

IMMOBILIZATION OF ARSENIC IN MINE TAILINGS USING STANDARD AND NANOSCALE METAL OXIDES

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ABSTRACT

IMMOBILIZATION OF ARSENIC IN MINE TAILINGS USING STANDARD AND NANOSCALE METAL OXIDES

Sevag Derghazarian

Elevated levels of arsenic can be found in mine tailings, sediment and soil samples. Leaching of arsenic from tailings can lead to the contamination of surface and groundwater. One potentially sustainable method is to add various agents to stabilize the waste and ensure that arsenic does not leach out of the waste. In the current study, the effectiveness of various types of metal oxides as immobilizing agents was tested. Leaching tests and SSE (Selective Sequential Extraction) were performed on different mixtures of mine tailings and metal oxides, using different weight ratios, reaction times, types of oxides. The mine tailings were taken from different sites in Canada.

The metal oxides used were either regular (commercial grade) or nanoscale powders. The additives evaluated were MgO, ZnO, Fe₃O₄, TiO₂, CaO and Al₂O₃. These additives were chosen for their successful use as commercial agents in chemical decontamination. The leaching tests were done using a solution of distilled water and sulphuric acid at a pH of 3 to simulate acid rain fall on the mine tailings that could occur. The concentration of arsenic in the leachate was measured using arsenic test kits and ICP-MS instrumentation.

It was found that both regular and nanoscale ZnO (zinc oxide) had the highest capacity to immobilize the arsenic present in the mine tailings, whereas the other metal oxides tested and Fe₃O₄ (magnetite) had little or no effect. Leaching tests performed on Noranda and Golden Giant mine tailings over a 24 hour period revealed that the addition of 7.5% in weight of nanoscale ZnO caused a 99.4% to 99.7% reduction in the amount of arsenic leached into solution of distilled water at a pH of 3. A 91% to 92% reduction was observed when the additives were left to immobilize the tailings for a period of 1 month.

SSE tests confirmed that ZnO is a very effective immobilizing agent in all of the five chemical phases and stable on a long-term basis. SSE tests showed a reduction in the amount of arsenic leached by a factor of more than 31 in the exchangeable phase, and by a factor of 4.9 in the water soluble phase, and 5.1 in the carbonate phase for Noranda mine tailings treated with 7.5% regular grade ZnO. Leaching from each of the other phases was also minimized. These results indicate the possibility of developing a sustainable remediation process for mining areas as well as other contaminated soil using ZnO. Further studies on immobilization are recommended using ZnO in conjunction with other metal oxides or compounds that would improve efficiency, reduce costs and minimize the leaching of zinc into the soil.

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It is my sincere wish that this work be of use to the environment and help in our ongoing battle against arsenic poisoning across the world.

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NOMENCLATURE

ACA	Ammoniacal Copper Arsenate
AZCA	Ammoniacal Zinc Copper Arsenate
B	Beringite
CCA	Chromated Copper Arsenate
CCME	Canadian Environmental Quality Guidelines
CED	Centre for Environment and Development
CEPA	Canadian Environmental Protection Agency
DMA	Dimethyl Arsenic
EDTA	Ethylenediaminetetraacetic Acid
ENVIRODAQ	Environmental Markets Index
EPA	Environmental Protection Agency
EXAFS	Extended X-Ray Absorption Fine Structure
FAAS	Flame Atomic Adsorption Spectrometry
HG-AAS	Hydride Generation Atomic Adsorption Spectrometry
IARC	International Agency for Research on Cancer
ICP-MS	Inductively Coupled Mass Spectrometry
IOCS	Iron Oxide Coated Sand
MITHE-SN	Metals in the Human Environment Research Network
MMA	Monomethyl Arsenic
SPLP	Synthetic Precipitation Leaching Procedure
SS	Steel Shots
SSE	Selective Sequential Extraction
WHO	World Health Organization

1 Introduction

1.1 Statement of purpose

Arsenic (As) is a highly toxic metalloid and is widely distributed in soil, rocks, water and the earth's crust (WHO, 2001). It is carcinogenic to humans and animals, and has been classified, along with its various compounds, as a Group I carcinogen (IARC, 1987).

Arsenic was first isolated in 1250 by Albertus Magnus, a Dominican Bishop from the Middle-Ages (Vidac and Pohland, 1996). Its most common natural occurrence is in the form of the natural mineral arsenopyrite (FeAsS). It is also found in arsenides of some metals such as cobalt, silver and nickel and also as sulfides. Its presence in organic form is very rare (Wang and Mulligan, 2006). It is introduced into water by the dissolution of ores and minerals.

The long term exposure to arsenic causes cancer of the kidney, lungs, skin and bladder. Acute arsenic poisoning causes bloody diarrhea, vomiting and abdominal pain. Other than these diseases, arsenic has also been associated with hypo and hyper pigmentation, keratosis, hypertension, cardiovascular diseases and diabetes (Jack et al., 2003). It has been estimated that 60 to 100 million people in India and Bangladesh alone are at risk from the consumption of water contaminated with arsenic (Ahmad, 2001; Chakraborti et al., 2001).

It has been found that drinking water with concentrations of arsenic in excess of 0.05 mg/L increases the risk of lung and bladder cancers and skin lesions. At this concentration, the risk of developing cancer is as high as 1/100 (Jack et al., 2003). The current guidelines for drinking water have been established as less than 0.01 mg/L by the WHO. However many developing countries still have the guidelines at 0.05 mg/L. Arsenic in drinking water can occur naturally or as the result of anthropogenic activity (WHO, 2001).

Therefore strategies for preventing arsenic from leaching into the environment are imperative, for the well-being of millions of people, as well as other living beings on this planet. Many technologies are available for the remediation of arsenic whether in soil,

water, or air. However, any proposed solution must be efficient as well as cost effective to be applied on a large scale and in any given environment.

A few of the methods for the removal of arsenic from water include flocculation, reverse osmosis filters as well as ion exchange (Naidu and Bhattacharya, 2006). In addition, low cost alternatives such as auto-attenuation or using natural geological material as adsorbents for arsenic are emerging especially in third world or developing countries (Genç-Fuhrman et al., 2004, 2005; Naidu and Bhattacharya, 2006; Vithanage et al., 2006).

Other methods aimed at remediating arsenic-contaminated soil are phytoremediation, chemical stabilization and burial. Except for phytoremediation, these methods can pose the risk of instability and chemical leakage (Allen, 2001; Förstner and Haase, 1998). In the case of stabilization, it is therefore important to ensure that it remains effective over time.

Currently the method of treated polluted waters is the favoured remediation strategy for many contaminants, including arsenic. Several treatments have been carried out such as sorption/desorption, ion exchange and membrane separation (Gupta and Chen, 1978; Jekel, 1994; Kartinen and Martin, 1995; Korngold et al., 2001). The sorption methods developed include the use of many different substances such as activated alumina, mesoporous silica, modified zeolites and activated carbon. Ferric oxides and hydroxides have been successfully used to remove both As (III) and As (V) from waters. However successful, the removal of arsenic from water is a costly method for even the most primitive installation (Seidel et al., 2005). Furthermore, such methods require continuous operation since the source of pollution is not attenuated and will continue to leach over time.

Less research has been done on treating arsenic at the level of the source materials using adsorbents. The current study's objective is to evaluate a few nanoscale materials as well as regular metal oxides and explore their potential in immobilizing high levels of arsenic

present in contaminated mine tailings. One additive, in particular, nanoscale magnetite (Fe_3O_4) has been used successfully as an adsorbent of As in water filtration systems. It, along with zinc oxide (ZnO), was especially evaluated for their effectiveness on a short and long term basis. Previous studies which have been conducted in this area are found in more detail in the literature review section.

Nanoscale metal oxides were selected for their high surface area per weight ratio and small size which could increase their mobility within the soil, as well as their chemical reactivity and adsorption potential.

1.2 Objectives

The main objective of this study is to determine the effectiveness of 8 metal oxides in immobilizing arsenic in mining residues. As mentioned in the introduction, it is important that the immobilization of arsenic caused by the additives remain stable over time, despite the effects of temperature variations, changes in pH and water. To determine the effectiveness of the different additives, leaching tests were carried out, and to test the chemical stability of the immobilized soil, Selective Sequential Extraction (SSE) tests were carried out after stabilization over a period of 1 to 2 months.

The specific objectives of this study are to:

- Determine the effectiveness of 8 different metal oxides at immobilizing arsenic in two selected mine tailings.
- Evaluate the stability of the most promising metal oxides added to the soil by performing SSE (Selective Sequential Extraction) tests.

1.3 Plan of Thesis

This thesis consists of five chapters, a list of references, appendices and a list of figures and tables. In Chapter 2, we present a literature review from various articles in regards to arsenic, its sources, concentrations in water and soil, and various established remediation methods. In Chapter 3, we present the methods and materials used to conduct the experiments and measure the results. We give a summary of each of the devices and experimental setups used to conduct the research. In Chapter 4, we present the results and

findings of this study, and give explanations and analyses. The last chapter contains conclusions of the thesis and recommendations for further work.

2 LITERATURE REVIEW

2.1 Arsenic - An Overview

Arsenic is produced commercially by the reduction of arsenic trioxide using charcoal. Arsenic trioxide is produced as a result of smelting operations. (Jack et al., 2003). Particularly in Canada, it is manufactured by the roasting of gold ores (Wang and Mulligan, 2006). Its production has varied tremendously from 1885 until the present, reaching nearly 7000 tonnes in the early in 1940s.

Arsenic can be found mainly in 4 oxidation states: (-III, 0, III, V). The -III oxidation state is present only in extremely reduced conditions and pure arsenic metal is rarely found in nature. As (III) and As (V) are the most common forms of arsenic to occur in nature (Boyle and Jonasson, 1973; Cherry et al., 1979). The toxicity and mobility of arsenic depends on its speciation and As (III) is considered many times more toxic and mobile than As (V). To be more precise, the toxicity of As (III) is 25 to 60 times more than As (V) (Dutre and Vandecasteele, 1995; Corwin et al., 1999). Generally, inorganic forms of arsenic are also many times more toxic to humans with the exception of a few organic methylated species of arsenic, such as the methylated species MMA, DMA MMA (III) and DMA (III) (Jack et al., 2003). Table 2-1 summarizes the different levels of arsenic contamination in various countries around the world. The maximum permissible concentration of arsenic by the WHO is 10 µg/L.

Table 2-1 Arsenic contamination around the world in groundwater and coal and different populations at risk around the world

Country or Area	Exposed Population	Groundwater Conc. ($\mu\text{g As/L}$)
Argentina	2 000 000	100 – 1000
Bangladesh	50 000 000	1 – 4700
Chili	437 000	900 – 1040
China, Guizhou	20 000	100 – 10000 mg/kg
Hungary	220 000	10- 176
India, West Bengal	1 000 000	10 – 3900
Mexico	400 000	10 – 4100
Peru	256 000	500
Taiwan	200 000	10-1800
Vietnam	Millions	1-3050

Source: (Jack et al., 2003)

As explained in the introduction, arsenic is a highly toxic metalloid that can provoke many diseases.

2.2 Arsenic Sources in Canada

Since the present study was conducted on mine tailings in Canada, it was felt to be appropriate to present an overview of the problem of arsenic contamination in Canada. It also gives a better insight into where the current research can be applied locally.

Canadians are exposed to arsenic through air, water and soil. High levels of arsenic present in the environment can be either due to natural sources or to anthropogenic activity. In Canada, the main sources of arsenic are from anthropogenic activity: from the roasting of arsenious gold ores, the use of arsenic based wood preservatives, the disposal of arsenic containing industrial and domestic wastes as well the processing and combustion of coal (Wang and Mulligan, 2006).

The most common natural sources of arsenic are from volcanic rocks, marine sedimentary rocks, hydrothermal ore deposits and fossil fuels (coal and petroleum) (Korte and Fernando, 1991; Smedley and Kinniburgh, 2002). The most common arsenic containing rocks are arsenopyrite (FeAsS), orpiment (As_2S_3) and realgar (AsS). Very

high levels of arsenic have been reported in Canada up to $6.5 \mu\text{g}/\text{m}^3$ in the air, soils 25,000 mg/kg in soils and surface and groundwater 1570 mg/L (ENVIRDOQ, 1997; Coumans, 2003; Newhook et al., 2003). As a comparison, the average levels of arsenic in surface and groundwater in Canada range from .001 to 0.002 mg/L (BCMWLAP, 2002), $0.00062 \pm 0.00028 \mu\text{g}/\text{L}$ in Canadian air (Newhook et al., 2003) and 4.8 to 13.6 mg/kg in Canadian soils (CCME (1999/2002); CED (2003)). Some of the different sources of natural and anthropogenic arsenic are: mining, smelting, pesticides, fertilizers, wood, preservatives, volcanoes, fossil fuel, combustion, industrial process, municipal wastes, military activities and water treatment (Wang and Mulligan, 2006).

The most significant source of exposure for Canadians is through the ingestion of food and contaminated water. The global average arsenic concentration in soil uncontaminated through anthropogenic activities is about 5-6 mg/kg. The natural concentration of arsenic in various uncontaminated soils in Canada varies tremendously. An acid sulphate soil in Northwestern Alberta was found that contained a maximum of 37.9 mg/kg of arsenic. An extremely high level of arsenic up to 4600 mg/kg was found in the soil of A2 horizon in British Columbia (Wang and Mulligan, 2006). Global levels of arsenic in water were found to range from $0.02 \mu\text{g}/\text{L}$ to 5 mg/L. Elevated background concentrations were found in Mitchell Brook near Halifax, where levels up to 0.037 mg/L were reported (Wang and Mulligan, 2006). The arsenic which is naturally present in water is due to a number of geochemical processes. These processes include oxidation of arsenic containing sulphides, desorption of arsenic from hydroxides, leaching of arsenic from sulphides by carbonates as well as release of arsenic from geothermal waters and from evaporative concentration.

Other anthropogenic sources of arsenic contamination are from coal combustion, industrial emissions and wood preserving. Industrial emissions, particularly those of smelter and base metal refineries as well as thermal power stations are the main source of arsenic contamination in Canada. The amount of arsenic released into the environment through these means is tremendous, 15 tonnes a year in liquid effluent, 310 tonnes a year in air and 770 tonnes per year in soil (MacLachy, 1992). High levels of arsenic were

detected in the area surrounding the refineries and coal fire powered thermal generating stations. Near a copper-zinc smelter in Manitoba, concentrations in surface peats that were up to 70 times higher than the average background concentrations were detected (Zoltai, 1988).

Annual sales of arsenic pentoxide, used in arsenical wood preservatives between the years of 1984 and 1988 were between 650 and 1300 tonnes in Canada (CEPA 1993). It is estimated that in 1992, 59,000 tons of CCA (chromated copper arsenate) were used in Canada (Stephens et al., 1994.) Two other wood preservatives used in Canada are ammoniacal copper arsenate (ACA) and ammoniacal zinc copper arsenate (ACZA). Significant amounts of all of the above arsenical preservatives remain in the treated wood, ranging from 7800 to 78000 mg per kg of wood, with a leaching rate from 1.8% to 17.3%. This causes significant pollution to the surrounding environment. Leaching can happen in several ways: by the leaching of the compounds through rainwater, by spills of the preservatives around the treated area and by the dripping of freshly coated wood.

Coal combustion, a third source of arsenic contamination in the environment, is released during the processing and the combustion of coal. Arsenic concentrations in the order or greater than 6000 mg/kg were detected in Cumberland Basin in Nova Scotia (Hower et al., 2000). The arsenic came from bottom ash, fly ash and pulverised coal from coal fire powered thermal generating stations.

2.3 Mine tailings – History and Origin

Mine tailings are large amounts of crushed rock, which are left over when the metals of interest have been extracted from the mineral ores. The process is not 100% efficient so after the crushing and milling metal containing minerals are left behind as mine tailing particles. There are several factors that make mine tailings dangerous for the environment. In arid or semi-arid areas of the world, in particular in some southern states in the western part of United States, the mine tailings are prone to wind erosion and get carried in the air great distances from their original source. This results in significant

contamination of the surrounding environment and tests have shown elevated levels of toxic metals in human and animal life forms even great distances away from the original sites.

In historic gold mines in Nova-Scotia, tailings contain significant amounts of arsenic, due to mining activities from 1860 to the 1940s, where regulation on industrial activity was lacking (MITHE-SN Secretariat, 2009). The tailings, which are close to residential areas, playgrounds, are easily accessible, pose a health risk associated with oral ingestion or inhalation. The arsenic originally present in the tailings in the form of arsenopyrite was not a health concern, but the different forms of arsenic minerals created through years of weathering pose a risk to human health (MITHE-SN Secretariat, 2009).

