxicity characteristic leaching procedure (TCLP) could be used as the primary indicator that a WTP residual is not a hazardous material. The important link between this regulatory limit and a drinking water standard (MCL) is that the allowable concentration of arsenic in leachate of the residual must not exceed 100 times of the maximum contaminant level (MCL) of arsenic in the drinking water standard (Amy et al., 2000: 192): For example, the toxicity characteristic leaching procedure (TCLP) arsenic limit was set at 5.0 mg/L before October 31, 2001, or 100 times the drinking water MCL of 0.05 mg/L at that time. Similarly, the present USEPA regulatory limit of arsenic in drinking water is 10 µg/L, so a proportional reduction would mean that the TCLP limit would drop to 1.0 mg/L.

- 40 CFR 403: General Pretreatment Regulations for Existing and New Sources of Pollution:

Discharges to the sanitary sewer are subject to EPA's National Pretreatment Standards and any additional pretreatment requirements mandated by the state or wastewater treatment facility. Examples of arsenic limits from seven states reviewed in a recent USEPA publication , Science Applications International 2000, range from 0.051 mg/L for Albuquerque, New Mexico to 1.07 mg/L for Farmington, New Mexico. Residual arsenic levels in this range were attained through precipitation or adsorption treatments for all wastewaters examined in this work except Ion Ex . The requirements imposed on a wastewater treatment facility through a permit and/or local ordinance are necessary to enable the facility to achieve compliance with their National Pollutant Discharge Elimination System (NPDES) permit. Pretreatment required prior to discharge of liquid residuals into the environment is typically site-specific. Several states have a surface water quality arsenic standard of 0.05 mg/L for waters used as public water supplies (Science Applications International 2000 cited in Macphee et al. (2001: 46-48) .

- 40 CFR 503: Standards for the Disposal of Sewage Sludge:

This regulation describes comprehensive criteria for the management of biosolids. Under 40 CFR 503, biosolids can be either land applied in bulk form. sold. or given away. In order to utilize biosolids as land application materials, criteria for pollutant limits, pathogens. and vector attraction reduction must be met. There are nine metal pollutants regulated in this regulation and one of them is arsenic. Considering only criteria for arsenic. all biosolids that are to be land applied must meet the ceiling concentrations of 75 mg/kg. Bulk biosolids that are applied to agricultural land. forest. public contract sites. or reclamation sites must also either meet the pollutant limits of 41 mg/kg or be applied at rates so that the cumulative loading rates of 41 kg/ha are not exceeded. Bulk biosolids that are applied to lawn or home gardens must meet the pollutant limits of of 41 mg/kg. Biosolids that are sold or given away must either meet the pollutant limits of 41 mg/kg, or be applied so as not to exceed the annual pollutant rates of 2 kg/ha/year. while still meeting the ceiling concentrations of 75 mg/kg.

Similarly. Thailand established a set of regulations analogous to some but not all of the United States' to succeed in the management of waste in the environmental friendly way.

- The Notification of the Ministry of Industry No. 1. B.E. 2541(1998):

Under the Notification of the Ministry of Industry No. 1. B.E. 2541(1998). dewatered sludge from industrial wastewater treatment plants is allowed to be either disposed at a landfill or subjected to composting or land reclamation.

However, the waste that are managed by these methods must be nonhazardous as determined by the Notification of the Ministry of Industry No. 6, B.E. 2540 (1997).

- The Notification of the Ministry of Industry No. 6, B.E. 2540(1997):

The Notification of the Ministry of Industry No. 6, B.E. 2540(1997) identifies the solid waste materials which are subject to regulation as a hazardous waste. Like 40 CFR 261, a solid is considered a hazardous waste if it exhibits any of the characteristics of ignitability, corrosivity, reactivity, or toxicity as defined in The Notification of the Ministry of Industry No. 6, B.E. 2540 (1997). Like the TCLP, the Leaching Procedure under the Notification of the Ministry of Industry No. 6, B.E. 2540(1997), abbreviated as LP-NO.6, could be used as the primary indicator as to whether the sludge is a hazardous material or not. Nowadays, the drinking water MCL of Thailand is 0.05 mg/L, so LP-NO.6 arsenic limit was set at 5.0 mg/L.

- The Notification of the Ministry of Industry No. 2, B.E. 2539(1996):

Under the Notification of the Ministry of Industry No. 2, B.E. 2539(1996), considering only suspended solids and arsenic concentration, water discharged to the environment must have suspended solid no more than 50 mg/L and arsenic concentration no more than 0.25 mg/L.

2.9.2 Arsenic Residual Management Alternatives

Unfortunately, there is no study regarding the management of arsenic containing sludge done in Thailand. Therefore, all literature cited here comes from management experience in the United States.

There are several available alternatives for arsenic residual management, which complies with the United States' regulations discussed above. However, the factors determining whether an alternative is applicable to the residual from a particular location and removal technology or not are the states of the residuals, total concentration of arsenic (mg/kg) which varies from place to place and from one kind of removal technology to another, and the leachability of raw sludge itself depending on its immobilization efficiency.

Consequently, in the first part of this section, all available alternatives for liquid and semi-liquid residuals of both the conventional coagulation process and other removal technologies such as ion exchange (Ion Ex), reverse osmosis (RO), nanofiltration (NF), activated alumina (AA), and iron removal processes are summarized. Then, in the second part, all available alternatives for solid residuals of both conventional coagulation processes and other removal technologies are also reviewed.

2.9.2.1 Available Management Alternatives for Liquid and Semi-liquid Residuals.

For liquid and semi-liquid residuals, disposal alternatives may include (Amy et al.,2000: 188):

- Discharge into receiving water
- Discharge into a sanitary sewer that conveys the liquid waste to a waste water treatment plant (WWTP)

- <u>Discharge into Receiving Water</u>

In the United States, discharge of the residuals to surface water requires a NPDES permit. NPDES permit requirements are based on stream flow conditions and provide maximum limits for solids discharge and contaminant loadings. The limits established in the NPDES for specific contaminants are determined by the water quality criteria established for the receiving water, ambient levels of the specific contaminants, the established low flow condition of the receiving water, and the design flow of the proposed discharge from the arsenic treatment process (Macphee et al., 2001: 49).

