SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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FORMATION OF IRON OXIDES UNDER VARYING CONDITION OF PH, TEMPERATURE AND NEUTRALIZATION DOSAGE

By

MOHAMAD NAZMIE BIN MOHD SHARIPUDIN

Supervisor: Dr Norlia binti Baharun

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Formation of iron oxides under varying condition of pH, temperature and neutralization dosage ”.I also declare that it has not been previously submitted for the award of any Degree or Diploma or other similar title for any other examining body or University.

Name of Student: Mohamad Nazmie Bin Mohd Sharipudin Signature:
Date: 1st June 2017

Witness by:
Name of Supervisor: Dr. Norlia Baharun Signature:
Date: 1st June 2017

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ABSTRAK

Baru-baru ini, schwertmannite, minersl ferik sulfat halik, telah menarik perhatian meluas kerana kapasiti penyerapan yang tinggi untuk spesies toksik arsenic. Kerja-kerja penyelidikan telah dijalankan ke atas sintesis dan pencirian schwertmannite. Kajian ini melibatkan sintesis schwertmannite dengan pelbagai pemboleubah seperti kelajuan pergolakan, pH akhir, suhu dan dos peneutralan. Pembolehubah yang digunakan dalam kerja-kerja penyelidikan ini adalah kelajuan pergolakan (250 rpm dan 350 rpm), pH akhir (<3.5 dan> 3.5), suhu (25 ° C dan 60 ° C) dan dos peneutralan (1000 µL dan 2000 µL). Mineral schwertmannite sintetik telah disintesis menggunakan kaedah peneutralan yang telah diubahsuai. Kerja-kerja penyelidikan ini melibatkan percubaan awal dengan menggunakan kaedah peneutralan dan juga pengubahsuaian. Dalam sintesis menggunakan kaedah peneutralan, kira-kira 500 mL larutan 0.05 M $Fe_2(SO_4)_3$ telah dicampurkan dengan 5 mL larutan 0.01 M H_2SO_4 untuk mendapatkan larutan yang berasid. Kajian ini telah diikuti oleh proses pentitratan dengan 1 M Na_2CO_3 di bawah keadaan diaduk ke dalam larutan campuran pada setiap satu minit untuk menjadikan pH akhir 3-4. Kadar titratan adalah 1000 µL / min. Larutan campuran telah ditapis menggunakan kertas penapis dan diikuti dengan proses pengeringan dalam ketuhar selama 24 jam pada suhu 60 ° C. Sampel serbuk kekuningan telah dikisar sebelum proses pencirian. Proses pencirian yang terlibat dalam kajian ini berfungsi ialah X-ray diffraction (XRD), scanning electron microscopy dengan energy dispersive X-ray microscopy (SEM/EDX) dan analisis saiz zarah (PSA-MALVERN). Untuk XRD, sintetik schwertmannite telah menunjukkan kehadiran unsur-unsur seperti Fe, S dan O. Dari

keputusan analisis SEM/EDX menunjukkan kehadiran mendakan ferum. Analisis saiz zarah menunjukkan bahawa X_{50} daripada sintetik schwertmannite adalah di antara 1.4µm dan 2.2µm.

FORMATION OF IRON OXIDES UNDER VARYING CONDITION OF pH, TEMPERATURE AND NEUTRALIZATION DOSAGE

ABSTRACT

Recently, schwertmannite, a ferric oxyhydroxy sulfate mineral, has attracted attention broadly due to its high sorption capacity for toxic arsenic species. This research work has been carried out on the synthesis and characterization of schwertmannite. The present study involved the synthesis of schwertmannite at varying condition such as speed of agitation, final pH, temperature and neutralization dosage. The parameters that has been used in this research work are speed of agitation (250 rpm and 350 rpm), final pH (<3.5 and >3.5), temperature (25°C and 60°C) and neutralization dosage (1000 µL and 2000 µL). The synthesized schwertmannite was obtained using modified neutralization method. This research work involved preliminary trial runs using the neutralization method and also modification that have been carried out. In the synthesis using the neutralization method, about 500 mL of 0.05 M $Fe_2(SO_4)_3$ solution was mixed with 5 mL of 0.01 M H_2SO_4 solution to obtain an acidic environment in a reaction vessel. The experiment were followed by titration with 1 M of Na_2CO_3 under stirred condition into the mixing solution at every one minute to adjust the final pH to 3-4. The rate of the titration was 1000 µL/min. The residue were filtered using filter paper and followed by drying in the oven for 24 hours at 60°C. The yellowish powder samples were ground before characterization process. The characterization process that involved in this research works is X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray microscopy (SEM/EDX) and particle size distribution (PSA-MALVERN). For XRD, the synthesized schwertmannite has shown the mineral phases such as Fe, S and O. From SEM/EDX analysis results showed that iron

element was present in the precipitate. Particle size analysis shows that the X_{50} of the synthesized schwertmannite was in between 1.4 µm and 2.2 µm.

CHAPTER 1

INTRODUCTION

1.1 Introduction

In this research work, formation of iron oxides were done under several varying conditions. The parameter that were used in this experimental works are final pH, temperature, agitation speed and neutralization dosage. The parameter used is to studies the effective way in synthesis schwertmannite. Since schwertmannite is a metastable element, controlling the final pH is very important to synthesis schwertmannite.