Another effect would be the impact of abandoned mine tailings in the levels of arsenic present in Moira Lake in Ontario (Azcue and Nriagu, 1995). Arsenic has accumulated in the last 160 years in Moira Lake, ever since mining operations began there. Since 1837, hematite, magnetite, lead, gold and cobalt were mined in the Eldorado and Dorado region, with arsenic as a by-product. The mines were closed in 1961 but resulted in a large amount of arsenic and other wastes being abandoned on the site (Azcue and Nriagu, 1995). In 1979, the Ontario Ministry of Environment began cleaning up the area removing 15 tonnes of arsenic per year (Azcue, 1992). This was done through the treatment of groundwater containing anywhere from 50 to 3000 mg/L of arsenic. (Azcue & Nriagu, 1995). The arsenic concentration sampled in the winter upstream from the mining was 0.67 µg/L whereas the concentration sampled just after the mining area was 23.3 µg/L and it remains high for 23 km. This indicates how far reaching the impact of mine tailings can have on arsenic levels in water, and cause widespread contamination. The mining operations were shut down 31 years ago and there is still a high amount of arsenic transferred into solution.

Table 2-2 lists a few mines in Canada and the corresponding concentrations of arsenic in the tailings in increasing order.

Table 2-2 Arsenic concentrations in several mine tailings

Origin Of Tailings	Location	Conc. [mg/kg]
Iron Mine	Mont-Wright, QC	< 0.70
Gold Mine	Musselwhite, ON	63
Copper and Zinc Mine	Val D'Or, QC	270
Gold Mine	Marathon, ON	270
Copper Mine	Murdochville, QC	500
Lead Zinc Mine	Bathurst, NB	2200

Source: (Wang and Mulligan, 2004a)

2.4 Arsenic in mine tailings, soils and sediments

Arsenic in mine tailings is a source of major environmental pollution. In Canada, the extraction of gold from arsenious ores produces a large amount of arsenic trioxide. An example would be the Giant Mine in Yellowknife, North West Territories where 220 million tons of arsenic trioxide were stored in underground chambers after the closure of the mine, threatening the surrounding ground and surface waters. Silver mining in the Cobalt mining camp in northern Ontario has left large volumes of arsenic wastes around the waters of the area. This has led to significant contamination and the concentration of arsenic in the surrounding waters is greater than the acceptable Canadian threshold of 0.025 mg/L (Kwong et al., 2007).

The form of arsenic which occurs in mine tailings is from arsenopyrite (FeAsS), arsenates (AsO_4^{3-}), arsenian pyrite (FeS rich with As) and arsenic associated with iron oxyhydroxides. Several mine tailings were measured and their concentrations recorded by Wang and Mulligan (2004). Concentrations ranged from 63 mg/kg from a gold mine in Musselwhite Ontario, to 2200 mg/kg in Bathurst, New Brunswick to as high as 25,000 mg/kg in the Con Mine tailings in Yellowknife, NWT.

Natural arsenic concentrations in soils vary tremendously from area to area. Although minerals containing arsenic occur naturally, the anthropogenic contribution of arsenic to the environment is substantial. The worldwide contribution in the past was 82,000 metric tons (Nriagu and Pacyna, 1988). This has been due to various pesticides and insecticides (lead arsenate, sodium arsenate and calcium arsenate) as well as arsenic-based wood preservatives such as CCA (chromated copper arsenate) (Bhattacharya et al., 2002).

In addition, not only the use of the pesticides themselves, but also the waste from the manufacturing of the pesticides is responsible for the pollution of nearby soils and waters (Mahimairaja et al., 2005). The majority of arsenic soil pollution can be traced back to a time when there was no formal control over the use of arsenic (Meharg et al., 1994).

England, which was one of the pillars of the industrial revolution in the 19th century, left behind huge amounts of arsenic-contaminated soils. The mobilization of arsenic from the soils is a danger for human health, as it leaches into ground water and enters into the food chain. Further investigations are required in these areas to determine the solubility of the arsenic, and in which fraction it appears to assess its degree of mobility and hazard to human life (Bhattacharya et al., 2007).

Arsenic concentrations in soils and wastewaters were measured in two former arsenic mining and ore processing areas in Poland, Zloty Stok and Zeleznik to determine the environmental risk associated under changing redox conditions, pH and other factors (Krysiak and Karczewska, 2007). A large number of samples were collected from different sites and represented a variety of different soil properties and compositions, including mine tailings, natural soils, mine slags and spoils. Analysis of different species of arsenic was done using the Selective Sequential Extraction (SSE) technique and analysis of the change of solubility was performed under various pH values (2 to 8). It was found that the soils contained extremely high levels of arsenic from 100 to 43500 mg/kg. The tests from SSE extraction revealed that the majority of the arsenic in the soils was bound to Fe oxides, whereas the arsenic in the mine tailings was mostly in the residual form, i.e. tightly bound to the soil via specific adsorption in the soil mineral lattice. Arsenic mobilization was found to be high for low or elevated pH levels (i.e. $\text{pH} < 2$ or $\text{pH} > 8$). High pH promotes solubilisation of arsenic under reducing conditions (little or no free oxygen), whereas in neutral or acidic soils the risk of solubilisation is minimized. Arsenic mobilization was high for $\text{pH} < 2$ because of the increase in solubility of the iron oxides to which the arsenic was bound (Xu et al., 1991).

2.5 Remediation Methods for Contaminated Soils

As seen, arsenic distribution and toxicity is a major concern worldwide and a significant health hazard. There are many strategies which are currently being explored to be used to remedy the situation. The selection of the most appropriate remediation method depends on many characteristics, such as the nature of the site, the final use of the site after the treatment, the concentration and the chemical form of the pollutant. A few of these technologies include immobilization, physical separation, extraction, isolation and toxicity reduction (Mulligan et al., 2001). The following sections describe these techniques in more detail.

Containment

One of the methods used is containment. Containment is a physical separation process whereas an impermeable barrier made of steel, concrete, bentonite or grout can be used for capping and containing the waste horizontally or vertically. The purpose of this technique is to reduce the flow of groundwater through the contaminants and the spread of pollution outside the contaminated area. Vertical barriers reduce the flow of contaminated and uncontaminated groundwater through the contaminated area. They must be combined with the natural clay, bentonite or bedrock barrier to prevent the leaching of contaminants past the vertical layer (Rumer and Ryan, 1995). Horizontal barriers have not been proven as effective as vertical barriers and consist of restricting the downward movement of contaminants by acting as an underlying layer of low permeability.

Solidification/Stabilization

In solidification and stabilization techniques, the contaminants are physically bound into a solidified mass or treated chemically which makes them less mobile, toxic and soluble. It was shown, through TCLP tests, that this technology is capable of reducing the levels of arsenic in soil below 5 mg/L which is the drinking water threshold in many countries (EPA, 2002).

Solidification or stabilization techniques are a more popular alternative as they contain the contaminants themselves rather than just the polluted area. Arsenic, as well as chromium (VI) and mercury are not very suited to this form of treatment since they do not form hydroxides. Soils can be treated either in situ or ex situ (Mulligan et al., 2001).

Vitrification

Vitrification is a high temperature treatment which involves the insertion of electrodes into the soil to carry a high current which melts the soil and turns it into chemically durable and leaching resistant vitreous mass. This technique has been used at a full scale for the treatment of arsenic, lead and chromium contaminated soils. Wastes which contain a combination of contaminants cannot be effectively treated through stabilization/solidification can be treated this way. This method is very effective for shallow depths and large volumes. One of the disadvantages of this method is the large requirement for energy and the generation of toxic off-gases during the intense heat that contain arsenic (Mulligan et al., 2001); (EPA, 2002). Fig. 2-1 illustrates the steps involved in the vitrification process.

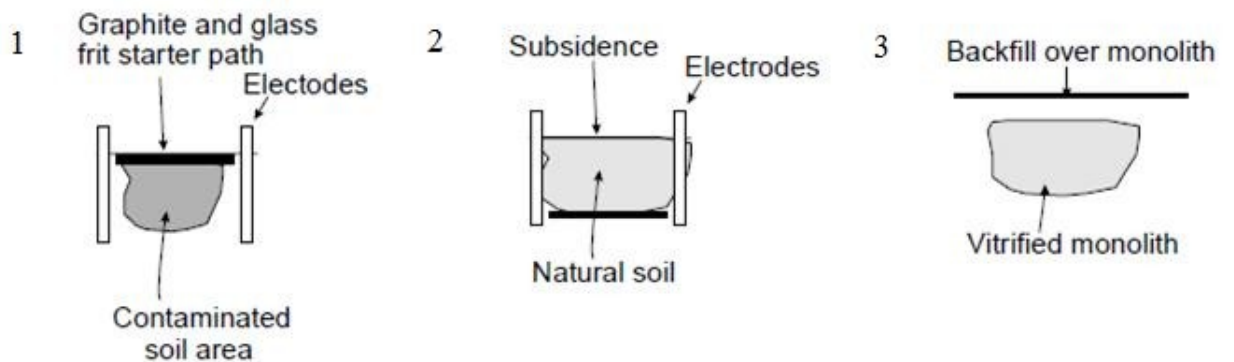


Figure 2-1 Several steps in the vitrification procedure for metal, which includes: 1) Insertion of electrodes, graphite and glass frit starter path to start vitrification, 2) Soil subsidence due to vitrification 3) Placing of a backfill over vitrified monolith (Mulligan et al., 2001)

Mechanical Separation

Mechanical separation is another form of remediation whose purpose is to separate larger cleaner particles from smaller, more polluted ones. This process requires a characterization in terms of size and level of contaminant present in each size fraction. Different methods such as hydrocyclones, fluidized bed separation which function either through centrifugal force or gravimetric settling and flotation, are used to accomplish this separation. Certain chemicals are also added which along with aeration cause the contaminated particles to float. Magnetic separation allows the separation of the metal contaminants from ferrous materials. This method, based on physical separation, is becoming more and more common as they can be used alone or in combination to reduce the volume of soil to be treated by other methods (Mulligan et al., 2001).

Pyrometallurgical Separation

Another form of remediation is called pyrometallurgical separation. It uses heat to volatilize the metals in the contaminated soil using temperatures of 200-700°C. Metals that are recovered after volatilization can be reused and sold. This method is most effective for mercury because it transforms easily to its metallic form when heated, but in the case of arsenic the metals refinement process has to be modified using fluxing or reducing agents to help in melting. This type of treatment is usually performed off site and for high concentrations of metals (Smith et al., 1995). Rotary kilns, hearth furnaces and arc furnaces are usually used for this type of treatment. The factors that affect the performance of this type of remediation are particle size, moisture content, thermal conductivity and the presence of impurities (EPA, 2002).

Chemical Treatment by Reduction/Oxidation

Another form of treatment is chemical treatment by reduction or oxidation to detoxify the contaminants and decrease their mobility (Evanko and Dzombak, 1997). This is a treatment most often used for wastewater treatment. Oxidation reactions involve the use of hydrogen peroxide, chlorine gas, and potassium permanganate. Neutralization reactions are performed to adjust the pH of the soils. Reduction reactions are performed

through the addition of salts of alkali metals elements such as sodium, and compounds such as sulfur dioxide and ferrous sulphate. Arsenic is most suited to chemical oxidation since As (V) is less toxic than As (III). The combination of As (V) either with Fe (III) (Fe_2O_3) or ferric hydroxide ($\text{Fe}(\text{OH})_3$) results in the production of arsenic ferrihydride, a compound that is very resistant to leaching.

Reactive Barriers

Another form of treatment is the introduction of a permeable barrier that contains a reactive substance. The barrier allows water to pass, however intercepts the plume of contaminants and removes them through ion-exchange, precipitation, adsorption or degradation. Some of the chemical and reactive substances used to treat the contaminants are zero valent iron, limestone, basic oxygen furnace slag, surfactant modified zeolite and ion exchange resin (EPA, 2002). The advantage of this technique is that it is done onsite, without the need for excavation and transport. More research is needed to identify which medium is compatible with which contaminant (Mulligan et al., 2001).

Electrokinetics

Another remediation method which involves the use of an electric current is called electrokinetics. It is based on the theory that passing a low intensity electrical current through contaminated soil will mobilize contaminants in the form of charged particles. Two electrodes are inserted into the soil and current is passed through them. Cations in the soil move towards the negative electrode whereas anions (positive ions) move towards the positive electrode. Four types of processes take place in the electric field generated by the electrodes: electrophoresis (charged particle movement), electromigration (charged chemicals movement), electro-osmosis (movement of fluid) and electrolysis (chemical reactions due to electric field). The metals in the solution then arriving at the electrodes can be removed by precipitation, coprecipitation, adsorption, electroplating, electrodeposition or by pumping of water near the electrode (EPA, 2002). This process removes metals as ions bound to hydroxides, oxides and carbonates and it is effective with clays that have low permeability. The main use of electrokinetics is with

saturated soils that have low groundwater flow rates. It is used in Europe for the remediation of arsenic, copper, zinc, chromium and lead (Mulligan et al., 2001). It is still though an emerging technology for arsenic treatment limited by a number of soil and contaminant characteristics (EPA, 2002).

Phytoremediation

Phytoremediation involves the use of specific plants that have the capacity to extract, degrade, contain or immobilize heavy metals. They can be considered as an indirect form of remediation. Once they are sufficiently contaminated with the pollutants, they are disposed of safely (EPA, 2002).

Soil Washing and Soil Flushing

Soil flushing and soil washing are yet another set of techniques that involve the addition of water, and/or various additives as the flushing solution. These additives may include strong acids or bases, chelating or complexing agents such as EDTA, surfactants or reducing agents to help in the desorption, dissolution and chemical extraction the metals present (EPA, 2002). Biodegradable surfactants have been successfully used to remove metals from hydrocarbon-contaminated soils (Mulligan et al., 1999). For soil washing to be successful, certain conditions of the soil must be met such as low contents of cyanide, fluoride and sulphide, the CEC (cation exchange capacity) must be 50-100 meq/kg, particle sizes must be 0.25 -2 mm, and contaminant solubility in water must be greater than 1000 mg/L (Hazardous Waste Consultant, 1995).

Other methods for the remediation of soils include biochemical processes, which will be very briefly mentioned. Bioleaching and biosorption (adsorption of metals on biomass which is either dead or alive) are the main methods used for this type of treatment. Methylation (addition of a CH₃- methyl group) is used to make the metals more mobile, however in the case of some metals like arsenic, the by-products are more toxic, so it is not recommended. Table 2-3 summarizes and compares the different treatments mentioned above.

Table 2-3 Comparison of different remediation methods

Remediation Method	Description	Application	Cost (US \$/Ton)
Physical Containment	Prevents movement by preventing fluid flow	Landfill covers and slurry walls	10-90
Vitrification	High temperature treatment that involves applying electrical current to solidify the contaminants into a vitreous mass	Shallow, soils contaminated with metal, metals with low volatility	400-870
Encapsulation	Making the waste inert	Injecting solidifying chemicals	60-290
Soil Washing (ex-situ)	Adding surfactants and different additives to solubilize	For water soluble contaminants	25-300
Physical separation (ex-situ)	Includes gravity separation, froth flotation, screening	For high metal concentrations	60-245
Pyrometallurgical treatment (ex-situ)	Processing for metal removing and elevated temperature extraction	Highly contaminated soils (5-20%)	200-1000
Reactive barriers (in-situ)	Creation of a wall containing reactive media to intercept contaminant plume	Degradation or sorption of contaminants	60-245
Soil flushing (in situ)	Involves the extraction of organics from soil using water without excavating the contaminated material.	Used for soluble contaminants	100-200
Electrokinetics (in situ)	Application of electrical current between two electrodes inserted into the subsurface.	Applied to saturated soils with little groundwater flow	NA
Physical Containment	Prevents movement by preventing fluid flow	Landfill covers and slurry walls.	10-90

Source: (Mulligan et al., 2001)

2.6 Immobilization of Arsenic

The usual approach for remediating contaminated land is excavation followed by replacing the area with clean soil. This is however, a tremendously expensive method and is quite disruptive to the environment (Vangronsveld and Cunningham, 1998). As seen in Table 2-3, there are many different alternatives for treating soils contaminated with heavy metals, such as arsenic. A more sustainable method is in situ metal inactivation or in other words, immobilization of metals.