Most NPDES permits limit solids discharge to around 30 mg/L (Amy et al., 2000: 188); as a result, waste streams with solids concentrations greater than this cannot be discharged. In addition, to determine whether the residuals can be disposed by this method, the water quality criterion presented in table 3.3 will be used by state regulators to establish discharge limitations for arsenic based on classification of the receiving water. The established arsenic limit will then be written into the NPDES permits. The discharge limitation are calculated by the following equation (Amy et al., 2000: 189)

$$M_2=(O_3M_3-Q_1M_1)/Q_2 \qquad (2\text{-}39)$$

Where M_1 = the background arsenic concentration in the receiving water, µg/L.
Q_1 = the low-flow condition of the receiving stream, mgd.
M_2 = the allowable arsenic concentration of the discharge, µg/L.
Q_2 = the design flow rate of the arsenic treatment facility discharge, mgd.
M_3 = the arsenic water quality criterion of the receiving stream, µg/L.
$Q_3 = Q_1 + Q_2$, mgd.

In addition, a discharge is required to pass the whole effluent toxicity (WET) test. The WET test will determine the toxicity of the effluent regardless of the arsenic concentration and possible synergistic impacts with other contaminants in the water (Amy et al., 2000: 189)

Amy et al. (2000: 205-217) evaluated the possibility of residuals from each type of removal technology in the United States to be discharged into the receiving water. Below is the summary of its study.

Considering the residuals produced at a conventional coagulation process reported by Amy et al. (2000: 206), it was revealed that the solids concentration of such residuals was around 0.5 percent solids or 5,000 mg/L. Therefore, these residuals could not be discharged to a receiving stream because their solids concentration was much greater than 30-mg/L limit mentioned above.

In the same way, because of its high arsenic concentration and high salt content together with assimilation efficiency of the receiving water depending on flow rate, the waste brine from ion exchange seemed to fail the WET test and therefore could not be disposed of by this method, nor could the residuals from activated alumina and iron oxide coated sand.

In contrast, the residual from nanofiltration and reverse osmosis was supposed to have such a low concentration of arsenic that it was not anticipated that toxicity caused by arsenic would occur. Therefore, it is possible to discharge the residuals from nanofiltration and reverse osmosis to a reciving stream by assimilating 200,000 gal of rejected water produced for every 1 mgd of drinking water production with a dilution flow of 3.8 ft^3/s.

- Discharge to a Sanitary Sewer

In the United States, the major factor controlling whether the residuals can be discharged to a sanitary sewer or not is the Technically Based Local Limits (TBLL) of the current industrial pretreatment program. The purpose of TBLL is to prevent unacceptable concentrations of contaminants from entering the WWTP treatment process. Those guidelines protect the operation of the WWTP from inhibition of the biological processes used to treat municipal wastewater, prevent violations of the WWTP NPDES permit, and prevent unacceptable accumulation of contaminants in the WWTP biosolids. The TBLL for arsenic will typically be limited by contamination of the wastewater treatment plant biosolids rather than discharge limitations or process inhibitions (Chwirka 1999 cited in Macphee et al., 2001: 49).

The TBLL of one city may be significantly different from that of another city owning to the fact that the factors influencing the development of the TBLL as well as level of treatment achieved for the water supply may vary from place to place. Some of the factors are arsenic concentration of the water supply and the treatment technology. Table 2.15 shows arsenic TBLL for various cities in the United States.

Table 2.15 Arsenic TBLL for some cities (Amy et al., 2000: 191)

City	Arsenic TBLL, μg/L
Albuquerque. N.M.	51
Anchorage. Ark.	1.700
El Paso. Tex.	170
Lakeland. Fla.	120
Newark. N.J.	150
Orange Country. Calif.	2.000
San Jose. Calif.	1.000

Amy et al. (2000: 205-217) evaluated the possibility of residuals from each type of removal technology in the United States to be discharged to a sanitary sewer. Below is the summary of their study.

For a conventional coagulation plant. it was found that the blowdown arsenic concentration for these residuals was around 9.2500 mg/L. which was much higher than the arsenic TBLL. Therefore. the study suggested that it was very unlikely that the residuals could be managed by this option.

In addition. their study concluded that the residuals from both ion exchange and activated alumina could not be managed by this alternative because of the fact that both the waste brine from ion exchange and waste regenerant solutions had an arsenic concentration of around 10 and 9.52 mg/l. respectively; these concentrations were much greater than typical TBLLs.

In contrast. the residuals from iron oxide coated sand as well as nanofiltration and reverse osmosis could be managed by this alternative due to the fact that both the waste stream from the iron oxide coated sand and rejected water from iron oxide coated sand had an arsenic concentration of around 1.9 mg/L and 98 μg/l. respectively; these concentrations were in the upper range of typical TBLLs.

It should be noted that only a few types of liquid residuals produced from such arsenic removal technologies could be managed by either of the alternatives discussed above. Therefore. coagulation and co-precipitation with ferric salts was usually applied. However. the same study reported that the sludge produced usually had either too many percent solids to be discharge to receiving water or too high level of arsenic concentration to be discharge to a sanitary sewer. Consequently. this semi-liquid sludge is required to be dewatered and disposed of by one of the three available alternatives for solid residuals discussed in next section.

2.9.2.2 Available Management Alternatives for Solid Residuals.

For solid forms of arsenic residuals. disposal alternatives may include (Amy et al. .2000: 188):

- Land application or land disposal with other residuals
- Disposal at a landfill
- Disposal at a hazardous waste landfill.

- <u>Land Application or Land Disposal with Other Residuals</u>

In the United States. the blending of arsenic residuals with other water treatment residuals may be managed by land application. However. land application of WTP residuals is dependent on the state regulatory guidelines. The general criteria for allowing WTP residuals to be land applied are based on the following Federal regulations which were discussed in the previous section:

- EPA CFR 40 261 - TCLP Hazardous Determination

- EPA CFR 40 503 -Biosolids Metals Concentrations

- EPA CFR 40 257 - Solid Waste Disposal

Amy et al. (2000: 205-217) evaluated the possibility of residuals from each type of removal technology in the United States to be subjected to land application and concluded that almost all kinds of arsenic residuals were able to be disposed of by this option. Table 2.16 summarizes the condition of the residuals from arsenic removal processes for land application.

However, for nanofiltration and reverse osmosis rejected water, the disposal of these wastes on the land application site was unlikely to be appropriate because the reject water would need to be applied at a rate matching the evapotranspiration requirements of the cover crop grown, and it would also be limited to a arsenic loading of 41 kg/ha.

- Disposal at a landfill

Municipal solid waste landfills in the United States are under a set of disposal guidelines. The basic guidelines for disposal include the following:

- No free liquids (must pass paint filter test)
- TCLP nonhazardous (EPA CFR 40 Part 261)
- Non-corrosive, non-reactive, non-ignitable (EPA 261)

Thus, liquid or semi-liquid WTP residuals would require mechanical or nonmechanical dewatering prior to acceptance. If the WTP residuals exceeds the TCLP limits established by EPA 40 CFR 261, then the material would have to be disposed of in a hazardous waste landfill.