Schwertmannite normally forms as a product of iron sulphide or pyrite weathering in normal environment. A few chemical formula can be describe for this complex process of FeS_2 oxidation. This complex process was investigated in numerous works. In the reaction [1-1] of one mole of pyrite (FeS_2) reacting with 3.75 mole of oxygen gas (O_2) and 3.5 mole of water (H_2O) produce one mole of iron hydroxide [$Fe(OH)_3$] and two mole of sulphuric acid (H_2SO_4).

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \leftrightarrow Fe(OH)_3 + 2\ H_2SO_4 \qquad (1.1)$$

$Fe(OH)_3$ represent the term for various Fe(III) oxides, hydroxides and Fe(III) sulphates. They are considered as ‘secondary minerals of pyrite oxidation’. Crystallization of the mineral goethite, jarosite, akaganeite, ferrihydrite and schwertmannite occurred depending on the chemical environment (Regenspurg. 2003). For example, jarosite is formed at pH between of 2-3, schwertmannite is formed at pH between of 3-3.5 and goethite is formed at pH between of 3.5 and above.

Naturally occurring soils, sediment or organic substrates (for example peat) that are formed under waterlogged conditions are called acid sulphate soils (ASS). These soils contain iron sulphide minerals which is mineral pyrite as the major mineral or their oxidation products. These secondary minerals play an important role in neutralizing the soil due to its potential in liberating acidity. Acid sulphate soil is a serious threat to agriculture, ecological system and infrastructure. Acidification and increase metal concentration in water (rivers, lakes and sea) can cause death of fish and other aquatic species and increase the risk of diseases among the aquatic species. Soil scalding, poor growth and shortening the life span of vegetation also occur as the result of severe acidification in terrestrial environments (Vithana, 2014).

Arsenic occurs in the natural environment in the oxidation states -3, 0, +3 and +5 and is found in about 200 different minerals including elemental arsenic, arsenides, sulphides, oxides, arenates and arsenites (Anonymous 2000; Riedel 1994). The most abundant mineral is arsenopyrite, $FeAsS$, which is often the host for gold. Arsenic is a well-known poison and is not element essential for the human body (Anonymous 2000). In water, arsenic is found in two oxidation states +3 and +5 (>11). The trivalent form, arsenic is hydrolysed as arsenous acid H_3AsO_3 and is present as the free acid or as one of the species resulting from its dissociation. The pentavalent form, arsenic is also hydrolysed as arsenic acid H_3AsO_3, and occurs as the non-dissociated acid or as their dissociated species. However, the two acids show completely dissociation patterns. Arsenic acid is almost completely dissociated at pH values >4, while arsenous acid shows substantial dissociation only at pH values >8. (Deschamps , Matschullat, 2011)

Schwertmannite, $Fe_8O_8(OH)_{8-2x}(SO_4)_x$ with x typically 1-1.75, is poorly crystalline Fe(III)-oxyhydroxysulphate mineral often formed in acidic iron and sulphate-rich (1000-3000 mg/L) environments (Bingham and Nordstorm, 2000; Bingham et al.,1990, 1994). Schwertmannite is a metastable phase and over weeks or months (Liao et al., 2011) it readily undergoes phase transformation to more stable iron oxides such as goethite under some pH and oxidizing conditions. (Antelo et al., 2012). However, it has been found that arsenic incorporated into schwertmannite retards or significantly inhibits the transformation into goethite (Fukushi et al., 2003; Regenspurg and Peiffer, 2005). Extremely high arsenic concentrations in acid mine effluent have been reported to be naturally decreased to background level by incorporation into schwertmannite (adsorption capacity up to 60 mg-As/g) within meters downstream of effluent outlets (Fukushi et al., 2003). The overall uptake of arsenic into schwertmannite is controlled by ligand exchanges with surface or structural SO_4^{2-} and/or surface precipitation (Carlson et al., 2002)

1.2 Problem Statement

Arsenic is an element that occurs naturally in sulphide minerals in soil and bedrock formations and has been deposited in the soil and bedrock layers over millions of years. Traces of arsenic are found in groundwater, lakes, rivers and ocean water. Around one-third of the world’s population drinks water from groundwater resources. Of this, about 10 percent, approximately 300 million people, obtains water from groundwater resources that are contaminated with unhealthy levels of arsenic or fluoride. These trace elements derive mainly from minerals. Extensive arsenic contamination of groundwater has led to widespread arsenic poisoning in Bangladesh and neighbouring countries. It is estimated that approximately 57 million people in the Bengal basin are drinking groundwater with arsenic.

Arsenic occurs in several types of geological deposits as porphyry copper or epithermal gold deposits. Oxidation of arsenic-sulphide in mine wastes stored at the surface and exposed to atmospheric conditions can release arsenic in the drainage water, Acid Mine Drainage (AMD).

Elevated arsenic content in surface and ground water is found in most gold mining project in Malaysia. The waste water from the mines are released or discharged to the nearby river. It may affect human if they drink the water from the river that contain arsenic. Long-term exposure to arsenic in drinking water can cause cancer in the skin, lungs, bladder and kidney. It can also cause other skin changes such as thickening and pigmentation. Regular exposure leads to cancer and other toxic health effects, including cardiovascular disease, skin hyperpigmentation, keratoses, neurological problems, and developmental disorders.

Mamut Copper Mine is one mine that has been closed because of the arsenic-contained acid mine drainage (AMD) in Malaysia. The mine is located in Sabah. During its operational phase, various environmental issues associated with the mine has been reported. The issues associated with the mine are water quality degradation and siltation. The major problem is acid mine drainage. Inputs of acid mine drainage (AMD) can adverse impact to the water quality and aquatic life of the receiving rivers. In fact, acid mine drainage (AMD) pollution is gradually becoming evident at Mamut Copper Mine (Jopony & Tongkul, 2009).