This is a process whereby the toxic metals presents in the soil are transformed into a more stable and less soluble form, by the addition of additives. The toxic metals bind to the additive, thus reducing their mobility in the soil. Immobilization can occur by solidification/ stabilization (e.g. with cement-like materials), or through absorption, adsorption or ion exchange. The process allows the mobility and the toxicity of the contaminant to be greatly reduced, which in our case is arsenic. The mobility of the contaminant is very important as helps to determine its bioavailability, as elements which are dissolved into solution are taken up by plants or humans (Boisson et al., 1999). The speciation determines the mobility of the trace elements and the speciation is dependent on several factors, such as the pH of the soil, the Eh (redox potential) and the mineral composition of the soil. The effect of soil additives is thus to alter the physical and chemical properties of the soil and thus reduce the mobility of the contaminant. It is very important that the immobilization have long term stability when applied to soils. The result will be a long-term reduction in the overall leaching to the groundwater, surface water and surrounding environment and allow for previously contaminated site to be possibly made safe enough and sufficiently decontaminated for human use.

Immobilization studies conducted using Iron Oxides and Zero Valent Iron

A study was conducted whereby soils were amended using several additives to immobilize the arsenic in the soil. The additives used were steel shots (1% w/w), beringite (5% w/w), a combination of steel shots (SS) and beringite (B) (1% SS + 5% B) and hydroxyapatite using 3 different weight ratios (0.5, 1 and 5% w/w). Steel shots are an

iron bearing material with traces of manganese used to polish metallic surfaces. Three soils were tested used to test the additives: Rep 1 (from a former Zn smelter mine in Belgium), Rep 2 (from a former As refinery) and Port (from the spoilheaps of a gold mine in Portugal). The effectiveness of the additives was tested using chemical extraction with distilled water (Boisson et al., 1999). After performing leaching tests, the lowest amount of arsenic leached from the soils mixed with B, SS and a combination of the two. The effect of B, however, was dependent on the type of soil, it worked well with soils Rep1 and Rep 2 of but increased leaching in the Port soil. The most successful additive found was SSB in all of the cases. To ensure the success of a particular additive both economically and in terms of its effectiveness, it is important to do tests on many different types of soil.

Another study was done using Fe precipitates (iron oxyhydroxides) to immobilize arsenic in tailings, thus preventing the generation of polluted waters. The efficiency of Fe (II) treatment was studied at different molar ratios of Fe: As, by adding CaCO_3 and also by the degree of arsenic desorption by continued leaching of the treated mine tailings (Seidel et al., 2005). It was found that arsenic could be effectively stabilized by treating the mine tailings with Fe (II) salt solutions. It was found that the most effective ratio of As: Fe was 4 and it was also found that the degree of immobilization depends on the amount of Fe added. It was also found that adding CaCO_3 to the soil increases the solubility of arsenic (V) but decreases the solubility of the more toxic As (III) and prevents the leaching of other heavy metals into solution.

A few studies have been carried out using Fe (II) salts, to prevent arsenic mobilization in the soils through chemical fixation. One study was carried out with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Moore et al., 2000). Arsenic in two different soils originating from mine waste was successfully treated using iron oxyhydroxides, aluminum hydroxides and naturally occurring clay minerals (Garcia-Sanchez et al., 2002). Immobilization was tested by subjecting the treated soils to water extraction one month after treatment. The best results were found using goethite ($\alpha\text{-FeOOH}$). A proposed remediation strategy is to precipitate Fe oxides in

the soil by adding ferrous sulphate and lime (Warren and Alloway, 2003; Warren et al., 2003). The bioavailability of the arsenic was tested using greenhouse studies involving the plants and by measuring their degree of uptake. It was found that adding the above substances caused a significant reduction in the degree of As uptake. However, it was essential to add both ferrous sulphate and lime simultaneously. Another study was done on sulphur rich mines acidified mine tailings to investigate the effect of amorphous Fe precipitates using ferric and ferrous sulphate solutions and adding them to the tailings. The efficiency of immobilization was tested by SSE procedures (Kim et al., 2003). However, there are no available studies on the stability of As leaching from mine tailings over an extended period of time.

A study has also been conducted on the amendment of metal contaminated soils using several iron bearing compounds, such as goethite (α -FeOOH), iron grit, Fe (II) and Fe (III) sulphates, and lime at a weight percentage of 1% w/w. They were selected because of their known potential for adsorbing arsenic. In fact, iron surfaces have been known to be involved in the adsorption of arsenic (Elbassam et al., 1975; Jacobs et al., 1970; Lumsdon et al., 1984; Waychunas et al., 1993), and iron hydroxides applied to garden soils have shown a decrease by as much as 50% of the water soluble arsenic concentration, as well as the degree of arsenic bioavailability (Mench et al., 1998). These compounds were first evaluated for their effectiveness as additives as well as their immobilizing capability through short and long term leaching tests. Column experiments also revealed that the iron oxides had a long term stabilizing effect on the soils; however the amended soils showed a higher concentration of both lead (Pb) and cadmium (Cd) suggesting that the treatment might have increased the mobility of other heavy metals (Hartley et al., 2004). Several leaching tests were used in this study that would best determine the mobility of the metals in groundwater as well as their bioavailability. The leaching tests that were used include the UK Environmental Agency 1 hour test, the ASTM (American Society of testing Materials) extraction test (Eisenberg et al., 1986), and a modified Dutch Environmental Agency test (NEN 7343; Netherlands Standardization Institute, 1995).

Zero valent iron has also been used as another strategy to immobilize calcium, copper and arsenic in soil. Chromated copper arsenate contaminated soils were treated with zero valent iron (Fe^0) using iron grits using a 1% w/w additive to soil ratio. It was found that the addition of these additives decreased the As by a factor of 98% in the leachate, by 99% in soil porewater and by 84% in plant shoots. Because stabilization of soils does not decrease the concentration of elements, the effectiveness of the treatment depends on the reduction on the amount of mobile or bioavailable fractions of the contaminants. Selective sequential extraction and leaching tests were the chemical tests used to measure the amount of metals released from the soil and into the groundwater. Since chemical tests can only estimate the bioavailability of the metals, a combination of tests are used, chemical, biochemical and biotoxicity tests (Kumpiene et al., 2005). Plant based studies are increasingly being used to determine the success of soil amendments (Adriano et al., 2004). Also several studies have shown that soil contamination leads to a decrease in soil hydrolytic enzyme activity (Tyler et al., 1989), and therefore the level of enzyme activity is a potential indicator of the bioavailability of the toxic metals in the soil (Nannipieri, 1995).

Synthetic Iron Hydroxide and Aluminium oxide

Synthetic aluminium hydroxide ($\text{Al}(\text{OH})_3$) as well as synthetic iron oxyhydroxide (FeOOH) has been shown to be very effective in the immobilization of arsenic, reaching an efficiency of nearly 100% in immobilizing the water soluble arsenic component of one of the mining soils studied. The synthetic hydroxides and oxyhydroxides were prepared by precipitation in their chloride solutions using the method of Sims and Bingham (1968). They were chosen for the study because of their purity as compared with their natural counterparts. The surface areas of the synthetic compounds were, respectively, $140 \text{ m}^2/\text{g}$ and $114 \text{ m}^2/\text{g}$ (Garcia-Sanchez et al., 2002).

Manganese Oxides

The capacity of manganese oxides to adsorb arsenic has not been as extensively studied as iron oxides, but they were found to adsorb high levels of arsenic (Chiu and Hering,

2000). Whether applied alone or in combination with Fe oxides, these can significantly reduce the toxicity and mobility of arsenic in soil (Mench et al., 2000). This was shown to be achieved by a variety of different reactions. Manganese oxides can adsorb As through bridging complexes similar to those formed with iron oxide and hydroxide surfaces (Manning et al., 2002; Foster et al., 2003), they can oxidize As (III) to As (V) reducing the toxicity (Tournassat et al., 2002), and they can also coprecipitate arsenic by forming $\text{MnHAsO}_4 \cdot 8\text{H}_2\text{O}$ (Tournassat et al., 2002) or a highly insoluble mineral: $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Porter et al., 2004).

Alkaline Minerals

The studies using alkaline minerals reveal contradictory results. It is generally thought that alkaline minerals are not appropriate for immobilization because they increase the pH of the soil which leads to more leaching, since the mobility of arsenic increases with the pH (Seaman et al., 2003; Hartley et al., 2004).

However, one study done shows that the addition of lime decreases the leaching of As by a factor of 8% (Mench et al., 2003). This is due to the formation of insoluble complexes (CaHAsO_4) and calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$) which precipitate (Porter et al., 2004). However, the total amount of arsenic removed in this way is still too small for it to be considered as a feasible alternative.

Clay Minerals

The toxicity of arsenic is lower in clay than in regular soils, because of the binding capacity that clay has to arsenic. Different types of clay were found to have different capacities to immobilize arsenic. Two different soils were studied to which were added two clay minerals, bentonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) and limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$). In both cases, it was found that the addition of 10% w/w of the above minerals reduced the leaching by a factor of 80% for limonite and 50% for bentonite. More acidic soils also reduced the immobilizing capacity of the clays, and in the case of bentonite, a pH of 3.8 rendered it ineffective (Garcia et al., 2002).

Zinc

The presence of zinc has been found to increase sorption of arsenic to goethite by a factor of 5 at a neutral pH, through the formation and precipitation of Zn-AsO₄ complexes (Gräfe et al., 2004).

2.7 General adsorbents used for removal of arsenic

The literature available for the removal of arsenic from water is much more vast and complete than the studies conducted on soil, and we will present here some of these findings will be presented, to help in identifying potential soil additives. The following adsorbents have been tested for removal of arsenic from water, and have the possibility of immobilizing the mineral in soil. However, further tests can identify their suitability as immobilizing agents.

Commercial Activated Carbon

Commercial carbons derived from coal have been used extensively for adsorption of As (III) and As (V). It was measured that the capacity of this activated carbon was huge, in the order of 2880 mg/kg. The same activated carbon coated with silver and copper was also successfully used to decontaminate water with arsenic (Rajakovic, 1992). A combination of carbon and steel wool was also successfully used to remove arsenic from water (Campos, 2002). The steel wool was used because of its ability to form Fe-As bonds (Mohan and Pittman, 2007).

Agricultural products and by-products

Rice husks have been successfully used for the removal of arsenic from water. They were most effective when combined with 0.01 mol/L of H₂SO₄, HClO₄, HNO₃ or HCl and for 1 g of adsorbent for 5.97 x 10⁻³ mol/L of arsenic and kept at a pH of 6.5 for As(III) removal and a pH of 6.0 for As(V) removal (Nasir et al., 1998).

Blast Furnace Slag

Steel plants generate a large volume of granular blast furnace slag, which is used to produce cement. This steel slag was also converted into an effective adsorbing agent for the removal of arsenic from water. (Zhang, 2005; Ahn et al., 2003). An adsorbent was synthesized for removing aqueous arsenic by adding iron (III) oxide into melted municipal waste slag. This combination led to the formation of Fe-Si complexes which tightly bind the iron to the slag. The loading of iron (III) oxide onto the slag caused a much better adsorption rate due to an increase in the surface area of iron (III) oxide by 68%. This caused a 2 to 3 times higher adsorption rate than for regular amorphous iron oxide.

Sand

A different variety of sands were applied for arsenic remediation. Two different types of sand coated with iron oxide (IOCS-1, IOCS-2) was used for dimethylarsenate removal from tap water (Thirunavukkarasu, 2002). Sand coated with manganese (Green Sand) was also tested for removal of arsenic less than 25 µg/L (Thirunavukkarasu et al., 2005).

NanoActive metal oxides

These are a line of nanocrystalline or nanoscale metal oxides manufactured by Nanoscale Corporation. They have a very small particle sizes (2 to 10 nm) and agglomerate into micron sized clusters with very high porosity, up to 1.5 cm³/g. This results in a very high reactivity and they have been shown to destructively adsorb a wide range of contaminants. The different powders manufactured have various particle sizes, porosities and molecular weights. The process by which they adsorb contaminants is a 2 step process: first the contaminants are physically adsorbed onto the powders (physisorption), and then they chemically react with the powders (destructive adsorption). This allows the removal of the toxic contaminants from the solution independently of the rate of the chemical reaction. This also allows for the nanoscale powders to remain active even at very low temperatures and independently of the substances used, which is very useful when there are variable conditions. The powders used are nanocrystalline forms of

aluminum oxide (Al_2O_3), magnesium oxide (MgO), zinc oxide (ZnO), titanium dioxide (TiO_2), calcium oxide (CaO) and cerium oxide (CeO_2). They will be discussed in more detail in the Materials and Methods section of the thesis.

Clay minerals

Clay minerals in general are hydrous aluminosilicate materials that have a layered structure and vary small particle size (Encyclopaedia Britannica Online, 2010a). Some clay minerals are illite, montmorillonite and kaolinite. Clay minerals and their oxides have large surface areas suitable for adsorption. They absorb neutral metal species, as well as their anions and cations. They are widespread in nature. Their sorption capacities, binding capacities, cationic and anionic exchange capacities vary. There have been many studies done on arsenic removal from groundwater using clay minerals (Singh et al., 1996; Manning and Goldberg, 1997). It has been shown that arsenic anions readily sorb to Al, Fe and Mn oxides, hydroxides and clay phases (Wang and Mulligan, 2006c).

Zeolites

Zeolites are hydrated aluminosilicate minerals. They are known for their ability for ion exchange (Encyclopaedia Britannica Online, 2010b). More than 30 species are available in nature, but only seven of them are in sufficient abundance to be used. When modified by ion exchange, they act as great adsorbents that can remove metal ions. Removal of arsenate and arsenite was tested using iron treated activated carbon as well as zeolites. Activated carbon removed 60% of arsenate compared to 50% for the zeolite chabazite, whereas for arsenite, 60% was removed by activated carbon, and only 30% was removed from the zeolite (Payne and Abdel-Fattah, 2005).

Manganese Dioxide (Birnessite)

Manganese oxides minerals easily absorb many species including As (III). The oxidation of As (III) by manganese oxide is an important reaction in the cycle of arsenic as well as for reducing the concentration of As (III) in water. The removal of arsenic using synthetic birnessite was studied by Manning et al. (2002) using Extended X-Ray Absorption Fine Structure (EXAFS) spectrometry as well as a conventional stirred reactor. The reactions

of As (III) and As (V) were measured. It was observed that As (III) was oxidized by MnO_2 , and the product, As (V), was adsorbed onto the solid phase of the birnessite. It was also found that the treatment of MnO_2 with As (III) caused a reductive dissolution of the latter into solution, creating fresh adsorption sites for As (V). Therefore, the presence of As (III) proved to enhance the effectiveness of As (V) adsorption and suggested the potential advantage of using birnessite to treat waters that are contaminated by both As (III) and As (V) (Manning et al., 2002).

Activated Alumina

Activated alumina is prepared by thermal dehydration aluminium hydroxide and has a high surface area and a good distribution of both macropores and micropores. Activated alumina was classified by the UNEP as one of the best techniques for removal of arsenic from water. However sorption of As (III) depends on the pH and is highest when the pH was 7.6 (Singh and Pant, 2004). Studies have been done on the removal of As from water using iron coated aluminum oxide powder. The adsorption capacity of iron coated alumina was 12 mg/g versus 7.6 mg/g for regular alumina (Singh and Pant, 2004).

Titanium Dioxide

Nanoscale titanium dioxide was evaluated for its ability to remove As (III) and As (V) from water. Batch experiments were conducted by using suspensions of TiO_2 in a solution of sodium chloride (NaCl). The adsorptive capacity of nanoscale titanium dioxide was much greater than that of fumed TiO_2 as well as ferric oxide (Mohan and Pittman, 2007).

Bimetallic adsorbent

A Fe-Ce bimetallic oxide adsorbent was investigated. The bimetallic oxide adsorbent showed a significantly higher capacity of adsorption than individual metals for As (V) (Zhang et al., 2005).

Magnetite

Experiments were conducted on the adsorption of arsenic on magnetite nanoparticles (Fe_3O_4) (Mayo et al., 2006). The influence of this compound was tested on the adsorption/desorption of As (III) and As (V). It was also discovered that when the particle size was decreased from 300 nm to 12 nm, the adsorption capacity of the nanoparticles increased 200 times.