Amy et al. (2000: 205-217) evaluated the possibility of residuals from each type of removal technology in the United States to be subjected to municipal solid waste landfills and concluded that almost all kinds of arsenic residuals were able to be disposed of by this option. Table 2.17 summarized the results of TCLP test for the residuals from several arsenic removal technologies.

Although nowadays the results of TCLP are the main indicators indicating whether the residuals can be classified as nonhazardous waste or not, there are some critics of the TCLP test. There are three reasonable reasons supporting the belief that the TCLP might underestimate leachability of the arsenic containing residuals.

First, the TCLP test may not mimic conditions in non-hazardous industrial landfills (Itle, Novak, and Edwards, 2001: 3). The pervious statement is supported by Hooper's study (1998 cited in Itle et al., 2001: 3). By making the comparison between the TCLP extracts and actual municipal solid waste leachate, he concluded that the TCLP was not an appropriate simulation of landfill conditions because it failed to extract oxyanion-forming elements such as arsenic. Theoretically, oxyanion-forming elements such as arsenic can combine with oxygen to form negatively charged solutes that can not complex with the negatively charged acetate solution used in the TCLP test.

Second, Meng, Korfiatis, Jing, et al. (2001: 3480-3481) suggested that the fact that the TCLP test was performed without paying attention to headspace in the extraction vessel or the exclusion of oxygen from the extraction system might underestimate the leachability of arsenic in the anoxic sludge collected from sludge ponds because of the oxidation of Fe(II) and As(III) to Fe(III) and As(V) by oxygen. This oxidation results in the decrease in Fe and As concentrations during the extraction. When ferrous was oxidized, it might subsequently precipitate as ferric oxyhydroxide. Then, the soluble As(V) and As(III) could be removed by this newly formed ferric oxyhydroxide. In addition, in the presence of oxygen, As(III) might also undergo oxidation to As(V) which was more effectively removed by ferric oxyhydroxide.

Table 2.16 Condition of the Residuals from the Arsenic Removal Processes for Land Application (Amy et al.,2000: 205-217)

Removal Technology	Arsenic concentration in the residuals (mg/kg) dry-weight basis	amount of sludge allowed for each acre of land (kg)	Land (acres) required per year for 1-mgd treatment facility
Conventional coagulation	1,850	8,967	3.3
Ion exchange brine	10	438,000 (gal)	3.3
precipitation of Ion exchange brine	64,000	NA	NA
Activated alumina waste regenerant	9.52	460,000 (gal)	3.3
Precipitation of activated alumina waste regenerant solutions	14,250	NA	NA
Iron oxide coated sand waste solutions	1.9	2.3 (mil gal)	3.3
Precipitation of Iron oxide coated sand waste solutions	14,250	NA	NA

Table 2.17 TCLP Result for Residuals from Several Arsenic Removal Technologies (Amy et al., 2000: 205-217)

Removal Technology	Total digested concentration		TCLP extact		
	mg Fe/kg dry solids	mg As/kg dry solids	% dry solids	Fe (mg/L)	As (µg/L)
Iron coagulation	19,350	337.8	100	182.4	1,559.6
Fe/Mn removal	37, 345	369.0	66.3	2.4	44.4

Removal Technology	Total digested concentration			TCLP extract		
	Fe (mg/L)	Al (mg/L)	As (mg/L)	Fe (mg/L)	Al (mg/L)	As (µg/L)
Iron oxide coated sand column regenerant	8.4	1.9	13,018	0.1	0.6	9,246.2
Activated Alumina column regenerant	1.8	271	12,708	0	0.1	24.2
Membrane fliter rejected residuals	N/A	N/A	837.5	12	0.3	17.9

Last but not least. the TCLP does not account for oxidation/reduction reactions that occur in landfills. Actually, this is probably the most serious failure of the TCLP due to the fact that arsenic is more soluble under reduced conditions (Itle et al., 2001: 3).

Although the TCLP is widely used throughout the United States, the State of California developed an alternative extraction procedure named the Waste Extraction Test (WET) in the 1980's. The California WET is likely to be a more aggressive test than the TCLP because of a longer mixing period, higher sample to extraction fluid ratio, and a different extraction fluid containing citric acid, which is a stronger chelating agent in comparison to acetic acid used in the TCLP. A comparison of the TCLP and California WET is shown in Table 2.18.

Hooper (1998 cited in Itle et al., 2001: 4) found that the California WET could extract two to ten times as much arsenic as the TCLP test, even after the TCLP value had been multiplied by two to account for the different dilution factors in the two tests. In addition, he compared the California WET with the actual municipal solid waste leachate and concluded that the California WET generally extracted higher amounts of arsenic than was found in the actual municipal solid waste leachate.

- Disposal at a Hazardous Waste Landfill

If arsenic-containing residuals fail to pass the TCLP or WET tests, they are disposed of at a designated and licensed hazardous waste facility. Moreover, their transport to the hazardous waste facility must be manifested, and the owner may never be free of the responsibility of such waste. Consequently, the cost of this method of disposal is usually much higher than that of a typical solid-waste landfill.

According to the TCLP test in Table 2.17, none of arsenic-containing residuals should be subjected to a hazardous waste facility. However, it should be kept in mind that although the residuals subjected to the TCLP test mentioned in this review might claim to be good representatives of the arsenic-containing waste in the United States, they might not be good representatives of the arsenic-containing waste throughout the world due to the distinction of the residuals from place to place discussed above. Therefore, using the results of these studies to deal with residual management in other regions should be done with great care.

Table 2.18 The comparison between the TCLP and California WET (adapted from Itle et al.. 2001: 4)

California WET	TCLP
One set of extraction fluid. Citric Acid Buffer pH 5.0	Extraction fluid selection depends on sample pH: a. Acetate buffer pH 4.93 b. acetic Acid solution pH 2.88
Sample to extraction fluid ratio is 1:10	Sample to extraction fluid ratio is 1:20
Does not specify extraction vessel design	Requires extraction bottles made of glass or polypropylene
Requires use of 0.45 µm membrane filter for extract after extraction	Requires use of 0.6 to 0.8 µm glass fiber filter
Uses mechanical shaker for extraction	Requires rotary end over fashion at 30 rpm
Extraction period of 48 hours	18 hours
Does not required acid digestion after extraction for metal	Requires acid digestion after extraction for metals other than mercury

2.10 Solidification and Stabilization

If the sludge becomes classified as hazardous, it may present the responsible parties with the negative economic impact from its management because of the disposal waste at a hazardous waste landfill is much more expensive than that of non-hazardous waste management with as disposal at a sanitary landfill or land application For this reason, to reach a compromise between reasonable operation costs of waste management and sufficient long-term stability of the waste itself, it is preferable to consider other management strategies.