1.3 Research Objectives

The objectives of this research paper are:

- To synthesize schwertmannite at varying condition which is pH, temperature, speed of agitation and neutralisation dosage.
- To characterize schwertmannite by using four method of testing which is X-ray Diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Particle Size Analyse (PSA-MALVERN).

1.4 Significant of Work

Significant of this project are as follows:

- Outcome of this work would be used to remove arsenic contamination in mine water waste that flows to the nearest river. This is the major problem for most of mining companies around the world since arsenic is very dangerous to people especially people surrounding the mine.
- Avoid from using a lot of chemicals which can cost huge amount of money to treat the contamination of water with arsenic. This project can able to be implement in large industry scale.

- To prevent surrounding people from the exposure of arsenic by drinking water which contain contamination of arsenic. Arsenic poisoning or arsenicosis occurs when someone is exposed to high levels of arsenic, typically by unknowingly ingesting it.

1.5 Scope of Work

In this research work, the chemical reaction of acid solution and base solution are involved in synthesis of schwertmannite. The method that take place in this research work is neutralization method. Neutralization method is a chemical reaction in which a base solution was titrated into an acid solution.

For this research work, there are three chemicals involved such as iron (III) sulphate, sulphuric acid and sodium carbonate. Before the experiment begin, preliminary trial runs have been conducted in the laboratory in order to understand the basic methodology in the synthesis of schwertmannite.

Iron (III) sulphate, sulphuric acid and sodium carbonate were diluted to a certain concentration. Iron (III) sulphate was mixed with sulphuric acid to obtain an acidic environment and followed by titration of sodium carbonate for every minutes until reach pH around 3.5 under stirred condition of 250 rpm. The schwertmannite produced was filtered using a filter paper and dried for 24 hours in the oven at temperature of 60 °C. The dried samples then ground with agate mortar and pestle. Then were analysed using x-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray Spectroscopy (SEM/EDX) and particle size analyser (PSA-MALVERN) to know the morphology of the dry samples. Detail explanations on this experimental procedure were discussed in chapter three.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Schwertamnnite

Schwertmannite is naturally found as secondary iron mineral in pyrite oxidizing environments with the general formula $Fe_8O_8(OH)_6SO_4$ (Regenspurg et al. 2004). Schwertmannite is a ferric oxyhydroxysulphate mineral and was first found during the characterisation of ochreous precipitates collected from aid coal mine drainage in Ohio, United States of America (USA). Schwertmannite has attract so many interest in recent years due to high sorption capacity for toxic arsenic species (Houngaloune et al. 2014). Schwertmannite is a hazy tetragonal mineral regularly occurring as caramel yellow encrustations. The Mohrs hardness of the schwertmannite is between 2.5 and 3.5 and a specific gravity in between 3.77 and 3.99. There are two types of schwertmannite which are natural schwertmannite and synthetic schwertamnnite.

2.1.1 Natural Schwertmannite

Natural schwertmannite is a poorly crystalline Fe(III)-oxyhydroxysulphate mineral oftern produced in acidic iron and sulphate-rich environments (Houngaloune er al. 2014). The existence of schwertmannite as an ochreous precipitate has been widely documented in acid-sulphate system, including acid mine drainange (AMD) streams, waters and sediments of mine-pit lakes, acid-sulphate soils and associated waterways as well as bioleaching environments and in the layers covering wetlands treating acid mine drainage (AMD) (Houngaloune et al. 2014).

The composition of this poorly crystalline Fe(III)-oxyhydroxysulphate is uneven and the chemical formula that represented it is $Fe_8O_8(OH)_{8-2x}(SO_4)_x$, where x ranges is between 1 and 1.75. It is usually found in sulphate-rich environments such as lakes and water streams affected by acid mine drainage (AMD), and in acid sulphate soil systems, in which the precipitates has pH in between three to four. In order of its metastable nature, schwertmannite can undergo phase transformation to goethite, jarosite or to other more crystalline minerals within weeks or months, depending on the pH and oxidizing condition of the medium. Variations in the composition of the aqueous phase, mainly in total Fe, SO_4 and H^+, has been reported to occur through the transformation process.

The importance of schwertamannite is its ability to absorb the metal ions present in acid mine drainage (AMD) onto its surface. The schwertmannite works by lowering the aqueous concentration of such ion of these traces metals during the transformation of schwertmannite to other mineral phases. It is accepted that the more crystalline phases will have a lower capacity to retain trace elements either in their structure or on their surface. It is very important to be able to accurately anticipate the reactivity of schwertmannite to some target species and how this reactivity may be affected by the medium to long term mineral transformations that are likely to occur in such environments.

A few transformation research has been improvised to identify the mineral phase that determine the mobility and fate of contaminants in different natural environments, nearby surface waters and acid mine drainage (AMD). In order to modifying the rate of the transformation from schwertmannite to the more crystalline form, several factors were applied. The factors are pH value, temperature and the presence of organic matter, silica, Fe (II) and other ionic species. The transformation of schwertmannite which lead to the appearance of goethite in less than 100 days. The most unfavourable conditions are required much longer time such as up to years (Antelo et al. 2013).