No studies could be found that investigated the effect of various nanoscale metal oxides, as well as magnetite in immobilizing arsenic in mine tailings. The current study attempts to analyze the effectiveness of these additives in stabilizing waste on a short and long term basis. Specific tailings were used from various mines in Canada.

3 MATERIALS AND METHODS

The main objective of the current research is to determine the effectiveness of metal oxide additives for immobilizing arsenic in mine tailings. The present chapter focuses on presenting the methods and materials used and describing the experimental design. The chapter is separated into three parts: the first part is focused on the measurement of arsenic in the solid tailings using an X-Ray Fluorescence (XRF) device, the second part is focused on presenting the leaching tests conducted to measure the effectiveness of arsenic immobilization and the last section is focused on the presentation of the analytical methods for measurement of the arsenic concentration.

3.1 Characterization of Mine Tailings Using XRF

Before any of the tests were carried out, the metal content of the mine tailings was measured using an XRF analyser (NITON XLP 700 series). Mine tailing samples from four different areas in Canada were analyzed and scanned by XRF. These tailings are shown in Table 3-1.

Table 3-1 Mine tailings characterized by the XRF device

Mine tailings	Type of Mine	Location
Louvicourt	Copper and Zinc	Val D'Or Quebec
Golden Giant	Gold Mine	Ontario, near Thunder Bay
Noranda	Copper and Gold	Rouyn Noranda, Quebec
Mont-Wright	Iron Ore	Fairmount, Quebec

The XRF spectrometer used for this study is a Niton XLP 700 series machine. A beam of high energy X- Rays is emitted and bombards the soil sample which emits secondary characteristic X-Rays (fluorescence), detected the device. Measurements were taken of all the metals in the soil.

3.2 Preparation of samples for analysis

The samples were prepared in a way to make them suitable for analysis by the Niton XLP 700 spectrometer. This was done in several steps. First the mine tailings were crushed using a grinder. Then they were air dried for a few days. The air dried mine tailings were passed through 3 sieves to filter out the portion that is equal to or smaller than 250 μm . The filtered tailings were placed in a small plastic holder, and then sealed at the top with a clear Mylar film. The prepared container was placed in the Niton XLP 700 holder and the XRF device was aimed at the sample and triggered. Measurements of all the elements present were displayed on the screen of the device taken.

3.3 Leaching and Extraction Tests

3.3.1 Immobilization of mine tailings

The mine tailings (Noranda and Golden Giant) were mixed with various metal oxides at different weight percentages. The mine tailings used were air dried samples, and the additives were dry crystalline powders. They were mixed together (2 g of mine tailings, 0 – 0.2 g of additives) and then combined with a very small quantity of water (1-2 ml) to allow the powders to react. Depending on the length of the test, they were either left to react for 24 h, 1 month or 2 months after which they were subjected to leaching tests and SSE (Selective Sequential Extraction) tests. The time periods for the tests were chosen as far apart from each other as possible to take into account the effect of time. Details on the types and weights of powders used are given in the sections below.

3.3.2 Preliminary Leaching tests

Preliminary leaching tests were carried out on untreated mine tailings and from tailings combined with various additives, over a 1 day or 1 month or 2 month period. These tests are meant to simulate the leaching of arsenic into ground and surface waters in acid rain conditions and are a modified version of the Synthetic Precipitation Leaching Procedure (SPLP) method. The role of the leaching tests was to determine which of the additives

was the most promising, in order to do more complete SSE tests on a few selected long term samples.

A solution of distilled water acidified to pH 3 was used instead of 4.2 (recommended by the SPLP method for mine wastes). The reason for choosing such a low pH was that the degree of leaching at pH 4.2 was too low to be adequately measured using the arsenic test strips, one of the test methods used in the study. It was found that a solution having pH 3 provoked enough leaching to provide readable results. Furthermore, the pH of distilled water was adjusted using pure sulphuric acid instead of a 60/40 ratio of sulphuric acid to nitric acid. This is because the presence of nitric acid interfered with the measurements made by the Hach EZ Arsenic Test Kit strips.

These leaching tests are not considered as standard tests since the pH used was much lower than what is usually found in nature. However they give a good idea which additives have the highest potential for immobilization. They also serve as a good selection method to narrow down the number of additives to be measured by more thorough tests.

3.3.2.1 Experimental Procedure

Dry mine tailing samples weighing 2 g in total were mixed with 0.2 g (10% w/w) of a variety of additives. They were then combined with 1-2 ml of water and left to react either for 24 h or 1 month. The additives used were nanoscale metal oxides and non-nanoscale metal oxides. The non-nanoscale metal oxides were manufactured by Fisher Scientific and the nanoscale metal oxides were manufactured by the company Nanoscale Corporation with the exception of the nanoscale magnetite (Fe_3O_4) which was supplied by Sigma-Aldrich. Details and properties are found in Table 3-4.

As explained in the previous section, these materials were chosen for their high surface area and promising results for adsorbing a wide range of contaminants, including organic compounds and heavy metals.

The additives were then mixed with 8 ml of a solution of distilled water acidified to pH 3 using pure sulphuric acid. The samples were then agitated for a period of 24 hours in 50 ml tubes at 150 rpm.

At the end of the agitation period, the whole sample was centrifuged at 4000 rpm for 15 min and the leachate was separated from the solid and measured by Hach EZ Arsenic Test Kit strips and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Table 3-2 summarizes the tests conducted over a 24 h period at a fixed additive/ tailing weight ratio of 10%.

Table 3-2 Summary of the first leaching test conducted using 5 metal oxides at a 10% weight ratio immobilized for a period of 24h.

Sample #	1	2	3	4	5	6	7	8
Noranda Tailings	0% additive	10% regular TiO ₂	10% nano TiO ₂	10% regular ZnO	10% nano ZnO	10% nano MgO	10% nano CaO	10% nano Al ₂ O ₃
Sample #	9	10	11	12	13	14	15	16
Golden Giant Tailings	0% additive	10% regular TiO ₂	10% nano TiO ₂	10% regular ZnO	10% nano ZnO	10% nano MgO	10% nano CaO	10% nano Al ₂ O ₃

Further leaching tests were conducted on the additive that showed the most promise for immobilizing As. These tests were aimed at further narrowing down the amount of SSE experiments to conduct on the most promising additive weight percentages. One additional test was also carried out on magnetite.

Table 3-3 Summary of second leaching test conducted using a metal oxide at different weight ratios immobilized for a period of 24h

Sample #	1	2	3	4	5	6	7	8
Noranda Tailings +	0% additive	5% regular additive	7.5% regular additive	10% regular additive	0% additive	5% nano additive	7.5% nano additive	10% nano additive
Sample #	9	10	11	12	13	14	15	16
Golden Giant Tailings +	0% additive	5% regular additive	7.5% regular additive	10% regular additive	0% additive	5% nano additive	7.5% nano additive	10% nano additive

The same tests were carried out with similar weight percentages over a period of 1-2 months. Since an additive weight percentage of 10% did not show significantly better results than lower weight percentages, an additional weight ratio of 2.7% was explored instead. Since the additives that were retained for SSE analysis were already determined by the 24 hour leaching tests, the 1-2 month leaching tests were used to see whether the degree of leaching was stable over time. Table 3-4 is a list of the different additives used and some of their properties.

Table 3-4 Nanoscale Metal Oxides and their properties

Metal Oxide	Appearance	Specific Surface Area (m² /g)	Crystallite Size (nm)	Average Pore Diameter
NanoActive Aluminium Oxide	White powder	≥275	Amorphous	28 Å
NanoActive Calcium Oxide	White powder	≥20	≤ 40	165 Å
NanoActive Magnesium Oxide	White powder	≥230	≤ 8	50 Å
NanoActive Zinc Oxide	Off-White powder	≥70	≤ 10	170 Å
NanoActive Titanium Dioxide	White powder	≥500	Amorphous	32 Å
Nanoscale Magnetite	Black Powder	≥60	≤ 50	NA

Source : (Nanoscale Corporation, 2010)

Once the leaching procedure was completed, the concentration of arsenic in the leachate was measured using the Hach EZ Arsenic Test Kit strips and ICP-MS analysis. The results were compiled and are presented in the results section of this thesis.

3.3.3 Selective Sequential Extraction (SSE) tests

The goal of SSE tests is to determine the different fractions of a specific element in a given solid sample to determine their effects (Tessier et al., 1979; Yong and Mulligan, 2004). Since arsenic is mainly in the form of anions, SSE procedures used for phosphorus retention have been modified for use with arsenic. The procedure uses specific chemical reagents to release heavy-metal fractions in the soil once the binding phase is destroyed. It does not allow determination of each of the phases very precisely. However, despite these difficulties, the method still gives a very good idea concerning the leaching potential of the heavy metal into the surrounding soil and water environment as a result of changing chemical conditions (pH, temperature etc.) (Yong et al., 1993). The most widely used method is by Tessier et al. (1979). The procedure used in this study was a modified and adapted version (Yong et al., 2003). Table 3-5 summarizes each of the steps.

Table 3-5 Adapted SSE procedure

Sequence #	Fraction	Chemical Reagents
1	Water soluble	8 ml of distilled water shaking at room temperature for 30 min
2	Exchangeable	8 ml of 1M MgCl ₂ shaking at room temperature for 1 hour
3	Carbonate associated	8 ml of 1M NaOAc (sodium acetate) adjusted to pH 5 with acetic acid, and shaking at room temperature for 5 hours.
4	Oxide and Hydroxide associated	8 ml of NH ₂ OH.HCl in 25% v/v acetic acid in a water bath for 6 h at 96°C
5	Organic matter and sulphide associated	3ml of 0.02M HNO ₃ and 5ml of 30% H ₂ O ₂ adjusted to pH 2 with HNO ₃ and then 5ml of 3.2M NH ₄ OH in 20% (v/v) HNO ₃ diluted to 20 ml at room temperature for 30min.
6	Residual Fraction	Digestion at 90°C with 25ml of dilute reverse aqua regia (5% v/v HCl, 20% v/v HNO ₃ and 75% v/v water) for 3 hours.

Source: (Yong et al., 1993)

Each of the different phases and their significance are explained in more detail below.

Exchangeable phase:

This phase is associated with metals that are ion exchangeable and not specifically adsorbed, so they can be readily replaced by competing ions provided by the reagent. For this phase, neutral salts are usually used such as MgCl₂, CaCl₂ and NaNO₃, which displace the cations of the heavy metals which are electrostatically bound to the negatively charged sites on the soil (Yong et al., 1993). In this study a solution of MgCl₂ was used at a pH of 7.

Associated with carbonates

This phase is associated with metals which are bound to carbonates and can be released by the application of acidified acetate solution. Usually the most generally used solution is a solution of sodium acetate brought to a pH 5 by the addition of acetic acid. This is

sufficient to release metals bound to carbonates without attacking the hydroxide or organic matter phases (Yong et al., 1993).

Associated with metal oxides (hydroxide-oxide phase)

The metals in this phase are bound to poorly crystallized and amorphous phases of Fe, Mn and Al. The extracting compound in this case should not attack the organic matter or silicate phases. What is usually used is a combination of 25% acetic acid and an acid reducing agent (e.g., hydroxylamine hydrochloride) to remove the metals bound to ferromanganese oxides. The technique has been confirmed not to reduce the natural organic carbon in the sediments (Tessier et al., 1979). When digestion is done at high temperatures, Al and Si may also be released into solution.

Associated with organic matter (organic phase)

Metals in this phase are bound to organic matter, e.g. humic acid. The mechanisms of binding in organic matter are three fold: adsorption, complexation and chelation. Because of these different mechanisms, there will be overlapping effects from the methods designed to release the metals bound to the exchangeable phase (Tessier et al., 1979).

Residual fraction

The metals in this phase are tightly bound within the lattice of the silicate minerals, and can only be release by digestion with strong acids at high temperatures. In most cases, the fraction is not considered to be significantly large, but in the case of the current study which uses mine-tailings, this fraction is expected to be the largest (Tessier et al., 1979).

3.3.3.1 Experimental Procedure

The adapted SSE procedure outlined in Table 3-5 was performed on various combinations of mine tailings and additives after they were left to rest for a period of 1 -2 months. The goal of this process is to test the long term stabilizing potential of the additives and also to determine in what form the arsenic is bound to the soil particles. Fourteen different samples were prepared for each metal oxide analyzed. Each sample contained a particular form of metal oxide (nanoscale or regular), a specific mine tailing

and different weight percentages of additives (weight additive/weight of tailings $\times 100\%$). Table 3-6 illustrates the different samples created using a particular additive.

Table 3-6 Fourteen different samples created by varying one additive weight and the type of mine tailing.

Sample #	1	2	3	4	5	6	7
Noranda Mine Tailings	0% additive	2.7% regular additive	2.7% nanoscale additive	5% regular additive	5% nanoscale additive	7.5% regular additive	7.5% nanoscale additive
Sample #	8	9	10	11	12	13	14
Golden Giant Mine Tailings	0% additive	2.7% regular additive	2.7% nanoscale additive	5% regular additive	5% nanoscale additive	7.5% regular additive	7.5% nanoscale additive

The samples were prepared at the beginning of the experiments using a combination of additives and tailings. Two grams of air dried mine tailing samples were inserted into fourteen 50 ml plastic centrifuge tubes (Fisherbrand centrifuge tubes). Two of the most promising additives that were selected from the preliminary leaching tests, were mixed with the above mine tailing samples at various weight ratios. Two out of the fourteen samples were not mixed with additives and were kept as control samples. All of the tubes were moistened with 1-2 ml of water to allow the additives to react with the soil as they would in natural conditions of rain or surface water. They were then allowed to rest for 1-2 months at the end of which the SSE extractions were performed. Between each successful extraction, the samples were centrifuged for 12 min at 4000 r/min. The supernatant was drained into separate tubes and the remaining samples were washed with 8 ml of distilled water. The extract and the wash solutions were pooled together and the concentration of arsenic was determined using a combination of ICP-MS, hydride generation, and flame atomic absorption spectrometry. The weight percentage of arsenic in each phase was determined based on the total metal content calculated from adding all

of the phases together. In steps 4, 5 and 6, a water bath was used to maintain a stable temperature.

3.3.3.2 Calculation of weight percentage of arsenic in each phase

After the samples were digested and the concentrations measured in the different phases, the following formulas were used to calculate the weight of arsenic in any given phase:

$W_p = V \times [As]$, where V is the volume of the extracted supernatant and $[As]$ is the concentration of arsenic in the supernatant, expressed in mg/L. The percentage of arsenic in each of the phases was calculated using the following equation: % in phase $p = (W_p/W_T) \times 100\%$.

Once the different weight percentages of arsenic in each of the phases were determined, they were used to plot graphs of the variation in the percentage of each of the phases as a function of the type and amount of additives added. This was later used to select an additive that is most promising for use in the actual field.

3.4 Analytical Methods

The different instruments which were used to measure the concentration of arsenic in the leachate were Hach EZ Arsenic Test Kits, ICP-MS, HG-AAS and FAAS.

3.4.1 Hach EZ Arsenic Test Kits

The first method used to measure arsenic concentrations were Arsenic test strips (Hach EZ Arsenic Test Kits, High Range and Low Range Models, Cat# 282000 and 280000). They are an inexpensive and easy alternative to use to obtain quick measurements. They were used at the beginning of the study along with the preliminary leaching tests to filter out ineffective additives and retain the most promising ones for further tests. Since many times these tests did not provide very clear results, the same samples were sent for a more precise analysis using an ICP-MS.

These test kits were used to measure the amount of arsenic in the leachate collected from the above leaching tests. The test kits were composed of a reaction vessel and cap, a series of 5 different reagents and a box of test strips. 50 ml of leachate was poured into the reaction vessels, and the different reagents (such as sulfamic acid and silver nitrate)

were systematically added into the liquid and shaken vigorously. The cap was then fitted onto the vessel along with a test strip attached to it. The cap has a hole which allows an area of the test strip to come into contact with the air in the reaction vessel. The combination of the reagents and the dissolved arsenic in the liquid produce arsine gas (AsH_3) reacts with the mercury bromide on the test strips to produce different colors. According to the concentration of the arsenic present in the leachate, the color produced will range from white to dark brown. There is a color chart present on the test strip bottles which can be used to compare and estimate the concentration. The readings are only as accurate as the person who reads them as well as the accuracy of the produced colors, and are not very accurate when the values are very similar. However they can give a good idea when comparing samples where the concentrations are significantly different.