Of all available alternatives, the solidification/stabilization (S/S) technique identified as the Best Demonstrated Available Technology for treating a wide range of Resource Conservation and Recovery Act (RCRA) non-wastewater hazardous waste subcategories (USEPA, 1993: 1) seems to be one of the most practical options to achieve that goal. The reason supporting this belief is the fact that not only is the solidified matrix considered stable and safe for public and environmental health but also its physical property is suitable for an application in the field of civil engineering. As an added value, the reutilization of solidified-waste products may help to relieve the economic impact discussed above.

Stabilization is a process employing additives (reagents) to reduce the hazardous nature of a waste by converting the waste and its hazardous constituents into a form that minimizes the rate of contaminant migration into the environment, or reduces the level of toxicity. In contrast, solidification is described as a process by which sufficient quantities of solidifying materials are added to a hazardous material resulting in a solidified mass of material Solidifying the mass is accomplished through the addition of reagents that increase the strength, and decrease both the compressibility and the permeability of the waste (LaGrega, Buckingham, and Evans, 2001: 677-678). The difference between the these two terms is that the solidification process may not necessarily decrease leachability, and stabilization generally refers to a purposeful chemical reaction that has occurred to make waste constituents less leachable. The binders and reagents generally used in the solidification and stabilization process of arsenic are cement, fly ash, lime, sulfur, phosphate, and pH adjustment agents.

Of all these additives, the most frequently used binders for the S/S of arsenic are pozzolanic materials such as Portland cement and lime (USEPA, 2002: 4-1) because they are inexpensive and have an extensively documented history of use and draw upon readily accessible technology. However, the major difference between these two additives is that lime acts as a stabilization agent more than a solidification agent because lime limits the solubility of the contaminants in the leaching water by the formation of an insoluble compound while Portland cement acts as a solidification agent more than a stabilization agent owing to the fact that the hydration reaction produces the monolithic solid mass, reducing the mobility of the contaminants by encapsulation in the resulting monolithic matrix, and thereby improves the handling and physical characteristics.

Mixed with water, Portland cement which has idealized compositions close to Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$, and $Ca_2(Al,Fe)O_5$ (Free lime, CaO, normally comprises less than 2-3% of the clinker) becomes solid due to the hydration reaction. Undergoing hydrolysis, each anhydrous composition of Portland cement transforms into a hydrous phase as a schematic representation in Figure 2.7.

When undergoing the reactions in Figure 2.7, roughly two thirds of the cement will have hydrated in approximately 28 days and the compressive strength of the solidified matrices will increase with the age of curing as long as hydration is in progress. For this reason, solidification by Portland cement makes it possible for solidified waste to be utilized as construction materials.

Generally speaking, there are two matters of concern regarding the utilization of a solidified waste form as a construction material. First, the solidified products must meet the physical requirement in terms of strength. For example, according to TIS 827-2531 (1988), the required unconfined compressive strength of a product to serve as an interlocking concrete paving block is around 410 ksc.

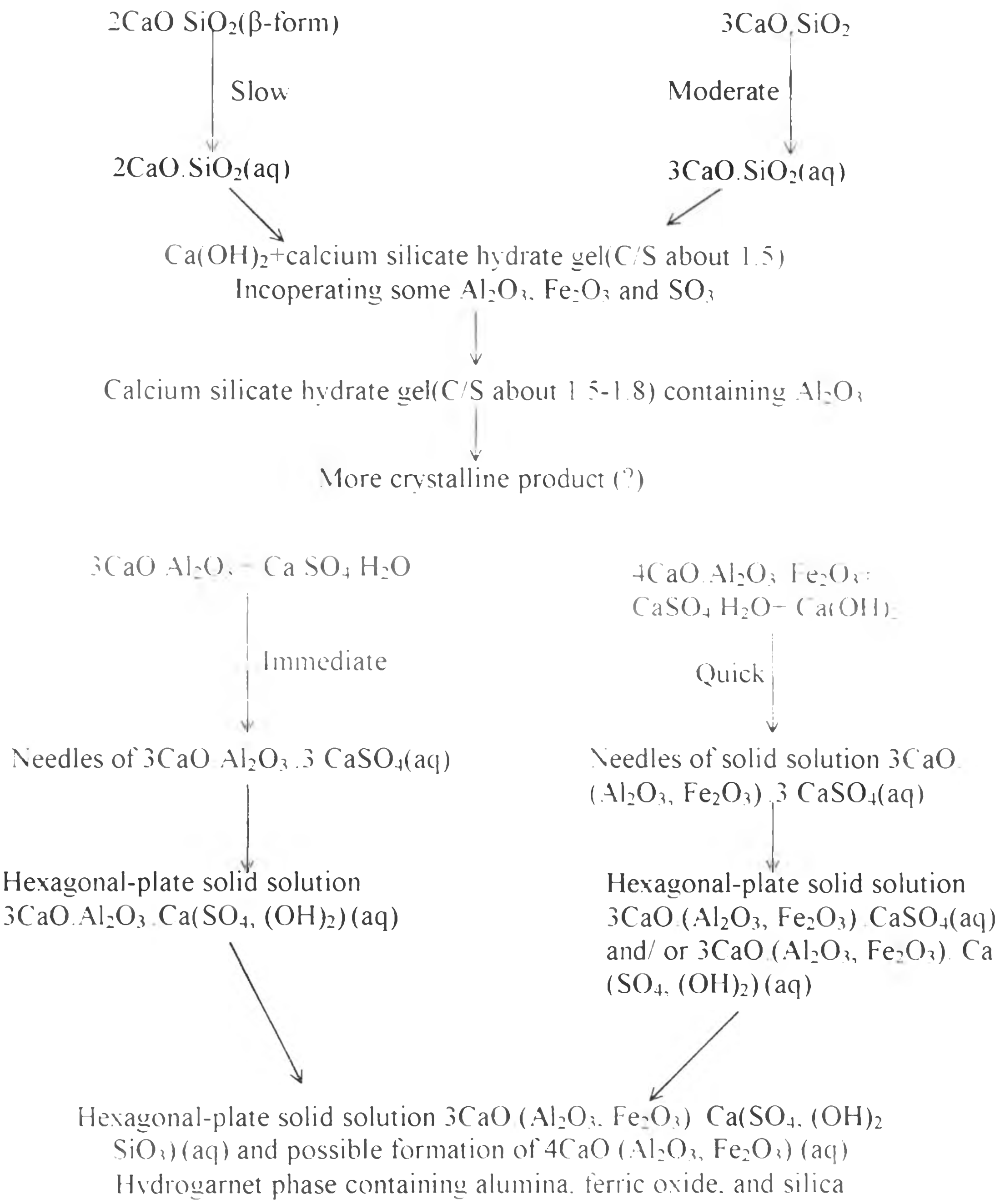

Figure 2.7 The schematic representation of the reaction during the hydration of portland cement at ordinary temperatures (Lea, 1970)