Iron oxyhyroxides or known as ochreous are important products from the weathering of sulphide minerals such as pyrite, arsenopyrite, chalcopyrite, pyrrhotite and marcasite (Jonsson et al. 2005). The chemical composition of acid mine drainage (AMD) is fully controlled by the iron oxyhydroxides (ochreous) precipitates, among which the mineral schwertmannite plays an important role. Due to high surface area and specific structure with tunnels cavities of schwertmannite, it is classified by an exceptionally high sorption capacity. It may well hunt toxic components release in the weathering zone, avoiding them from migrating into surface or groundwater fast. Nevertheless, this mineral is metastable, thus its solubility due to dilution of acid mine drainage (AMD) and increase of pH, leads to a steady release of absorbed components (Parafiniuk & Siuda 2006).

Since the first explanation as a pure mineral phase, schwertmannite has been discovered in a number of environment, mostly overestimated by acid mine drainage (AMD) but also under undisturbed conditions. Naturally, it is in acidic form, sulphate-rich water draining through iron sulphide containing rocks and soils. Formation of schwertmannite seems to be directly related to the bacterially catalysed oxidation of Fe (II) (Regenspurg et al. 2004).

Schwertmannite has a massive reactive surface and capable of searching significant quantities of arsenic and other trace elements. Furthermore, schwertmannite can likewise affect extraordinarily on causticity flow by means of Fe (III)/Fe (II) cycling at the oxic/anoxic interface. Schwertmannite changes in this manner emphatically control water quality through controls on follow elements mobility and acidity dynamics (Burton et al. 2008).

Schwertmannite is a mineral of "weak crystallinity" which influences its complex identification. This can be clarified by its crystal structure as depicted which started to be isostructural to the mineral akaganéite (β-FeOOH). Its structure comprises of chain iron (III) oxide-adhydroxide-octahedra which are somewhat associated in a specific conduct to shape cavities between them. In these cavities anions are put away which for the most part comprises of chloride on case of akaganéite and of sulphate on case of schwertmannite. The capacity of sulphate causes a little modify in grid constants or in special crystal growth direction, separately.

Schwertmannite can enhance a variety of (potentially toxic) compounds by sulphate substitution as well as adsorption. In this manner this mineral could be of incredible importance as a sink in acidic waters. Nevertheless, as a result of ageing or because of changes of the hydrochemical condition, schwertmannite breaks down or changes into another mineral. In this manner, schwertmannite could discharge the prior improved components and therefore (also) act as source for these potentially toxic compounds. Consequently, a neutralization of acidic waters could demand an expansion of their harmfulness.

There have been widespread studies of the reactivity of the schwertmannite with heavy metal and hazardous anions schwertmannite in natural AMD or wastewater under acid pH conditions. Schwertmannite assumes a fundamental part as an actually occurring attenuator for species, for example, arsenate and metals in AMD systems. As a result of its highly particular surface area (e.g., 240–320 m^2/g for engineered and 125–225m^2/g for characteristic examples) and its positive surface charge in these acid systems, schwertmannite can competently expel oxyanions from acid waters. Schwertmannite may hold-up the portability of anions and cations exhibit in these systems, by co-precipitation with the iron mineral oxide or by adsorption procedures to the previous schwertmannite. It has been accounted for that gigantically high arsenic focuses in acid mine effluents was normally diminished to foundation levels by consolidation into schwertmannite (adsorption limit up to 60 mg/g) inside meters downstream of gushing outlets. The general take-up of arsenic into schwertmannite is constrained by ligand trades with surface or structural ${SO_4}^{2-}$or potentially surface precipitation (Houngaloune et al. 2015).

2.1.2 Synthetic Schwertmannite

Synthetic schwertmannite is the same with natural schwertmannite. The distinction is synthetic schwertmannite is integrated by experiments in a laboratory with the controlled factors or parameters. The synthetic schwertmannite is created through cutting edge research and described to recognize the potential or capacity as passage depressions. There are three techniques to synthesis schwertmannite which is neutralization, dialysis and oxidation.

Neutralization method is a chemical reaction in which an acid and a base respond quantitatively with each other. In a reaction in water, neutralization results in there being no excess of hydrogen or hydroxide ions present in solution. The pH of the neutralized solution depends on upon the acid strength of the reactants. The neutralization method is a faster technique than other two technique and it might takes around 20 to 30 minutes in one running experiments depends on the controlled variables or parameters.

Schwertmannite was synthesized as follows: 500 mL of solution containing 10 mM H_2SO_4 and 50 mM Fe^{+3} was prepared and heated up to 65 °C in a beaker under magnetic stirring at 250 rpm. After discontinuing the magnetic stirring 1 M Na_2CO_3 was titrated to the solution for adjust the last pH to 3-4 with the titration rate of 1500 µL/min. The resulting suspension was left to resolve and several millilitres of supernatant were collected for analysis. Subsequently, the solution remaining in the beaker was replaced with deionized water and this rinsing procedure was repeated 5 times to eliminate soluble ions.

It is critical to locate an appropriate method to control or balance out the dangerous arsenic species that could be discharged from such gigantic measures of waste at copper mines. Stabilization of arsenic has been anticipated with an assortment of methodologies, for example, solidification/stabilization procedure, arsenic transfer as scorodite, immobilization by schwertmannite. Among the recent treatment processes for arsenic control at copper mine waste, retention of As by schwertmannite has fascinated much attention in recent years due to its strong binding affinity to toxic As species. It can likewise be savvy as it is conceivable to combine scwertmannite from arrangements produced in load drain operations. Such filter arrangements regularly contain high centralization of Fe^{+3} and ${SO_4}^{2-}$, the segments of schwertmannite (Houngaloune et al., 2014).