As was mentioned in the section about preliminary leaching tests, one of the limitations of the test kits is the interference of test measurements caused by the presence of certain compounds in the leachate, such as nitric acid. Nitric acid prevents the full reduction of arsenic to arsine gas and therefore gives lower results than in reality. Therefore, the leaching tests were carried out using a solution of sulphuric acid, rather than a mixture of nitric and sulphuric acids. Table 3-7 shows some technical information on the two types of Hach Test kits that were used.

Table 3-7 Arsenic Test Kit Types and Measurement Ranges

Test Kit Model	Range (mg/L)	Measurement Increment (mg/L)
Arsenic, Low Range	0-500ppb	0, 10, 30, 50, 70, 300 , 500
Arsenic, EZ, Dual Range	0-500ppb	0, 10, 25, 50, 100, 250, 500
	0-4000ppb	0, 35, 75, 175, 1500, 4000

Source: (Hach Company, 2009)

3.4.2 ICP-MS

ICP-MS is used for the determination of concentrations of elements in water samples or waste extracts. It can be used for concentrations below 1 µg/L (ppb). It is one of the recommended methods (Method 6020A) for measuring arsenic concentrations in waste (EPA Online, 2008). To measure the concentrations of dissolved elements in water, samples must be filtered and acid preserved before measurements are made. This method has been used to measure over 60 elements. Elements for which this method was shown to be acceptable are listed in Table 3-8.

Table 3-8 Some elements for which the ICP-MS method is applicable

ELEMENT	SYMBOL	ELEMENT	SYMBOL
Aluminum	Al	Manganese	Mn
Antimony	Sb	Mercury	Hg
Arsenic	As	Nickel	Ni
Barium	Ba	Potassium	K
Beryllium	Be	Selenium	Se
Cadmium	Cd	Silver	Ag
Calcium	Ca	Sodium	Na
Chromium	Cr	Thalium	Tl
Cobalt	Co	Vanadium	V
Copper	Cu	Zinc	Zn
Iron	Fe	Manganese	Mn
Lead	Pb	Mercury	Hg
Magnesium	Mg	Nickel	Ni

Source: (EPA Online, 2008)

It was developed in the late 1980's to combine the sample detection and analysis of ICP technology with the low detection limits of mass spectrometry. It has been widely used in many fields such as mining, metallurgy, drinking water, geology, food sciences and medicine. It is built using the same principles as atomic emission spectrometry, whereby samples are decomposed at high temperatures in an argon plasma and their contents are

analyzed based on their mass to charge ratios (EPA Online, 2008). Table 3-9 shows the sensitivity and the detection limits of ICP-MS for some elements.

Table 3-9 Detection Limits for various metals analysed by ICP-MS

ELEMENT	DETECTION LIMIT (PPT)
U, Cs, Bi	less than 10
Ag, Be, Cd, Rb, Sn, Sb, Au	10-50
Ba, Pb, Se, Sr, Co, W, Mo, Mg	50-100
Cr, Cu, Mn	100-200
Zn, As, Ti	400-500
Li, P	1-3 ppb
Ca	Less than 20 ppb

Source : (EPA Online, 2008)

The model used for this study was ICP-MS (Agilent 7500ce). The working concentration range is DL (Detection Limit) to 500 ppm. The sample is introduced using a peristaltic and HPLC pump. The samples for ICP-MS can be either liquid or solid. In this study, all the samples analyzed were liquid leachates. A small sample of the leachate, approximately 1 ml, was taken from the centrifuge tubes using a pipette. This sample was diluted between 2 to 401 times to bring the concentration of arsenic into the measuring range of the machine. A matrix of 1% nitric acid was used and samples were run in He mode, and a calibration of 0.1-500 ppb was used for arsenic.

3.4.3 Hydride Generation Atomic Absorption Spectrometry (HG-AAS)

As an alternative to ICP-MS, some low concentration samples were measured using HG-AAS EPA method 7061A). This method is also one of the methods recommended by the EPA (Method 7061A) for the measurement of arsenic in wastes, groundwater and soils. It is a low cost alternative to ICP-MS. The samples are digested using a mixture of sulphuric and nitric acid. It is applicable for samples that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt and molybdenum (EPA Online, 2008).

The arsenic in solution is converted, by the use of tin chloride, into a volatile gas (arsine) by the hydrogen produced by the reaction of zinc with hydrochloric acid. The arsine gas (arsenic hydride) is blown onto an argon-hydrogen flame in the path of an atomic adsorption spectrophotometer. The resulting arsenic concentration is proportional to the absorption of the lamp radiation (EPA Online, 2008).

This method has a typical detection level of about 2 ppb. The samples that were normally analyzed with ICP-MS were instead measured using a Hydride Generator connected to the Perkin Elmer AAnalyst 800 atomic absorption spectrometer with a longitudinal Zeeman graphite furnace. This was done as the ICP-MS became unavailable in the course of the study. As in the case of the FAAS, the samples were analyzed in the Trace Element Analysis Lab (TEAL) laboratory of the McGill Earth and Planetary Sciences department.

3.4.4 Flame Atomic Adsorption (FAAS)

For higher concentrations of arsenic, such as those that resulting from the digestion of the residual fraction of the mine tailings using reverse aqua regia, flame atomic adsorption was used. Flame atomic absorption is a commonly used technique for detecting metals and is very reliable. It is based on the fact that metals that are at their ground state absorb light only at certain specific frequencies. The metals present as ions in solution are converted into ground state metals through the flame in the atomic absorption device. The wavelength corresponding to the particular metal is supplied and the amount of light absorbed by the flame is used to determine the concentration of that element in the sample. The model of the FAAS used is the Perkin Elmer AAnalyst 100 Flame atomic absorption spectrometer at the McGill TEAL in the Earth and Planetary Sciences Department.

Each sample was prepared according to EPA method 3010, used for the analysis of extracts. The liquid leachate generated by the preliminary leaching tests and the SSE tests were added to a mixture of HNO₃, HCl and heat. The resulting samples were introduced into the machine and aspirated for analysis by an internal flame. Fig. 3.7 illustrates a

typical flame atomic adsorption instrument used at the Federal Institute for Materials and Research and Testing in Germany.

4 RESULTS AND DISCUSSION

In this chapter, the findings of the various experiments that were performed are presented as well their significance is discussed. As mentioned in the introduction, the main objective of this study is to determine the effectiveness of metal oxides at immobilizing arsenic in soil. To determine the effectiveness of the different additives, a variety of leaching tests were carried out, and to test the chemical stability of the immobilized soil, SSE tests were performed over a period of 1 to 2 months. Mine tailings were characterized using an XRF analyser (NITON XLP 700 series). Two out of the four tailings which showed the highest concentration of arsenic were selected for the study.

4.1 Characterization of Mine Tailings using XRF

The following measurements were taken from the XRF analyzer for four different mine tailings. As can be seen in Table 4-1, many different metals are present in each sample at different concentrations. In Golden Giant mine tailings, arsenic represents 0.027% of the total weight. The element with the highest concentration is iron, followed by chromium and molybdenum. Arsenic is the fifth most concentrated element, with a 9% the weight of chromium and 0.05% the weight of iron in the sample.

Table 4-1 XRF analysis results for mine tailings

Element	Conc. (mg/kg)	Error (±mg/kg)	Element	Conc. (mg/kg)	Error (±mg/kg)
Golden Gate Tailings			Louvicourt Tailings		
Rb	48	25	Zr	177	66
Hg	102	66	As	220	124
As	273	85	Pb	369	140
Sr	988	120	Cu	907	407
Mo	1070	67	Zn	2225	456
Cr	2896	1339	Mn	4266	1905
Fe	52k	3k	Fe	316k	8k
Noranda Tailings			Mont Wright Tailings		
Sr	178	79	Fe	349k	14k
Ag	1044	603	As	< DL	
Zn	1208	463			
Ti	1276	526			
As	2557	605			
Ba	4662	586			
Pb	11k	1k			
Ca	19k	3k			
Fe	385k	10k			

In the case of Louvicourt mine tailings, arsenic is 0.021% of the total weight. The highest concentration is again iron, representing 32% of the total weight, followed by manganese and zinc.

In Noranda mine tailings, the concentration of arsenic is 0.25% of the total weight of the tailings. Iron represents almost 40% of the weight of the mine tailings, followed by calcium at 1.8% and lead at 1.1%. Arsenic is the fifth most concentrated element by weight.

In the case of Mont-Wright tailings, the concentration of arsenic is below detectable levels by the XRF. The limit of detection is around 60 mg/kg for arsenic. The concentration of iron represents 35% of the total weight, with the remaining weight probably composed of non-metallic elements.

Two of the mine tailings with the highest concentration of arsenic, Noranda and Golden Giant tailings, were selected for this study. The concentration of arsenic in Noranda tailings is nearly 10 times that of Golden Giant tailings. The elements present in each of the tailings are very different, and have the potential to interfere with the immobilizing capacity of the additives.

Iron and calcium are the elements with the highest concentration in Noranda mine tailings. In the case of Golden Giant mine tailings iron and chromium are the elements which have the highest weight percentage.

4.2 Leaching Tests

These tests were performed in order to measure the leaching potential of the mine tailings with and without additives. The results are represented in the charts below. All errors are represented as average errors on the experimental values using a $\pm 5\%$ error margin. The points on all graphs are the average of duplicate tests.

4.2.1 Effect of Type of Metal Oxide Additives on Arsenic Immobilization at a fixed 10% weight additive/ weight tailing ratio

Measurements were taken with Hach EZ Arsenic test strips and ICP-MS. The reference point for each concentration was a mine tailing sample with no additives. The results are presented in Figs. 4-1 to 4-4.

According to the results obtained by the test strips, the greatest reduction in arsenic concentration in Noranda mine tailings is for regular and nanoscale ZnO. If we compare these results with those obtained using ICP-MS, we can see that both agree. As can be seen from Fig. 4-1, regular ZnO and nanoscale ZnO showed very promising results in terms of immobilization with a minimum reduction of 90% of the original arsenic respectively.

Golden Giant mine tailings showed slightly different findings. Considering the error margins, the most promising additive found according to the Hach test-strips is nanoscale TiO₂. However, the ICP-MS identified nanoscale and regular ZnO as the most promising additives. Since ICP-MS is a more sophisticated instrument calibrated to eliminate interferences it is most likely that the latter results are more accurate, in agreement with the findings for Noranda tailings. Measurements made using the Hach EZ test strips have a significant error margin since they are dependent on the ability of the reader to match the colors produced on the test strips to the color diagram. The discrepancy between both measuring methods is much greater in the case of Golden Giant tailings. This could be due to certain interferences of the compounds present in the tailings with the measurement method.

As is evident from all of the above results there is a significant difference in the degree of arsenic leaching from the mine tailings according to the type of additive used for a 10% weight additive /weight tailing ratio. Different interactions take place between the additives and the arsenic in the tailings that cause the immobilization. Depending on the interaction between the additives with the arsenic and other metals and compounds present in the tailings, the degree of effectiveness varies.

One interesting fact to note is that in the case of Golden Giant mine tailings, some additives increased rather than decreased the levels of arsenic in solution. In Table 4.6, nanoscale CaO and regular TiO₂ are examples of two metal oxides which increased the amount of arsenic leaching. One possible explanation to this phenomenon is that the additives increased the pH of the solution, thereby increasing the amount of leaching. It is possible that arsenic is more easily mobilized in Golden Giant mine tailings than in Noranda tailings, when the pH is thus increased from an original value of 3 to values above 7. Particularly in the case of CaO, a highly alkaline salt, when mixed with water generates a high pH, increasing the mobilization of arsenic. It has been shown in a number of studies that the mobility of arsenic increases with pH (Seaman et al., 2003; Hartley et al., 2004).

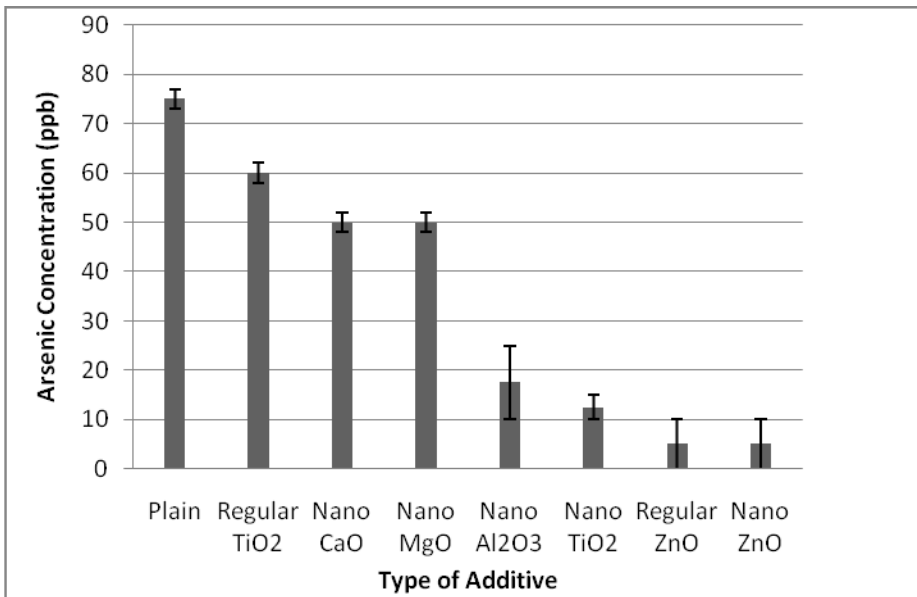


Figure 4-1 Arsenic concentration (ppb) leached from Noranda mine tailings according to type of metal oxide additive. Results were measured using Hach EZ Arsenic tests strips.

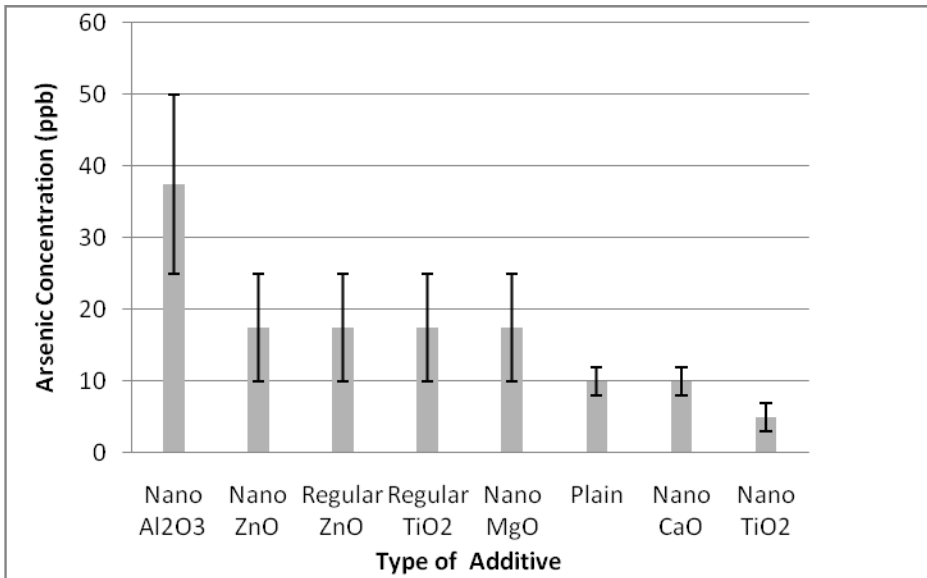


Figure 4-2 Arsenic concentration (ppb) leached from Golden Giant mine tailings according to type of metal oxide additive. Results were measured using Hach EZ Arsenic test strips.

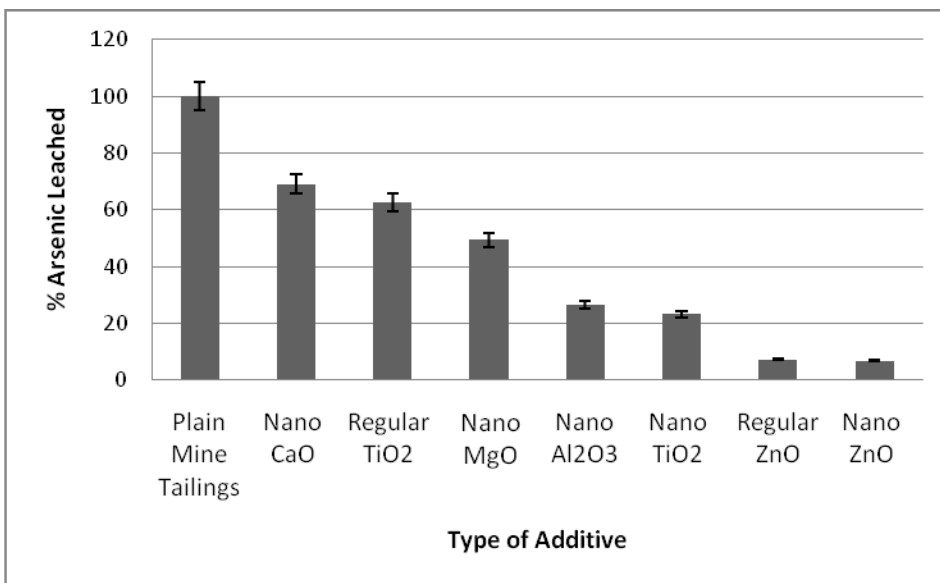


Figure 4-3 % Arsenic leached according to type of metal oxide additive, in comparison to plain Noranda mine tailings. Results were measured using ICP-MS.