Unfortunately, no research concerning the utilization potential of the solidified/stabilized matrix of arsenic containing waste has been conducted yet. In 1994 Melicher studied the compressive strength of solidified/ stabilized copper-chromium-arsenic (CCA) sludge from timber treatment plants under the method of cement-based stabilization/solidification; however, he did not draw any conclusion regarding the utilization potential of the solidified products. Mixed with 1 part of cement and 2 parts of sand, the contaminated cement-sand mixture hardened after two days of curing. He found that arsenate in the form of As_2O_5 in pure cement inhibited hydration. Although the contaminated cement-sand mix hardened after 2 days of curing, he witnessed the fact that its compressive strength was substantially reduced ($60\ N/cm^2$). In contrast, while arsenite affected the morphology of cement, the unconfined compressifve strength of As(III)-bearing cement–sand matrix was relatively high ($990\ N/cm^2$).

Second, the solidified product must not pose any threat to the environment during utilization. To determine whether or not the utilization has negative environmental impact, leaching test has to be performed. If the concentrations of arsenic in the leachate pass the regulatory limit, the utilization of the solidified waste form is supposed to pose no unacceptable threat to the environment.

Despite the fact that, generally, Portland cement itself has the potential to immobilize metal ions through lattice inclusion, precipitation, reaction with cement components to form solubility limiting phase, or sorption (Glasser, 1993: 1), it is proved ineffective in immobilizing arsenic without addition of lime. Dutre and Vandecasteele (1996) investigated the S/S process of an industrial waste material containing the large amount (32wt%) of arsenic, as As_2O_3, by Portland cement with and without the addition of lime. They conducted extraction test under DIN 38 414 S4 procedure, a German Standard, and found that the concentration of arsenic in the leachate (385-604 mg/l) of the S/S samples, in which no lime was added during solidification, was significantly higher than that of the other samples (close to 5 mg/l) in which lime was added. In the same way, Palfy, Vircikova, and Molnar (1999) investigated the test stabilizing potential of plain cement and found that the solubility of the solidified sludge from the carbon dioxide refining tower was practically equal to that of original sludge. This indicates that lime is essential for stabilizing arsenic containing sludge.

Although useless at improving the physical property of the solidified/stabilized waste form, the addition of lime is believed to result in the formation of $CaHAsO_3$, an insoluble compound, raise to a high pH value which is necessary for the cementation reactions, and buffer the pH of the solidified product (Dutre and Vandecasteele, 1996). These three phenomena play a crucial role on success of arsenic immobilization. Dutre and Vandecasteele (1995a) revealed that from the amount of 6 g of Ca added per 10 g of an industrial waste containing large amounts (42 wt%) of arsenic, where the pH had reached a value of 12.6. The concentration of As was lowered to a constant value of approximately 5 mg/l because a hardly soluble calcium-arsenic compound, $CaHAsO_3$ from As (III), was formed in the leachate. The solubility product Ks of such a compound was experimentally determined and amounted to 1.07 E-7.

To find the relation among Ca leaching, pH, and As leaching, Dutre and Vandecasteele (1998) interpreted the experimental results for arsenic and calcium in the leachate given along with the concentration versus pH curves for $CaHAsO_3$ and $Ca(OH)_2$+$CaHAsO_3$ precipitates, as calculated by using the MINTEQA2 program. They found that for S/S samples where less than 4 g of calcium was added per 10 g of waste ($pH<12$) the arsenic and calcium concentrations in the leachate closely followed the $CaHAsO_3$ curve. From an amount of 4 g of calcium per 10 g of waste (pH 12, saturation index of calcium hydroxide no longer negative), the concentrations fell on the curve of $Ca(OH)_2$+$CaHAsO_3$. The concentration of calcium in the leachate was thus determined by the solubility of calcium hydroxide, giving a calcium concentration of ca. 900 mg/l and a leachate pH value of ca. 12.5. Due to the presence of both $Ca(OH)_2$ and $CaHAsO_3$, the arsenic concentration [As(III)] was lowered to ca. 5 mg/l (at a pH of 12.5), whereas the minimum value for the arsenic concentration that could be reached when only $CaHAsO_3$ was present was ca. 55 mg/l.

Used together with lime as an arsenic precipitation agent, another type of additive used in the S/S of arsenic is ferric ion. Palfy et al.(1999) found that when the sludge contained 720 mg of Fe, the amount of arsenic that leached into the solution was only 4210 mg/l or 60% of the total arsenic, 6430 mg/l. Not all the content of arsenic presented in the waste enters the aqueous phase. They supposed that this was the case due to existence of poorly soluble complexes with iron. They also proposed the method of arsenic stabilization by a series of precipitation and solidification agents, calcium and ferric ion as precipitation agents and Portland cement as a solidification agent. They identified that it was possible to reduce original arsenic solubility of 6430 mg/l from untreated waste to 0.823 mg/l from final matrices by this technique. In the same way, Vegara (1992 cited in Palfy et al., 1999: 55) reported a substantial fall of As concentrations in leachate from high ferric precipitate in pHs over 10, when CaO was used for buffering.

Some other additives such as waste acid, aluminum, and barium were also studied to evaluate their possible use as arsenic S/S agents. Dutre and Vandecasteele (1995a) concluded that the addition of waste acid (5M HCl with Zn and Fe concentrations of approx. 60 g/l and a Pb concentration of 150 mg/l) and slang had only a negligible influence owning to the fact that the addition of waste acid to the mixture insignificantly lowered the concentration of arsenic of arsenic (from 10 to 5 mg/l). Slang was added to increase the silicon content in the resulting product. This promoted polymerization during the setting of the cement. However, the hardening process took weeks or months and could not be investigated in the short-term test (a one-week test). In conclusion, the addition of slang on a short-term basis had no significant influence on the concentration of the contaminants in the leachate. Moreover, they tried to use aluminum (Al) and barium (Ba) in the arsenic S/S process due to the possible formation of compounds with a lower solubility product, for instance

$$Al^{3+}_{(aq)} + AsO_4^{3-}{}_{(aq)} \longrightarrow AlAsO_4{}_{(s)} \qquad K_{sp} = 1.6 \times 10^{[illegible]} \qquad (2\text{-}40)$$

$$3\,Ba^{2+}_{(aq)} + 2\,AsO_4^{3-}{}_{(aq)} \longrightarrow Ba_3(AsO_4)_2{}_{(s)} \qquad K_{sp} = 7.7 \times 10^{-51} \qquad (2\text{-}41)$$