Schwetmannite can be synthesized by some different techniques, for example, dialysis b including ferric chloride/nitrate to sodium/potassium sulphate solutions at 60°C; oxidation of $FeSO_4$ solutions by H_2O_2; and biooxidation of $FeSO_4$ solutions by acidithioacillusferrooxidans. These methods may not suitable for schwertmannite era at porphyry copper mines. For instance, the dialysis strategy needs a time of over 30 days to be dialyzed against deionized water, which is a time-consuming and inefficient work on-site synthesis of schwertmannite at copper mines (Houngaloune et al. 2014).

On-site synthesis of schwertmannite is of financial and natural enthusiasm for As evacuation in porphyry copper mines. For the most part, effluents of copper heap leaching are complex solution, containing a scope of constituents, for example, Cu (0.5-4.0 g/L), Fe (0.5-10 g/L), S (2.5-20 g/L), and others. The leach solutions contains high concentrations of $Fe^{3+}$and ${SO_4}^{2-}$, the parts of schwertmannite, recommending that the solutions can be utilized for schwertmannite synthesis. On-site union is required to be performed by balance of the filter answers for pH 3-4. Be that as it may, the leach solutions likewise contain huge convergences of Cu^{2+} and Fe^{2+} as coinciding particles, and the impacts of these particles on schwertmannite is not notable.

On-site synthesis of schwertmannite is of productive and ecological enthusiasm for As evacuation in porphyry copper mines. Effluents of copper heap leaching are complex solutions, containing a scope of constituents, for example, Cu (0.5–4.0 g/L), Fe (0.5– 10 g/L), S (2.5–20 g/L), and others. The leach solution contain high concentrations of Fe^{3+} and SO_4^{2-} the segments of schwertmannite, suggesting that the solutions can be utilized for schwertmannite synthesis. In this way, this part gives close into the synthesis of schwertmannite in porphyry copper mines by exploring the impact of existing together metal particles (Cu^{2+} and Fe^{2+}) and the response temperatures (25˚C and 65˚C) on the union of schwertmannite by balance strategy.

2.2 Other Mineral

2.2.1 Transformation of Schwertmannite to Jarosite

Schwertmannite and jarosite are two of the primary optional iron(III) minerals for the most part found in acidic, iron and sulphate-rich conditions, for example, acid mine drainage (AMD) and coastal acid sulphate soils (CASS). Both minerals utilize real impact on the water and soil quality in these situations While there are many studies conducted on the stability of these two minerals under controlled laboratory circumstances, the behaviour of schwertmannite and jarosite under field circumstances and the factors influencing their behaviour have not been investigated directly (Vithana et al. 2015).

Schwertmannite ($Fe_8O_8(OH)_6SO_4$) and jarosite ($KFe_3(SO_4)_2(OH)_6$) are the two main secondary iron (III) minerals generally found in acid mine drainage (AMD). In natural environments, schwertmannite and jarosite are produced as a result of iron sulphide oxidation. Schwertmannite is also known to precipitate directly from acidic, sulphate rich waters (Vithana et al. 2015).

Both minerals will step by step change to goethite and additionally other thermodynamically stable mineral stages, resulting in the release of a considerable amount of acidity and previously held trace metals [Equations. (2.1) and (2.2)]. The release of acidity and mobilization of trace elements can have an effect on both terrestrial and aquatic environments (Vithana et al. 2015).

$$2H_2O + Fe_8O_8(OH)_6(SO_4) \rightarrow 8FeOOH + SO_4^{2-} + 2H^+ \quad (2.1)$$

$$3H_2O + KFe_3(SO_4)_2(OH)_6 \rightarrow 3Fe(OH)_3 + 2SO_4^{2-} + 3H^+ + K^+ \quad (2.2)$$

While both minerals are crucial sources of acidity, these minerals are additionally known to influence the mobilization of the toxic trace metals in the ASS, going about as scroungers. Schwertmannite, on because of its typically nano-particulate size and bigger surface region is a proficient sorbent for some follow metals. Jarosite has a chemical structure that allows the exchange of an variety of metals, thereby also acting as an effective scavenger for trace metals (Vithana et al. 2015).

Jarosite is partner of the iso-structural jarosite-alunite group. It has likewise been found on the surface of Mars in light of the spectroscopy finding by the opportunity meanderer. Schwertmannite has a passage arrangement likened to akaganéite (β-FeOOH) with high particular surface region, surface reactivity and poor crystallinity (Zhu et al. 2013).

Jarosite and schwertmannite have gained growing interest in geological, environmental, metallurgical fields in recent years, because it can scavenge heavy metals and some toxic ion efficiently by adsorption, co-precipitation or structural incorporation/substitution. Research shows that the most extreme adsorption limit of schwertmannite to arsenate can reach up to 113.9 mg/g. Both of trivalent and hexavalent chromium can be isolated from the aqueous solution by these iron oxyhydroxide materials. Cadmium and lead would be incorporated into jarosite amid its precipitation procedure. The adsorption conduct of copper to schwertmannite in presence of broke down natural matter has likewise been contemplated. Schwertmannite and jarosite have the adsorption capacity to all the heavy metals. The scavenging ability of these materials is strongly linked with their morphology, size, and crystallinity (Zhu et al. 2013).