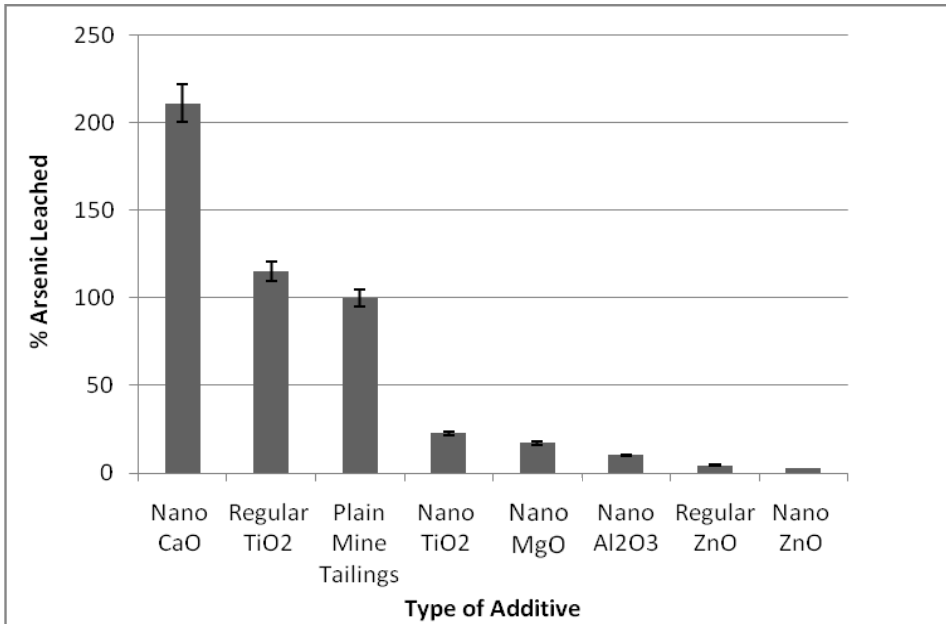


Figure 4-4 % Arsenic leached according to type of metal oxide additive, in comparison to plain Noranda mine tailings. Results were measured using ICP-MS.

4.2.2 Effect of Weight Additive/ Weight Tailing ratio on Arsenic Immobilization for two metal oxide additives over a period of 24 hours

It was determined from the previous experiment that the most promising additives are nanoscale and regular ZnO. In this section the results of further experiments on the immobilizing potential of ZnO using different weight ratios are shown. Using weight ratios of 5%, 7.5% and 10%, leaching tests were repeated for ZnO and Fe₃O₄. These tests were conducted over a period of 24 hours.

In Fig. 4-5, there is a decrease in the degree of leaching when the weight of ZnO is increased. A maximum reduction of 97.4% of the original concentration of arsenic occurs when a weight ratio of 7.5% nanoactive ZnO is used. For this particular test, nanoscale ZnO appears more effective at reducing leaching than regular ZnO.

In Fig. 4-6, there is a similar trend in the case of ZnO applied to Golden Giant tailings. The concentration of arsenic decreases from the value of 12.06 ppb for plain mine tailings to 0.28 ppb for tailings treated with 10% wt / wt nanoscale ZnO. This is a factor of reduction of 43:1 or 97.7%. It is interesting to note that there is less difference between the performance of nanoscale vs regular ZnO than in the case of Noranda mine tailings. This could be due to the different elements present in each of mine tailings and complex interactions between the additives and these elements.

By looking at Figs. 4-7 and 4-8, it is apparent that nanoscale and regular Fe₃O₄ do not act as a very effective additive for immobilizing arsenic in either Noranda or Golden Giant mine tailings. In the case of regular Fe₃O₄ applied to Noranda mine tailings, its addition even seems to increase the leaching of arsenic. The amount of arsenic leached from Noranda mine tailings without additives is 919.9 ppb. The amount of arsenic leached from a mixture of Noranda mine tailings and 10% regular Fe₃O₄ is 1170 ppb, an increase of 138%. One possibility could be that Fe₃O₄ has much a higher affinity to the other metals in the tailings, which take up the adsorption sites of arsenic. Another possibility could be that the surface area of regular Fe₃O₄ is not high enough for it to be an effective sorbent. Nanoscale Fe₃O₄, though with a slightly better performance than its non-nanoactive counterpart, could also have a reduced surface area and reactivity due to the formation of microsized nanoconglomerates. Agglomeration happens because of surface forces such as charge and Van der Waals forces, and even magnetic fields (Kindall and Kosseva, 2006). Many studies have shown that adsorption capacity of Fe₃O₄ increases manifold by particle size and that Fe₃O₄ with a low surface area is a poor sorbent for arsenic. In a particular study, when particle size decreased from 300 to 12 nm, the efficiency of sorption increased by a factor of 200 (Mayo et al., 2007).

In contrast to regular Fe₃O₄ its addition helps to decrease levels of arsenic to 66% of its original value, or from an initial value of 919.9 ppb to 603.8 ppb. Though a little more effective than regular Fe₃O₄, the nanoscale compound does not show much effectiveness.

In the case of Golden Giant tailings, the concentration of arsenic in the leachate diminishes from 61.4 ppb to 24.9 ppb for nanoscale Fe₃O₄, or to 40% of its original value. In the case of regular Fe₃O₄ the original concentration in the leachate drops from 61.4 ppb to 29.1 ppb, or to 47.3% of its original value. This is much less effective than ZnO. The results are shown in Fig. 4-8.

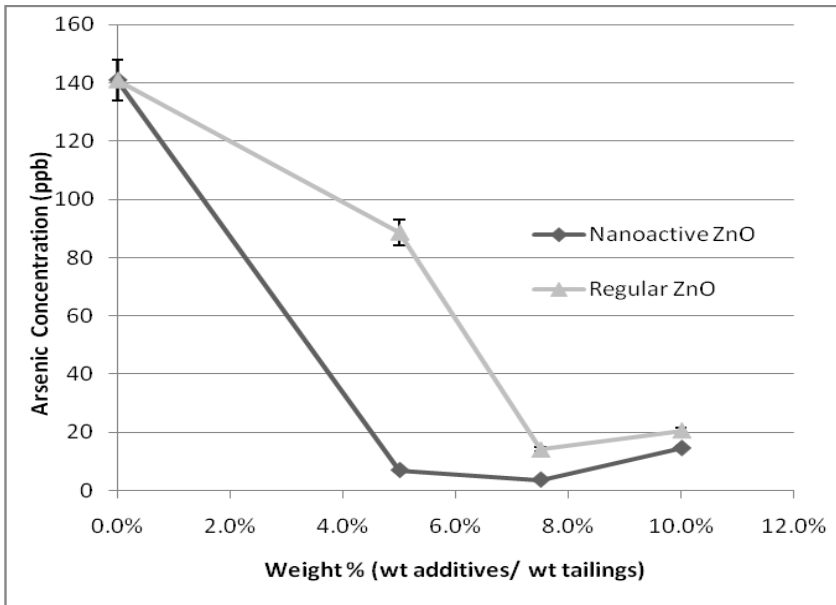


Figure 4-5 Arsenic concentration (ppb) leached from Noranda mine tailings according to weight percentage of nanoscale ZnO and regular ZnO after 24 hours.

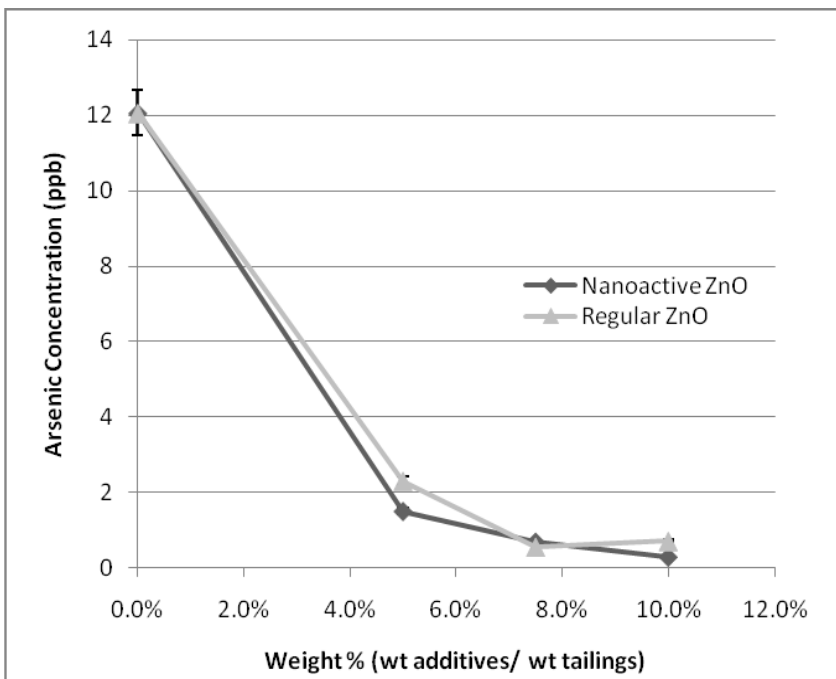


Figure 4-6 Arsenic concentration (ppb) leached from Golden Giant mine tailings according to weight percentage of nanoscale ZnO and regular ZnO after 24 hours.

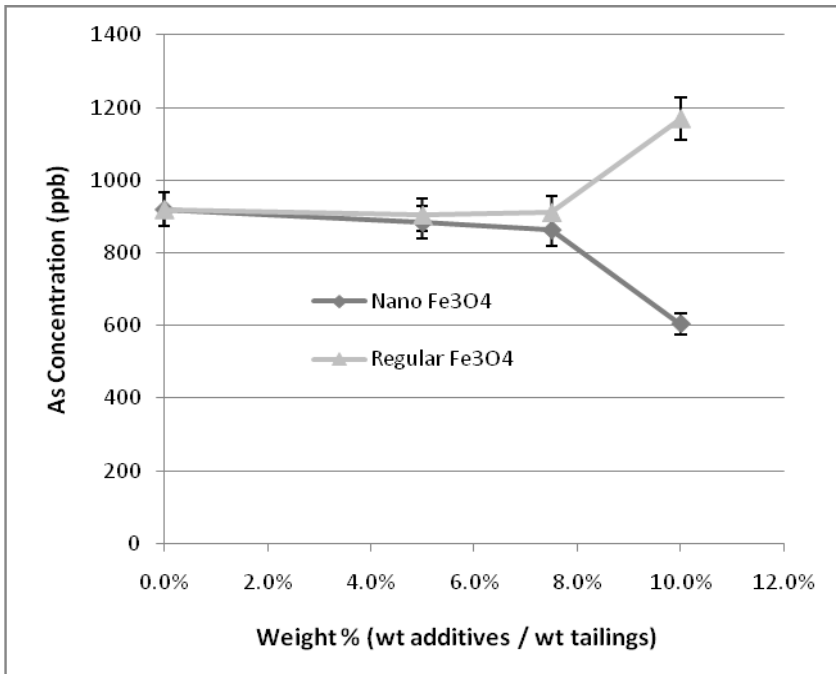


Figure 4-7 Arsenic concentration (ppb) leached from Noranda mine tailings according to weight percentage of nanoscale Fe₃O₄ and regular Fe₃O₄ after 24 hours.

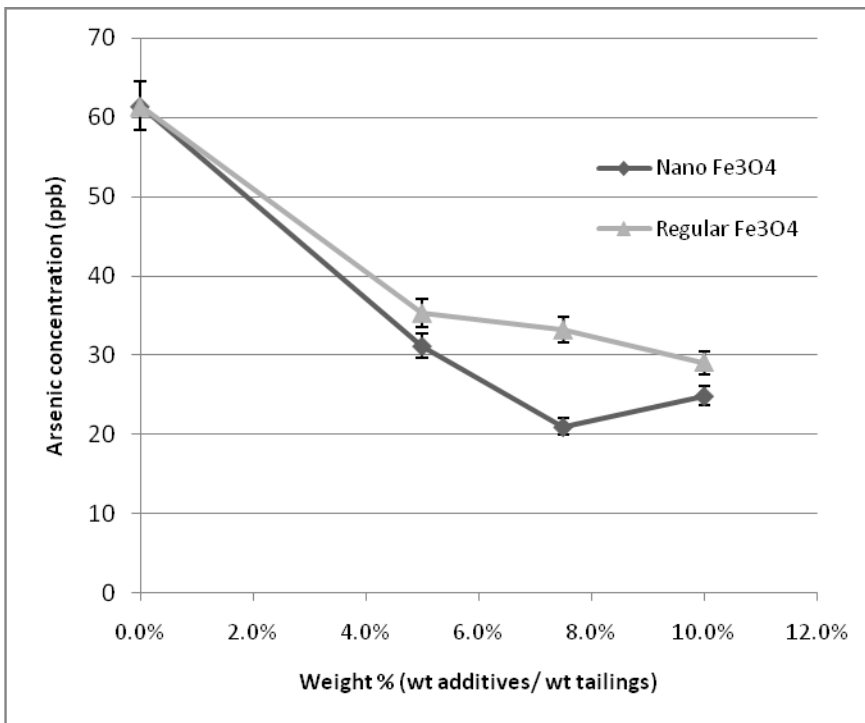


Figure 4-8 Arsenic concentration (ppb) leached from Golden Giant mine tailings according to weight percentage of nanoscale Fe₃O₄ and regular Fe₃O₄ after 24 hours.

4.2.3 Effect of Weight Additive/ Weight Tailing ratio on Arsenic Immobilization for two metal oxide additives over a period of 1 month

Leaching tests were conducted for a period of one month to determine whether the additives produced similar results if left to react over a longer period of time. The overall trend is similar in both the cases with a decrease in the concentration of arsenic in the leachate as the weight of the additives was increased. There is a substantial reduction in arsenic leachate levels with the application of regular and nanoactive ZnO to both Noranda and Golden Giant tailings. As in the case of the 24 hour leaching tests, Fe₃O₄ fared quite poorly and did not show any improvement when left over a longer period of time.

In the 1 month long study, the weight ratios of additives used were 1.3%, 2.7%, 5% and 7.5%.

As can be seen in Fig. 4-9, the effectiveness of the mine tailings increases with weight, with the arsenic in solution dropping from an initial value of 89.4 ppb to 8.41 ppb, when Noranda tailings were mixed with 7.5% w/w of nanoscale ZnO. This represents a reduction of 90.6%. When 5% wt/wt of nanoscale ZnO was used, the decrease was 89.8%.

In the case of regular ZnO, there is a similar trend with a decrease of 80% in the amount of arsenic leached when 7.5% wt/wt of the additive is mixed with Noranda tailings over a 1 month period. In contrast when the same additive is applied for a period of 24 hours, the decrease in arsenic leaching was 90%.

With Golden Giant tailings treated with ZnO, the results are similar. There is a slight decrease in the efficiency of the additives when they were tested after 1 month. Fe₃O₄ showed a similar performance when applied over 1 month as it did for 24 hours.

In general, the efficiency of immobilization seems to drop slightly when the samples are left for 1 month compared to 24 hours. This could be due to a change in the pH of the

mine tailings over time, reintroducing some of the arsenic that was initially immobilized. It is important to note that the difference in efficiency is only very minor.

The long term efficiency of the additives is investigated in more detail by the SSE tests in the following sections.