Using Al as an additive, they found that Al decreased the leaching of arsenic. This could probably be explained by the adsorption of arsenic on the aluminum hydroxide gel. Nothing, however, could be concluded on the oxidation state of arsenic - it was not clear whether this indicated the formation of $AlAsO_4$. However, the formation of the foamy, jellylike structure could indicate that an $Al(OH)_3$ gel was formed. Similarly, Ba lowered the concentration of arsenic in the leachate, but the values did not decrease below 200 mg/l. It appeared that the lower arsenic concentration could not be attributed to the formation of barium arsenate, because the concentration of Ba rose as the concentration of As reached a constant value. A possible explanation was that As was adsorbed on a barium carbonate precipitate. In the same way, several recent studies (Harris and Monette(1989); Emmett and Khoe (1994); and Khoe, Carter, emmett, Vance, and Zaw (1994) cited Palfy et al.,1999: 55) reported that by the presence of an element like Cd, Zn, Sr, Pb, Cu, or Mg, solubility of arsenic could be lowered significantly in wide interval of pH.

Besides the influence of such additives as described above, another factor controlling the immobilization efficiency of arsenic is the oxidation state of arsenic. The oxidation state of arsenic in the waste results in differences in the formation of arsenic compounds. Glasser (1993) concluded that most of the cationic electropositive elements with formal charge of 3 or more were well-insolubilized in cement matrices by a specific chemical mechanism. Anionic speciations were, however, less well bound. Examples include the semi-metals/ metal of the *p*-block. Thus, As occurring as AsO_3^{2} or AsO_4^{2}, was not well bound. Some arsenate, such as AsO_4^{-2}, would substitute for the sulfate phases of cement hydration products, but partition coefficients between aqueous and solid phases did not indicate good binding for large, tetrahedral species.

However, some researchers indicated that AsO_4^{2} was somewhat better fixed than AsO_3^{2}. For example, Dutré and Vandecasteele (1998) studied the effect of the oxidation state of arsenic. They oxidized arsenic-contained waste before solidification to convert As(III) to As(V) using H_2O_2 (30%) from 0 to 12 ml per 10 g of waste. The arsenic concentration in the leachate of the extraction test of an oxidized S/S sample was lowered to ca. 0.5 mg/l, a factor of 10 below the one for a non-oxidized sample.

They concluded that the decrease in the concentration in the leachate, mainly of As (V), was due to the formation of insoluble $Ca_3(AsO_4)_2$. With the MINTEQA2 program, calculations were made on the solubility of arsenic (V) in equilibrium with $Ca_3(AsO_4)_2$, and compared with As(III) in equilibrium with $CaHAsO_3$. Calculations were made for these precipitates alone and for these precipitates in the presence of 'infinite' amounts of calcium hydroxide. If arsenic were presented as As(V) the arsenic concentration was reduced from 30.3 mg/l only when a $Ca_3(AsO_4)_2$ precipitate occurred, to 0.47 mg/l in the presence of both $Ca(OH)_2$ and $Ca_3(AsO_4)_2$ precipitates.

Palfy et al. (1999) conducted bench-scale experiments similar to Dutre and Vandecasteele 's: per 100 g of wet sludge, 30% of H_2O_2 solution was used as an oxidation agent; calcium oxide was added in the form of dry powder, 40 % of ferric sulfate solution, and Portland cement was used for the solidification of the sample. After the bench-scale experiments, they extended the application to a semi-pilot plant test. This semi-pilot plant waste processing test was realized in a concrete mixer with a capacity of 150 L. Certain amounts of additives to stabilize and solidify 10 kg of sludge were composed of 38 L of H_2O_2, 6.4 kg of CaO, 40 kg of $Fe_2(SO_4)_3$,and 55 kg of cement under one hour's reaction time. The arsenic concentration of leachate was only 0.823 mg/l (from the original amount of 6430 mg/l) which was significantly lower than 5 mg/l of the environment limits for class III dump sites in Slovakia.

However, Dutré and Vandecasteele (1996) noted that the question of implementation of the oxidation method followed by solidification/stabilization on an industrial scale was unanswered. For example, during the mixing of the waste with hydrogen peroxide, a reaction occurred with a rather high heat development. The installation should be adapted to control these high temperatures and possible emissions that might result. Moreover, using hydrogen peroxide increases the cost of the overall treatment due to a more complicated solidification procedure and a more expensive installation.

In conclusion, after studying the use of many different additives as S/S agents, Dutre and Vandecasteele (1998) concluded that the addition of lime or lime and cement gave the best result in arsenic S/S. Similarly, Leist, et al. (2002) had tried to identify the most effective S/S formulation. They tried to use three combinations of additives. which were: (1) cement only, (2) cement and iron(II), and(3) cement together with lime, to solidify/stabilize four types of arsenic salts. which were sodium arsenate. sodium arsenite, arsenic trioxide, and arsenic pentoxide. They concluded that calcium is the key factor in arsenic immobilization. in that the higher the Ca:As mole ratios, the lower arsenic concentration in leachate. Therefore. it is now widely accepted that the formation of a calcium-arsenic compound. a solubility-limiting phase. is the main factor controlling arsenic mobility. However. the most controversial issue concerning the S/S of arsenic waste is uncertainty about which calcuim-arsenic compounds. especially for arsenate. are formed in the process.

While $CaHAsO_3$ was believed to be the calcium-arsenic (III) compound formed in the S/S process by most of the recent studies (Vandecasteele et al.. 2002; Palfy et al.,1998; and Dutré and Vandecasteele,1998). there was no consensus documented about the formation of a calcuim-arsenic(V) compound forming in the S/S process. While Dutré and Vandecasteele,1995; Zouboulis. Kydrous. and Matis. 1993: Sadiq, Zaidi. and Mian,1983; Robins, 1992; and Golovnev. 1994 cited in Bothe and Brown. 1999) concluded that $Ca_3(AsO_4)_2$ was the calcium-arsenic(V) formed in the S/S of arsenic. Guerin (1941. cited in Bothe and Brown. 1999) disputed their conclusion on the grounds that $Ca_3(AsO_4)_2$ was not stable. He suggested that the most possible form of calcium-arsenic (V) compounds scould be $Ca_3(AsO_4)_2.xH_2O$. Guerin's conclusion was in agreement with Bothe and Brown's observation in that there was no $Ca_3(AsO_4)_2$ formed in their experiment. Moreover. synthesizing several calcium arsenate compounds by mixing $Ca(OH)_2$ powder with o-arsenic acid and deionized water at a liquid to solids weight ratio of approximately 10 to result in attaining molar Ca/As ratios varying from 0.80 to 4.0. Bothe and Brown (1999) concluded that a variation of the initial Ca/As ration in the suspensions influenced the formation of calcium arsenic compounds. For the Ca/As ration between 2.00-2.50. a phase of pure $Ca_4(OH)_2(AsO_4)_2.4H_2O$ was formed; however. in some samples. the pure phase together with minor amounts of the apatite $Ca_5(AsO_4)_3OH$ was detected. While. for the Ca/As rations. between 1.67-1.90. $Ca_5(AsO_4)_3OH$ were identified. On the other hand. for the Ca/As ratios between 1.50 to 2.00. $Ca_3(AsO_4)_2.3^{2}/_{3}H2O$ and $Ca_3(AsO_4)_2.4^{1}/_{4}H2O$ were predominant phases.