2.2.2 Transformation of Schwertmannite to Geothite

Schwertmannite is also acknowledged as a metastable compound that is transformed to stable crystalline goethite via dissolution and re-precipitation. The overall reaction of the phase transformation can be expressed as:

$$Fe_8O_8(OH)_{8-2x}(SO_4)_x + 2xH_2O \rightarrow 8FeOOH + xSO_4^{2-} + 2xH^+ \qquad (2.3)$$

The transformation is a very moderate process requiring years or decades in acidic and oxic situations. This transformation procedure is regularly upgraded in higher pH situations, however needs over 100 days under close impartial, oxic conditions. It revealed that one-year time span for complete transformation of schwertmannite to goethite at pH-8. Schwertmann and Carlson watched entire change of schwertmannite to goethite in deionized water at pH 7.2 following 100 days. In contrast, incomplete change at pH 6 following 543 days of maturing was accounted for by Jönsson et al (2005). Subsequently, schwertmannite tends to accumulate and hold on in oxic and acidic conditions, for example, inside depleted acid sulphate soil (ASS) scene. Recently, it have been found that Fe (II)- catalysed change of schwertmannite can be massively fast under close impartial and anoxic conditions (Houngaloune et al. 2015). The plausible response for the change by these authors was:

$$Fe_8O_8(OH)_{5.5} + 2.5H_2O \rightarrow 8FeOOH + 1.25SO_4^{2-} + 2.5H^+ \qquad (2.4)$$

Other experimental studies on synthetic schwertmannite, the rate of the transformation into goethite was deliberately for high sulphate focuses, low pH and low temperature. High measures of As in synthetic schwertmannite have also been shown to delay or inhibit the transformation into goethite. The transformation of schwertmannite into goethite has also been recommended to happen in nature. For example, schwertmannite was found had transformed into goethite, in vertical sediment profiles of a developed mine seepage wetland (Acero, Ayora, Torrentó, and Nieto, 2006).

The adjustment of ferrihydrite to goethite occurs actually in acidic and basic solutions through reconstructive transformation including the disintegration of ferrihydrite and re-precipitation of goethite. At neutral pH, ferrihydrite is exceptionally insoluble and the change to goethite can only progress in the presence of a catalyst, for example, Fe (II)(aq). Since Fe (II) (aq) is stable and assembles in high focus under anoxic non-sulfidic conditions, this change pathway can assume an essential part in the development of goethite at redox transition zones. Although, the rate of transformation is inadequately restrained, to a great extent because of an absence of in situ continuous information (Yee et al. 2006).

In acidic sulphate solutions, the pH of schwertmannite presence extends in the range between 2.5 and 4.5, while jarosite exist at pH < 2.5 (Cravotta et al., 1999). Schwertmannite formation seems to be directly related to the bacterially catalysed oxidation of Fe^{2+}. Recently, its role in the electron cycling in the sediment of an acidic lignite mining lake (AML) had been strained, where schwertmannite serves as an electron acceptor for Fe (III) reducing bacteria. Its change to goethite discharges acidity, a procedure which seems to obstruct sulphate reduction in the sediment and to support an acidic iron cycle at the sediment-water boundary. Schwertmannite can be a key transitional in the movement process from iron reducing to iron oxidizing conditions (Regenspurg et al. 2004).

2.3 Introduction of Arsenic

Recently, the natural fate and behaviour of arsenic (As) is getting greater consideration because of the arsenic (As) contamination in South-East Asia. In spite of the fact that As defilement in nature has been expressed worldwide, be that as it may, arsenic contamination in groundwater has been a genuine wellbeing danger to the individuals in South-East, South-West and North-East USA, inward Mongolia (China), South-West Taiwan seaside locales, Sonora (Mexico), Pamplonian Plain (Argentina), West Bengal (India), Northern Chile, and Bangladesh. The World Health Organization (WHO) considered that As in Bangladeshi groundwater to be "the biggest mass harming of a population ever".

Arsenic is bottomless in the earth and profoundly poisonous to all types of the life. It is a crystalline "metalloid", a natural element with landscapes middle between metals and non-metals, occurs naturally as an element, ranks as the 20th most arising trace element in the earth's crust, 14th in seawater, and 12th in the human body. Arsenic exists in four oxidation conditions – arsenate(As^{v}), arsenite (As^{III}), arsenic (As^{0}), and arsine (As^{-III}) and its solubility be dependent upon the pH and ionic condition. Among them, the As^{V} being the most stable form.

As^{V} is thermodynamically steady in state in aerobic water, while As^{III} is significantly present in redox environment. Arsenic can be available in the earth in a few compound structures, for example, monomethylarsonic acid [MMA:$CH_3AsO(OH)_2$], dimethylarsinic acid [DMA;$(CH_3)AsOOH$], trimethylarsine oxide [TMAO;$(CH_3)_3AsO$], arsenobetaine [AsB:$(CH_3)_3As + CH_2COOH$], arsenocholine [AsC], arsenosugars [AsS], arsenolipids and so forth. In generally speaking, inorganic arsenicals are more poisonous than natural ones (Singh et al. 2015).

As^{III} is regularly more toxic than As^{V}, and dimethylarsinous acid (DMAAIII) and monomethylarsonous acid (MMAAIII) are more dangerous than their parents mixes (Petrick et al., 2000; Mass et al., 2001). Methylated As mixes, for example, MMA, DMA and TMAO are discovered once in a while as a minor component in soil, however can achieve high in concentration. Both MMA and DMA (otherwise called cacodylic acid) have been comprehensively utilized as pesticides and herbicides, the DMA additionally as a cotton defoliant (Singh et al. 2015).