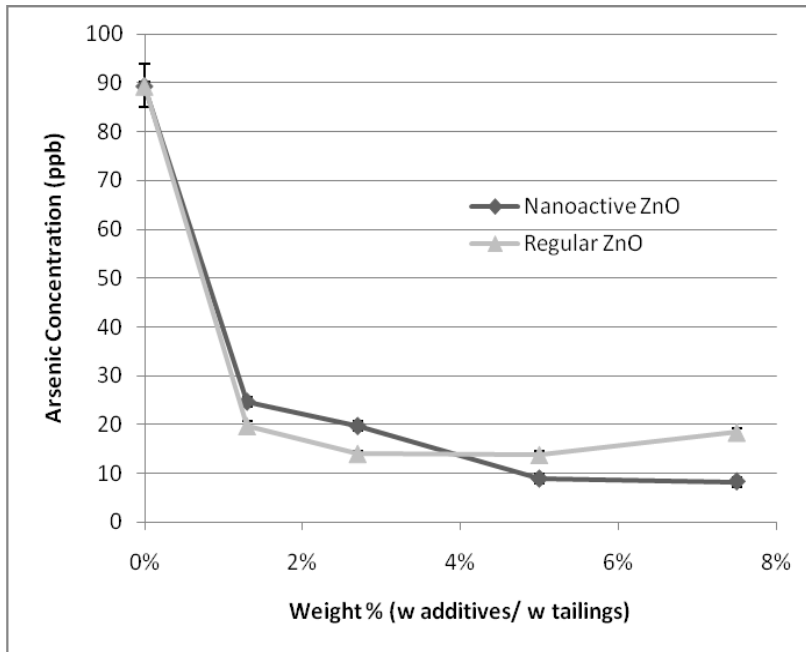


Figure 4-9 Arsenic concentration (ppb) leached from Noranda mine tailings according to weight percentage of nanoscale and regular ZnO after 30 days.

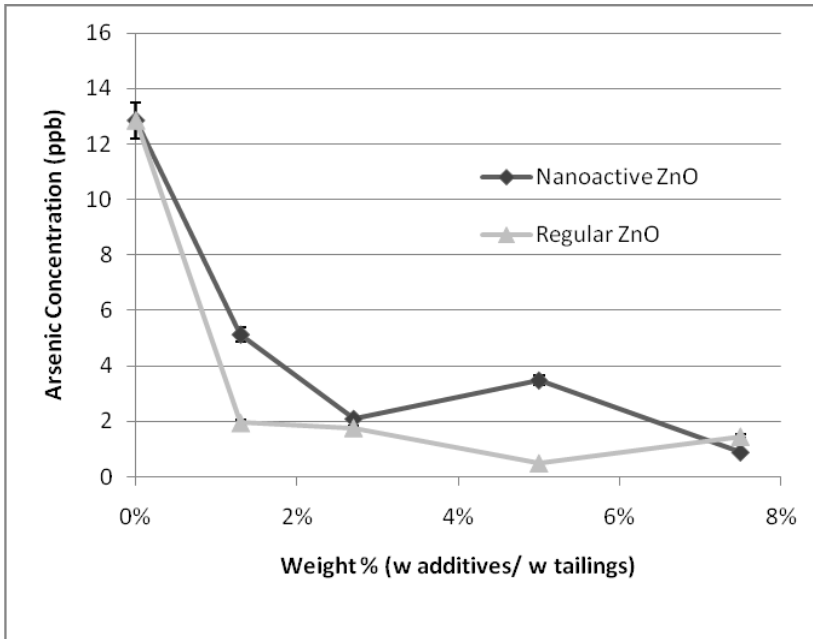


Figure 4-10 Arsenic concentration (ppb) leached from Golden Giant mine tailings according to weight percentage of nanoscale ZnO and regular ZnO after 30 days.

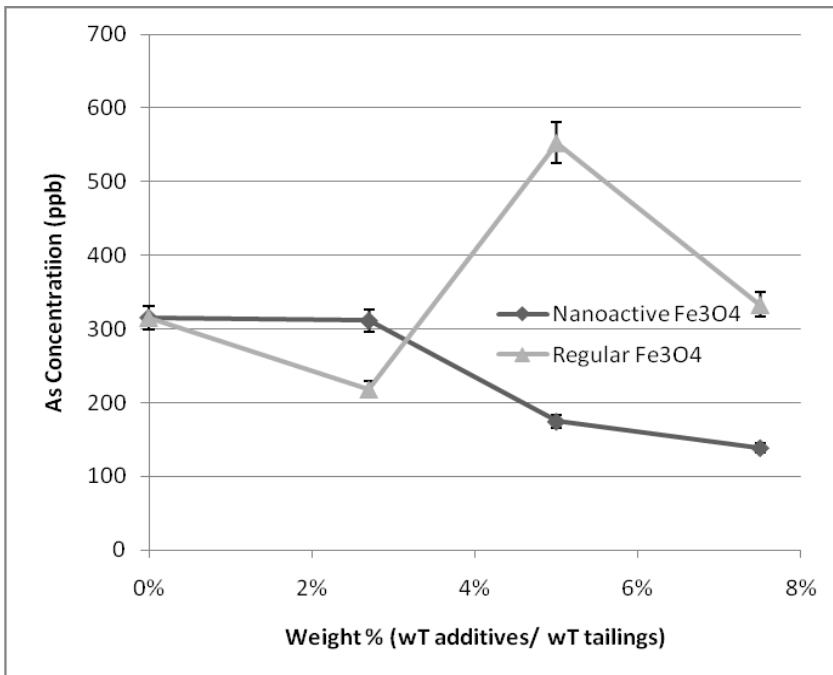


Figure 4-11 Arsenic concentration (ppb) leached from Noranda mine tailings according to weight percentage of nanoscale Fe₃O₄ and regular Fe₃O₄ after 30 days

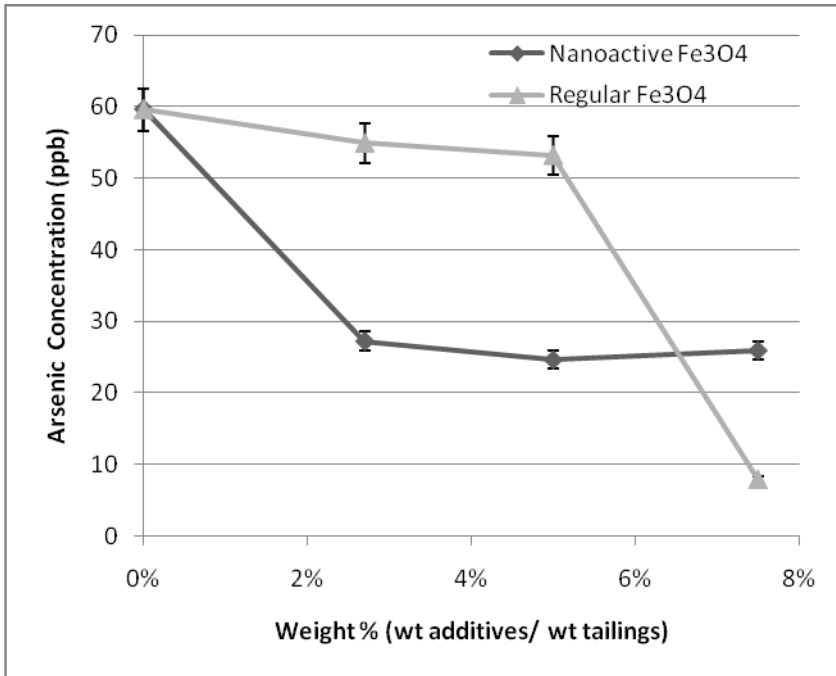


Figure 4-12 Arsenic concentration (ppb) leached from Golden Giant mine tailings according to weight percentage of nanoscale Fe₃O₄ and regular Fe₃O₄ after 30 days.

4.2.4 Concentration of Zinc Ions in Solution

Some measurements were taken in order to determine the concentration of zinc in solution after leaching tests were performed on the samples treated with different weights of ZnO over a period of 24 h. This was done to determine the potential for zinc leaching into the environment as a result of in situ treatment of the tailings. Table 4-2 shows the concentration of zinc and pH of the leachate following the 24 hour leaching tests.

The solubility of ZnO in distilled water is only 0.16g per 100ml, or 1.6 ppm. Higher values of zinc were detected in solution up to 340 ppm when the ZnO was added to Noranda mine tailings. This suggests that the pH of the solution has a significant effect on the solubility of ZnO.

In untreated Noranda mine tailings, the concentration of zinc is relatively low at about 9 ppm. In untreated Golden Giant mine tailings, the concentration is also low at about 0.226 ppm. This small quantity of dissolved zinc comes from the zinc present in the mine tailings themselves. The higher concentrations of zinc present in the Noranda mine tailings as compared to Golden Giant tailings are probably the reason for the higher

concentration of zinc in solution. Noranda mine tailings have a concentration of more than 2000 ppm of zinc.

When the same weight of ZnO was added to Noranda mine tailings as compared to Golden Giant mine tailings, the resulting concentration of zinc in solution was much higher. This suggests that the pH of the solution containing Noranda mine tailings is much lower since the solubility of ZnO increases with lower pH. This can be seen from Table 4-9 which contains the pH values of the mine tailings mixed with a solution of sulphuric acid and distilled water at pH 3. If we look at the results of the mixed samples containing additives, it is clear that the higher pH values reduce the solubility of ZnO, without decreasing the immobilizing effect of ZnO. Therefore, a possible solution for large scale remediation to reduce the zinc content in solution when dealing with acidic soils is to add calcium oxide or another neutralizing salt to raise the pH slightly without promoting mobilization.

Table 4-2 Concentration of zinc and pH of solution following the addition of ZnO additives at different weights after 24 hours. Tailings were mixed with distilled water combined with sulphuric acid at pH 3.

Mine Tailings	ZnO (wt/wt %)	As (ppb)	Zn (ppm)	pH at t = 0	pH at t = 24h
NORANDA					
Untreated Mine Tailings	0.0%	140.8	9.7	3.0	2.6
Regular ZnO	5.0%	88.6	233.3	3.0	3.7
Regular ZnO	7.5%	14.1	289.0	3.0	4.8
Regular ZnO	10.0%	20.6	301.7	3.0	4.5
GOLDEN GIANT					
Untreated Mine Tailings	0.0%	12.1	0.2	3.0	3.3
Regular ZnO	5.0%	2.3	46.1	3.0	6.2
Regular ZnO	7.5%	0.6	46.4	3.0	6.0
Regular ZnO	10.0%	0.7	48.7	3.0	6.0

4.3 SSE Tests

Heavy metals that occur in soil or mine tailings can be bound in several different forms. Through the SSE procedure, the effect of the additives on immobilizing the heavy metals bound to each specific component in the soil was determined. The results are represented in the charts below. All errors are represented as average errors on the experimental values using a +5% error margin. The points on all graphs are the average of duplicate tests.

4.3.1 SSE Tests on ZnO Additives and Noranda Mine Tailings

After leaving the mine tailings mixed with various weight ratios of ZnO for a period of 2 months, SSE extraction tests were performed.

In Figs. 4-13 – 4-18, the effect of the additives on the different fractions of arsenic in Noranda mine tailings is seen. There is an overall decrease in the water soluble arsenic fraction after the addition of ZnO. All values of arsenic leached are far below the concentration of arsenic leached from plain mine tailings. For example, in Fig. 4-13, as the weight of ZnO is increased from 0% to 2.7%, the concentration of arsenic in the water phase drops from 0.017 ppb to 0.001 ppb, only to increase to 0.005 ppb again. Because there is no steady decrease in values, no clear correlation can be made between the weight ratio of the additives and the concentration of arsenic.

A few possible explanations to this phenomenon could be the lack of precision of the SSE method, or complex interactions which would need to be further investigated into. It would be beneficial to repeat the same experiments with a wider spectrum of weight ratios to get a better idea if there really does exist a correlation between weight ratio and arsenic concentration.

The decrease of arsenic in the water soluble phase varies from factor of 2.7 for 5% nanoscale ZnO, to 18.7 for 2.7% regular ZnO to below detectable levels for 7.5% nanoscale ZnO. The large scale reduction calculated for 7.5% nanoscale ZnO could be

partly attributed to instrument or experimental error, and would have to be verified by further repetitions. The arsenic in the water phase is the arsenic which readily dissolves into pure distilled water upon contact with the mine tailings.

As seen in Fig. 4-14, the decrease in arsenic in the exchangeable fraction varies by a factor of 2.2 for 2.7% nanoscale ZnO, and a factor of 32 for 7.5% regular ZnO. A clear correlation can be observed between the increase in weight of the additives and a decrease in arsenic concentration. The exchangeable phase is associated with metal ions (arsenic ions in this case) electrostatically bound to the negative sites on the mine tailing sample. The larger concentration of MgCl₂ displaces the As (III) and As (V) ions from their sorption site on the tailings, and into the solution. The MgCl₂ solution used for extraction is not strong enough to release arsenic bound in any other forms (Yong et al., 1993).

The decrease of arsenic in the carbonate phase varies, as illustrated in Fig. 4-15, from a factor of 2.1 for 2.7% nanoscale ZnO, to 11.5 for 5% regular ZnO. ZnO effectively decreased the amount of arsenic bound to this phase on average by a factor of 6. As in the case of the water soluble component, a clear correlation cannot be observed between an increase in additive weight and reduction in arsenic concentration. Metals bound to the carbonate phase can be released by the application of a weak acid. In this case, a solution of acetic acid with a pH of 5 was used.

In the oxide and hydroxide phase, the level of arsenic in the leachate decreases constantly when the weights of both regular and nanoscale ZnO are increased. The highest decrease in arsenic concentration in this phase can be observed by the addition of 7.5% regular ZnO. The level of arsenic decreases by about 70%. The arsenic in this phase is bound to poorly crystallized Fe, Al and Mn oxides. The agents used in the SSE procedure remove the arsenic which is bound to the ferromanganese oxides in the tailings. The binding might be strong, moderate or weak. Therefore the decrease of arsenic leaching in this phase testifies to the effectiveness of immobilization by ZnO.

In the sulfide organic matter phase (Fig. 4-17) there is also a consistent decrease in the level of arsenic as different weight percentages of ZnO are used. However, the concentration of arsenic does not decrease proportionally as the weight percentage is increased. The highest decrease of arsenic is by the addition of 5% regular ZnO where a reduction of 46% is observed.

In the residual fraction, the addition of ZnO caused a higher amount of arsenic to be bound, which possibly indicates the formation of a stable geochemical species of arsenic with ZnO or with other compounds in the mine tailings. A similar conclusion was reached when zero valent iron was used in one study and nearly doubled the residual fraction of arsenic (Kumpiene et al., 2006). It was hypothesized that the arsenic in the study must be forming a stable Fe-As species.

Table 4-3 summarizes the average decrease in arsenic concentration in each of the different fractions of the mine tailings. As can be seen, the more tightly bound fractions are less affected by the addition of the additive. In all of the phases, with the exception of the residual fractions, the addition of ZnO additives improves the degree of immobilization of arsenic.

Table 4-3 Decrease in the different chemical fractions of arsenic in Noranda mine tailings after the addition of 7.5% wt / wt ZnO

Fraction	$C_{\text{Untreated tailings}} / C_{\text{Treated tailings}}$
Water Soluble	4.9
Exchangeable	31.9
Carbonate	5.1
Oxide/Hydroxide	4.8
Organic Matter/Sulfide	1.5
Residual Fraction	9.5×10^{-1}

Looking at Figs. 4-13 – 4-18, we can see that the efficiency of the additives to immobilize arsenic is quite high in all of the phases especially in the exchangeable phase. This behaviour confirms that ZnO is an additive of choice for the long term immobilization of Noranda tailings.