In addition, they studied the relationship between the forms of calcium arsenic compounds and their immobilization potential. They found that not only do the forms of the compounds influence the waste immobilization efficiency but so does the equilibrium pH. As shown in Table 2.19, Bothe and Brown also found that despite the formation of the same compound, the difference of the pH effected the immobilization efficiency. For examples, although $Ca_4(OH)_2(AsO_4)_2 4H_2O$ was formed in the two ranges of pH, 12.14-12.23 and 12.52-12.64, Arsenic immobilization in the latter pH range was more effective than in the former range.

Table 2.19 Formation of calcium-arsenic compounds, their equilibrium pH, and concentration of Ca, as well as, As at equilibrium condition (Bothe and Brown, 1999)

Solid-phase assemblage	Equilibrium pH	Equilibrium concentration	
		Ca(mg/L)	As(mg/L)
$Ca_4(OH)_2(AsO_4)_2 4H_2O$	12.14-12.23	310-320	0.40-0.12
	12.52-12.64	780-690	0.01
$Ca_5(AsO_4)_3OH$	9.54-9.87	18-26	19.5-10.5
	12.63-12.72	780-850	0.14-0.14
$Ca_3(AsO_4)_2 3^2/_3 H_2O$	11.18	32	3
$Ca_3(AsO_4)_2 4^1/_4 H_2O$	7.32-7.55	400-350	710-490

In the view of their studies, Dutre and Vandecasteele (1998) concluded that the optimum recipe to solidify and stabilize arsenic-containing waste (23-47% of arsenic of which 90-95% was in form of arsenite) was composed of 8 g of lime, 6 g of cement, and 20 g of water per 10 g of waste. Palfy et al (1998) studied the possibility of powder calcium oxide employment as a precipitation agent for industrial sludge containing arsenic. They concluded that the higher the molar ratio of Ca:As, the lower the residual concentration of As (g/l). Prior to a Ca:As ratio higher than 8, there was not a significant reduction in the residual concentration of arsenic in the solution. This implied that the maximum possibility to fix aqueous arsenic by precipitation with lime was 70%, because the remaining part of arsenic could not be bound by even the extensively increased addition of calcium ions. So the optimum Ca:As ration was 8. They also noted that the molar ratios, Fe: As = 4 to 6, gave the best results in case of using ferric sulfate in the S/S process.

It should be noted that all the literature reviewed above were investigated in macroscopic scale which was effective enough to provide a reliable answer regarding utilization potential issue. On the other hand, to further investigate mechanisms or phenomena taking place in the solidified/stabilized matrices, the experiment in microscopic scale is required.

Despite the fact that solidification/stabilization (S/S) has emerged and been applied to cope with various types of waste ranking from radioactive waste to biological organism for several decades, the physical and chemical phenomena as a result of the interaction between the priority metal pollutants, including arsenic with cement components, have not been fully characterized. According to the most recent studies in this field of several metal pollutants, the phenomena mentioned prior are believed to be the major factors contributing to the reduction of toxicity, dissolution, and release of metals into the environment (Cocke and Mollas, 1993). Figure 2.8 shows various possibilities for the interaction of hazardous substances with cement. It should be noted that the most important data emphasized in Figure 2.8 is the fact that there may be other possibilities of interactions occurring in the system which are still regarded as "Unknowns". However, based on present scientific knowledge, these interactions can be categorized under four headings: lattice inclusion, precipitation, reaction with cement components to form solubility limiting phase, and sorption (Glasser, 1993). Owning to the fact that the blending of dynamic cement chemistry with solution equilibrium and kinetic processes coupled with the surface and nearsurface phenomena makes the S/S process so complex that it is regarded as " a black box", our knowledge of these four important mechanisms is still far from complete.

Because of the complexity of the system, in order to gain better understanding of the mysterious areas discussed above, the combination of several characterization techniques, as shown in Figure 2.9, has been utilized to unveil information of molecular, surface, and structure useful for characterization of the four mechanisms.

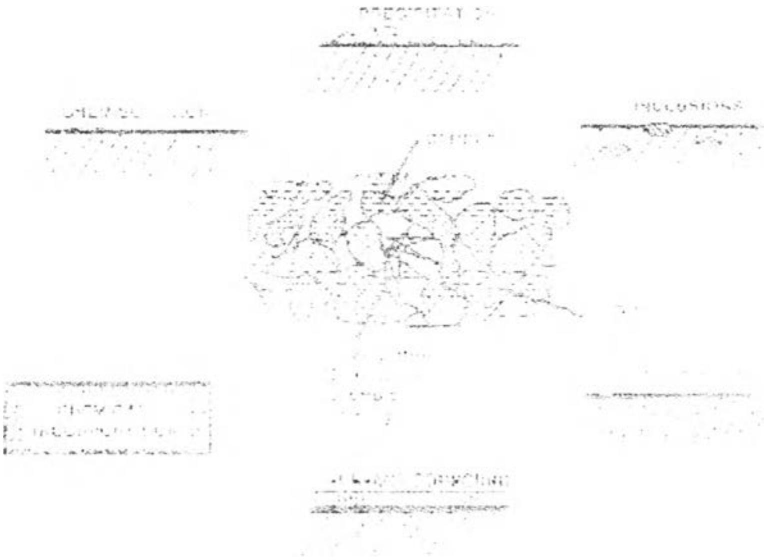

Figure 2.8 Various possibilities for the interaction of hazardous substances with cement (Cocke and Mollah, 1993)

One of most frequently asked questions is that which compounds are formed when the metals of interest react with cement components in the S/S process? X-ray Diffraction spectroscopy, one of the most popular techniques to acquire structural information, is usually used to answer this important question. With the application of this technique, several calcium-arsenic compounds have been identified and reported by several studies from the past to the present day as shown in Table 2.20.