Arsenobetaine, the preeminent As species in marine creatures, was originate to be present in an acidic fen soil with unclear origin. Arsenolipid, a lipid-soluble As compound, generally found in the marine organism, and its concentration may reach up to 16mg As/kg fish oil. Most recent discoveries prescribed the accompanying request as far as intense As harmfulness: MMA (III) > As(III) > As(V) > DMA(V) >MMA(V), where the MMA(III) metabolite is the most poisonous compound and a few scientists measured it to be the focal As method of activity (Singh et al. 2015).

The uses of arsenide is in solidifying of composites and underway of semi-conductors, colours, glass fabricating, pesticides, rodenticides and fungicides. Moreover, arsenic likewise utilized as an element of medications for the treatment of a few illnesses (e.g. dozing disorder and endless myeloid leukaemia). In light of its comfort and improvement, arsenic pollution is presently broad in the earth. In as much as poisonous mixes of arsenic could happen actually or anthropogenically in the earth, an insightful of its lethal impacts is justified (Duker et al. 2005).

Arsenic is a semi-metal. In its metallic form it is bright, silver-grey and brittle. Arsenic is a recognizable toxin. Arsenic mixes are every so often utilized as rodent toxic substances and bug sprays yet their utilization is extremely controlled. Out of the blue arsenic can likewise have restorative applications. In Victorian circumstances, Dr Fowler's Solution (potassium arsenate disintegrated in water) was appreciated cure-all tonic that was even utilized by Charles Dickens. Today, organo-arsenic mixes are added to poultry nourish to forestall illness and create weight pick up. Another employments of Arsenic is as a doping specialist in semiconductors (gallium arsenide) for strong state gadgets. It is additionally utilized as a part of bronzing, fireworks and for solidifying shot. Arsenic mixes can be utilized to make extraordinary glass and save wood.

A few researchers feel that arsenic might be a fundamental component in our eating routine in, low doses. In little dosages it is lethal and a speculated cancer-causing agent. Once inside the body it bonds to iotas in the hair, so investigating hair tests can indicate whether somebody has been presented to arsenic. A few nourishments, for example, prawns, contain a stunning measure of arsenic in a less hurtful, natural frame.

Arsenic was recognized to the old Egyptian, and is said in one papyrus as far of overlaying metals. The Greek scholar Theophrastus knew about two arsenic sulphide minerals: orpiment (As_2S_3) and realgar (As_4S_4). The Chinese likewise thought about arsenic component as the compositions of Pen Ts'aoKan-Mu. He accumulated all his awesome work on the common world in the 1500s, amid the Ming line. He noticed the danger related with arsenic mixes and specified their utilization as pesticides in rice fields.

Another hazardous type of arsenic, called white arsenic, has likewise been long notable. This was the trioxide, As_2S_3, and was a by-result of copper refining. At the point when this was blended with olive oil and warmed it yielded arsenic metal itself. The disclosure of the component arsenic is credited to Albertus Magnus in the 1200s.

Arsenic happens in two allotropic structures. Allotropes are types of a component with different physical and chemical properties. The more broad type of arsenic is a shiny, grey, brittle, and metallic-looking strong. The less broad shape is a yellow crystalline strong. It is shaped when vapours of arsenic are cooled all of a sudden. Whenever warmed, arsenic does not soften, as most solids do. Rather, it changes straightforwardly into a vapour (gas). This procedure is known as sublimation. Be that as it may, under high weight, arsenic can be compelled to dissolve at around 814°C (1,500°F). Arsenic has a thickness of 5.72 grams for every cubic centimetre.

Arsenic is a metalloid. A metalloid is a component that has properties of both metals and non-metals. Metalloids happen in the occasional table on either side of the staircase line that begins amongst boron and aluminium. At the point when warmed in air, arsenic implants with oxygen to frame arsenic oxide (As_2S_3). A blue fire is framed, and arsenic oxide can be perceived by its unmistakable garlic-like smell. Arsenic joins with oxygen all the more continuously at room temperatures. The thin covering of arsenic oxide that structures on the component keeps it from responding more. Arsenic does not break down in water or most icy acids. It reacts with some hot acids to frame arsenic acid (H_3AsO_3) or arsenic acid (H_3AsO_4).

Arsenic is fundamentally utilized as a part of compounds. A substantially littler amount of the element itself is utilized as a part of alloys. For instance, a few sections of lead stockpiling batteries utilized as a part of autos and trucks contain alloys of lead and arsenic. Arsenic likewise used to make lead shot before. The measure of arsenic utilized as a part of these applications is probably going to keep on lessening. It is too simple for arsenic to get into the earth from such applications.

Minute measures of arsenic are utilized as a part of the electronics industry. It is joined to germanium and silicon to make transistors. A compound of arsenic, gallium arsenide (GaAs), is likewise used to make light-radiating diodes (LEDs). LEDs deliver the lit numbers close by held calculator, clocks, watches, and various other electronic gadgets.

2.3.1 Sources of Arsenic

The primary source of As in the earth (hydrosphere, pedosphere, biosphere and environment) is the arrival of As from As-enriched minerals. The sources of As incorporates both normal i.e. from start to finish disintegration of As mixes adsorbed onto pyrite metals into the water by geochemical elements and anthropogenic i.e. amid utilization of bug sprays, herbicides and phosphate composts, semi-conductor ventures, mining and purifying, mechanical procedures, coal burning, timber additives and so forth. A study of occurrence of As in groundwater/drinking water, fresh waters, marine waters, soil and food stuffs is given below (Singh et al. 2015).