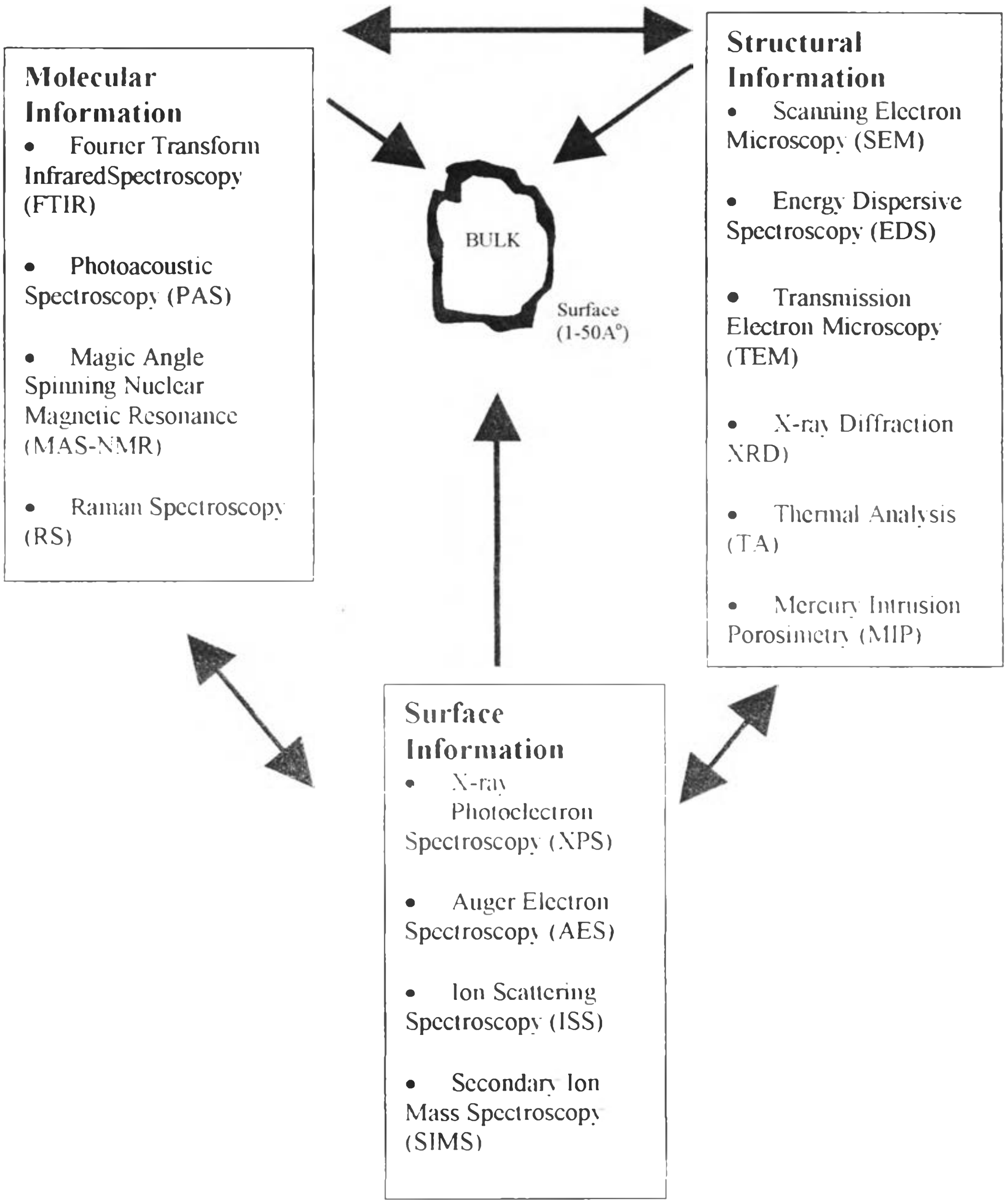

Figure 2.9 Illustration showing the range of characterization of techniques needed to study the binding chemistry and leaching mechanisms of stabilized and solidified hazardous substances (Cocke and Mollah, 1993)

Table 2.20 Some Calcium-Arsenic Compounds with Their *d*-spacings (A^{o})

Compound formula	3 strongest *d*-spacings (A^{o})			Source
$CaHAsO_4H_2O$	5.22	2.96	8.06	Berry, 1974
$CaHAsO_4 2H_2O$	4.32	3.09	2.71	Berry, 1974
$CaH_4(AsO_4)_2$	4.48	3.76	2.17	Berry, 1974
$Ca_3(AsO_4)_2$	2.90	2.82	3.51	Berry, 1974
$CaHAsO_4H_2O$	5.6	2.94	7.93	Mollah et al., 1998
$CaHAsO_4 2H_2O$	4.45	3.1	2.78	Mollah et al., 1998
$Ca_3(AsO_4)_2$	2.94	2.78	3.62	Mollah et al., 1998

After being able to identify the compounds as a result of the interaction of waste and cement components by XRD, the next step satisfying researchers' curiosity is to identify the morphologies of these compounds. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) can serve in this task. Bothe and Brown (1999) successfully photographed several calcium-arsenic compounds such as the well crystallized $Ca_4(OH)_2(AsO_4)_2 4H_2O$, of which crystallites ranged from approximately 0.5 to 4 µm in size, the large platy crystals of $Ca_3(AsO_4)_2 4^1/_4H_2O$ of which crystallites ranged in size from approximately 10-30 µm across; the smaller leafy crystals of $Ca_3(AsO_4)_2 3^2/_3H_2O$ of which crystallites are approximately 2 µm in size; and the fine needlelike crystals of $Ca_5(AsO_4)_3OH$

Another technique generally used to obtain information concerning the molecular characterization of the solidified/stabilized waste form is Fourier Transform-Infrared Spectroscopy (FT-IR). Jing et al. (2003) indicated the As-O-Ca bonds with the IR spectrum at 860 cm^{-1}. Similarly, Myneni, Trama, and Waychunas (1998 cited in Jing et al. 2003) reported the formation of the calcium arsenate mineral with the IR spectrum at 866 cm^{-1}. Moreover, Mollah et al (1998) noticed the hydration retardation in Portland cement type-V with the presence of sodiumarsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$). They found that the Si-O stretching band in the As-doped sample appeared at 950-970, while that of a control sample without the addition of arsenic salt appeared at 975-980. The decline of the Si-O stretching band in the As-doped sample in comparison to that of the control sample suggested that the decline of polymerization of the orthosilicate in cement occurred. This means that hydration retardation takes place in the As-doped sample.