(a) Groundwater/Drinking Water

As per the WHO rules, the recommended furthest reaches of arsenic in drinking water is 0.01mg/L. Be that as it may, the levels of As in unpolluted surface water and groundwater shift by and large from 1–10 μg/L. Groundwater convergences of As is accounted for to be enormous range from under 0.5–5000 mg/L covering normal As pollution found in more than 70 nations (Ravenscroft et al., 2009). The As sullying in groundwater in various parts of the world is brief in Table 2.1.Huge ranges of Bangladesh, West Bengal and different conditions of India and Vietnam depend on As debased groundwater for water system of staple harvests, for example, rice (Singh et al. 2015).

Defilement of drinking water is the fundamental source of As for individual however for the populace not revealed to lifted As in drinking water, utilization of nourishment developed in As-debased soil or inundated with As-polluted water speaks to the principle wellsprings of As admission for people, which causes an existence debilitating inconvenience for a huge number of individuals in vast ranges of South-East Asia. For instance, as of late inorganic As introduction drawn mindfulness through sustenance, since some nourishment things particularly rice and vegetables were accounted for to contain high inorganic As fixations in territories with hoisted As in soil and water system water (Singh et al. 2015). Figure 2.1 show the global probability of arsenic contamination of groundwater.

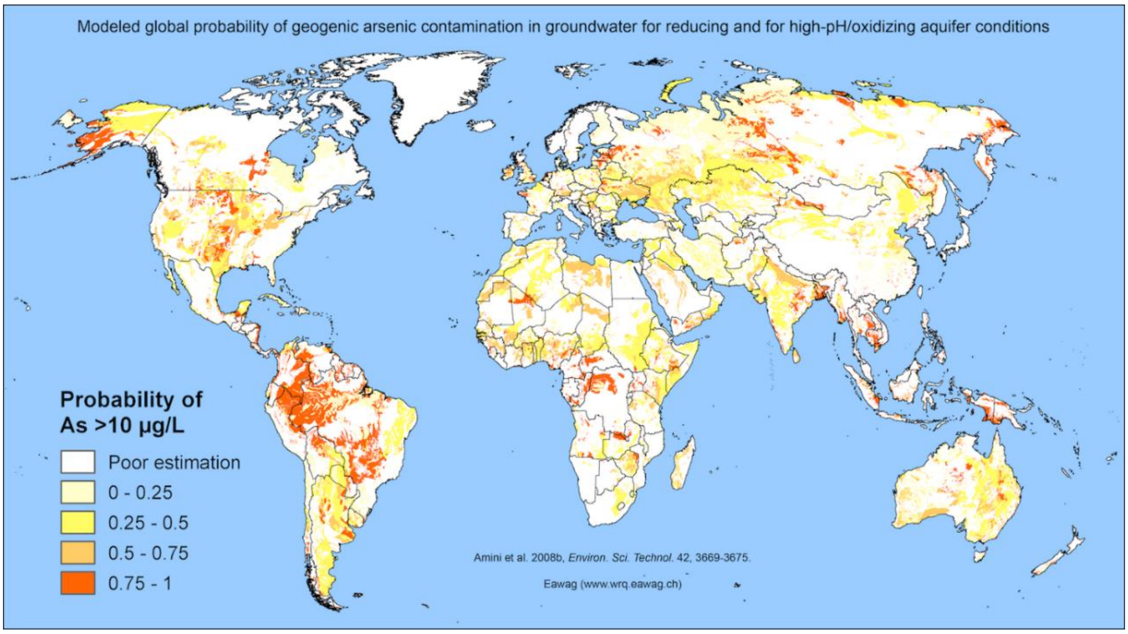

Figure 2.1: Global probability of arsenic contamination of groundwater.

(b) Freshwater

In freshwater systems (rivers and lakes), the distinction in As fixation is in the scope of 0.15–0.45 μg/L relying upon the source, accessibility, and geochemistry of the catchments. Fundamental As focuses in the water of an assortment of tainted streams go between 0.1 to 2.1 mg/L with a normal of 0.8 mg/L, which may be because of the source of contamination, surface revive, base stream, and the bedrock lithology. The geothermal data sources, dissipation, and groundwater defilement are the centre reason for high groupings of As in streams. For instance, in Lao River of Northern Chile the high groupings of As (up to 21,000 mg/L) is because of the previously mentioned forms. Mining action additionally given high possibility of the event of high As focuses in stream waters. For instance, water of Mole River, New South Wales, Australia has abnormal amounts of As (from 110–600 mg/Lupto 13,900 mg/L) from the mining and preparing of arsenopyrite metals (Singh et al. 2015).

As concentrations in lake waters are near or lower than that recorded for river waters. As concentrations was examined in lakes around British Columbia and Canada run in the vicinity of 0.2 and 2.08 mg/L, has been transported from the deserted Cariboo Gold Quartz mine tailings of that zone, and gets amassed in high concentrations (up to 1104 mg/g) in the base residue of the lakes. Geothermal sources and mining works have likewise rise the rate of convergences of As in lake waters. In mine influenced lake waters, the As concentrations are modestly low due to its adsorption onto Fe oxides under nonpartisan pH and furthermore from its aggregation in base residue (Singh et al. 2015)