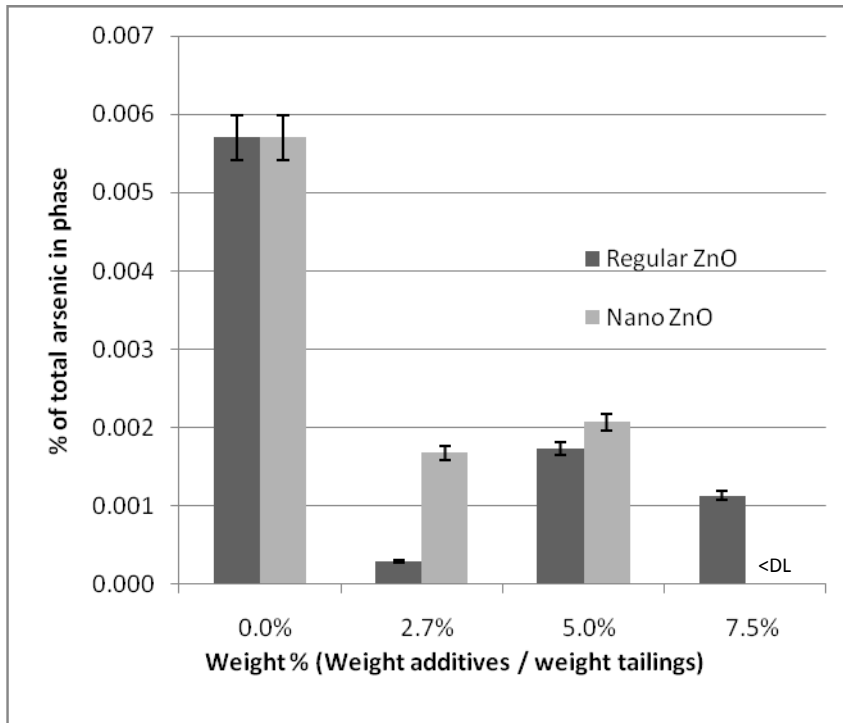


Figure 4-11 Effect of weight percentage of ZnO on water soluble arsenic fraction in Noranda mine tailings in SSE tests.

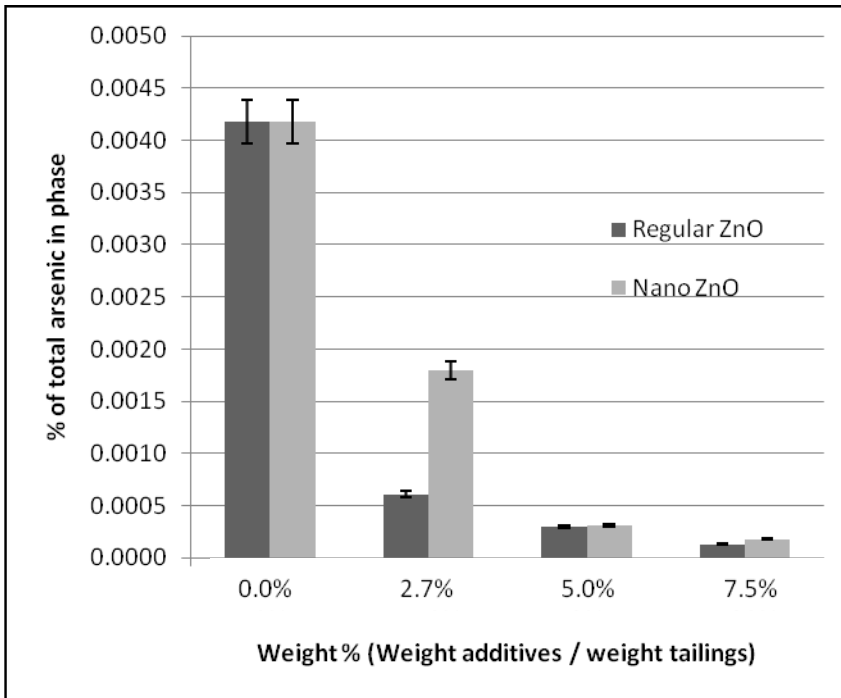


Figure 4-12 Effect of weight percentage of ZnO on exchangeable arsenic fraction in Noranda mine tailings following SSE tests.

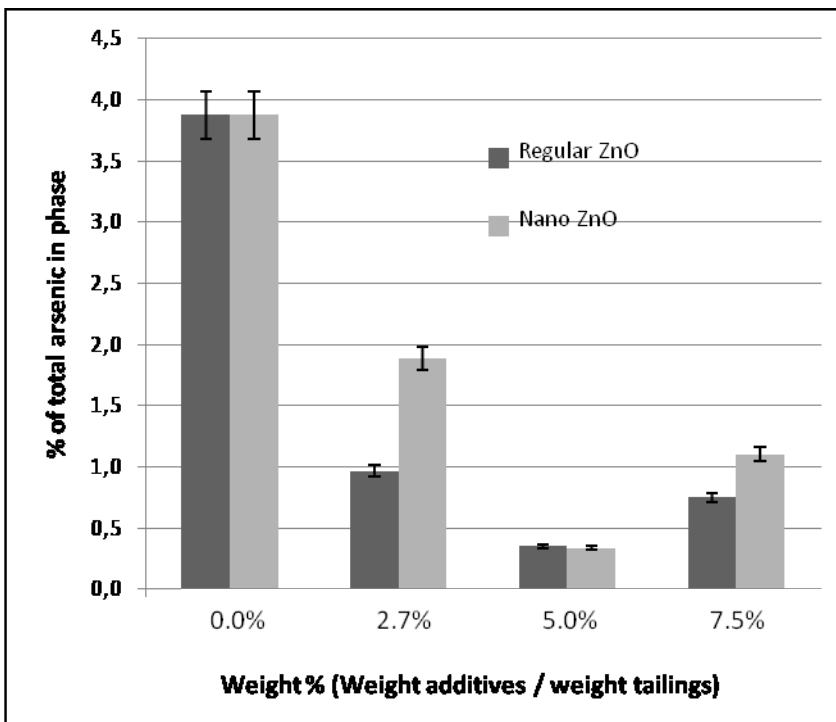


Figure 4-13 Effect of weight percentage of ZnO on carbonate bound arsenic fraction in Noranda tailings following SSE tests.

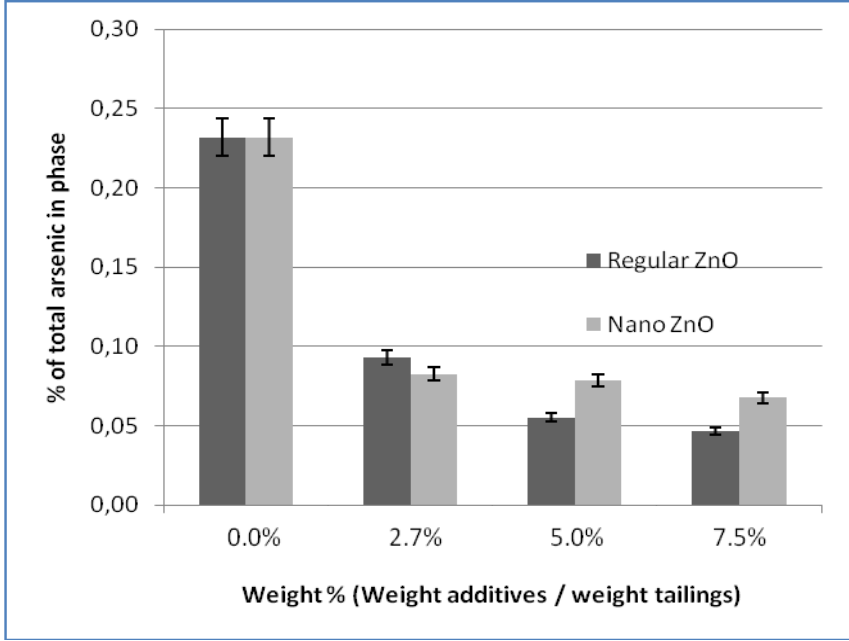


Figure 4-14 Effect of weight percentage of ZnO on oxide/hydroxide arsenic fraction in Noranda mine tailings following SSE tests.

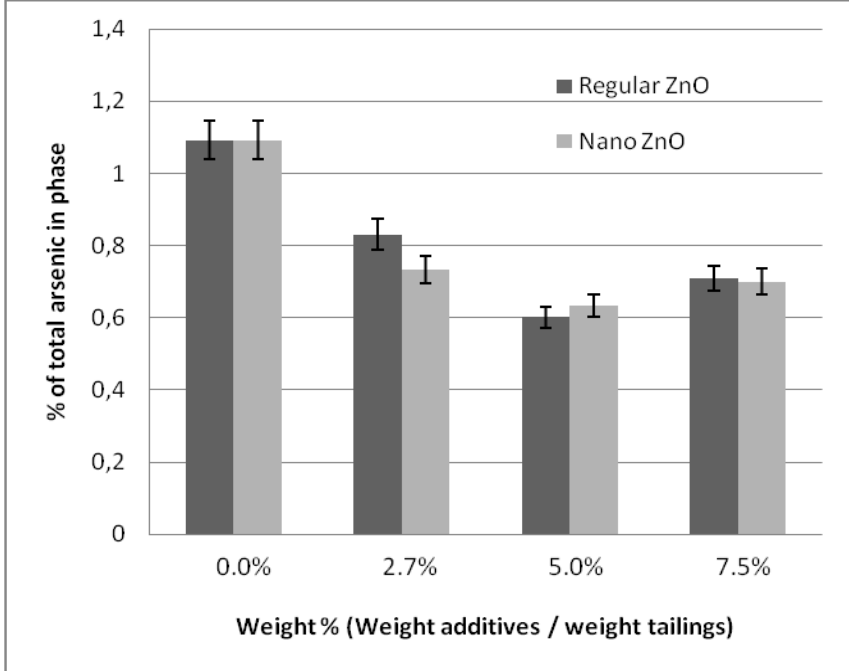


Figure 4-15 Effect of weight percentage of ZnO on sulphide/organic matter arsenic fraction in Noranda mine tailings following SSE tests.

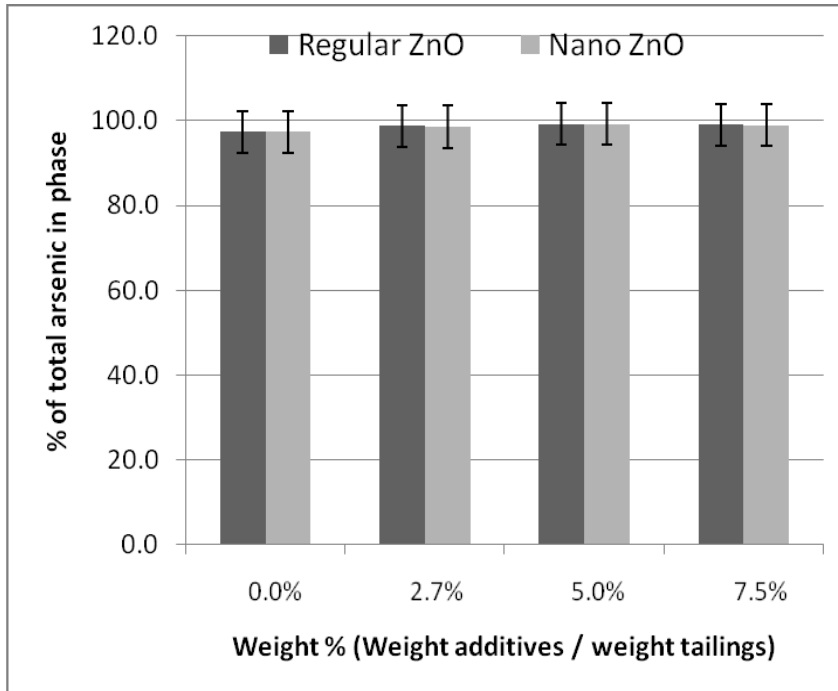


Figure 4-16 Effect of weight percentage of ZnO on the residual fraction in Noranda mine tailings following SSE tests.

4.3.2 SSE Tests on ZnO Additives and Golden Giant Mine Tailings

In this section, we examine the effect of ZnO additives when applied to Golden Giant mine tailings. Based on the results illustrated in Figs 4-19 – 4-24, we are able to conclude that contrary to Noranda tailings, ZnO additives do not seem to function well when applied to Golden Giant mine tailings. The only exception to this rule is the exchangeable phase in the SSE tests which shows a consistent decrease in arsenic levels for all additive weight percentages. The unsuccessful immobilization of Golden Giant tailings could be due to the composition, pH or other unique factors in the tailings. In a similar study that was done by Boisson et al. (1999), with different soils and additives, the immobilizing power of the additives was found to be soil dependent. Three different types of soils were immobilized in the study using three types of additives. Sample 1 was collected from the site of a former arsenic refinery, Sample 2 was taken from an agricultural site close to the former arsenic refinery, and Sample 3 or port substrate was taken from the site of a former gold refinery. It was found that in Samples 1 and 2, the most immobilization occurred with the addition of SSB (steel shots and beringite), followed by SS (steel shots)

and B (Beringite). In Sample 3, it was found that the addition of B, even increased the mobility of arsenic. It was hypothesized that this could be due to the low pH of the soil which leads to the formation of other metal oxides from zero valent iron to which arsenic has less affinity. The most probable explanation given for the immobilization of arsenic in the same study is through adsorption and co-precipitation on the formed iron oxides in the soil (Boisson et al., 1999).

A similar phenomenon could be taking place in the case of ZnO applied to Golden Giant mine tailings in the current study. The different pH of the soil and the different combination of metals could be having an unfavourable effect on the immobilization of arsenic, even to the extent of promoting mobilization of arsenic. There is the possibility of competitive sorption of certain metals present in Golden Giant mine tailings with arsenic on the surfaces of the additives, such as chromium.

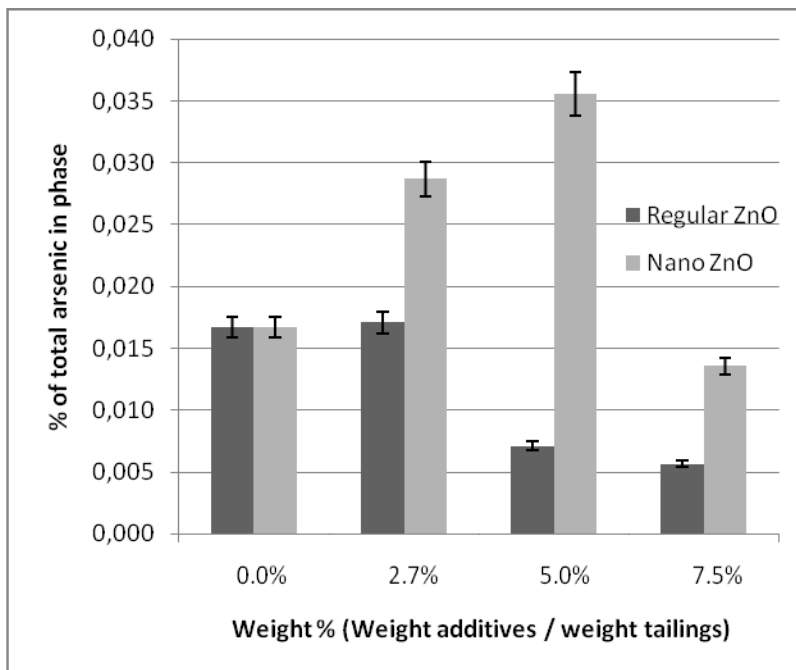


Figure 4-17 Effect of weight percentage of ZnO on the water soluble arsenic fraction in Golden Giant mine tailings following SSE tests.

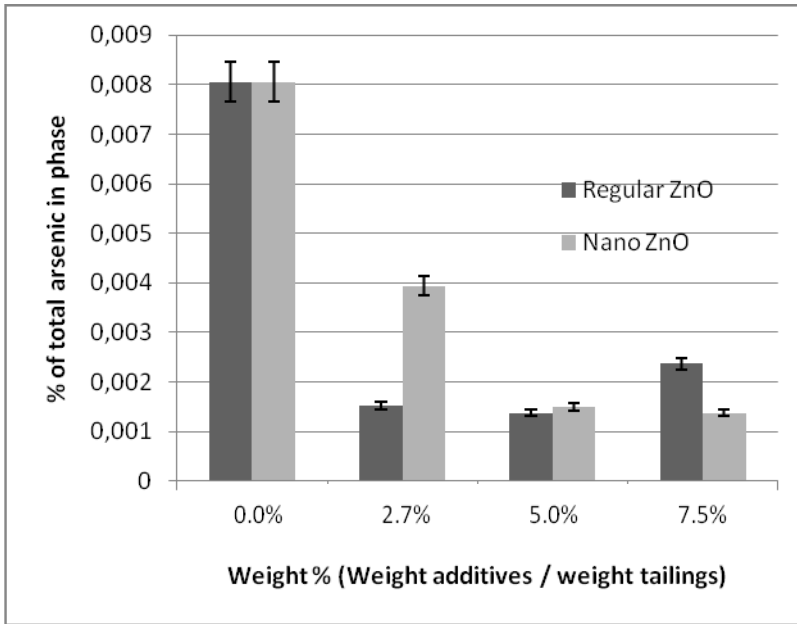


Figure 4-18 Effect of weight percentage of ZnO on the exchangeable arsenic fraction in Golden Giant mine tailings following SSE tests.

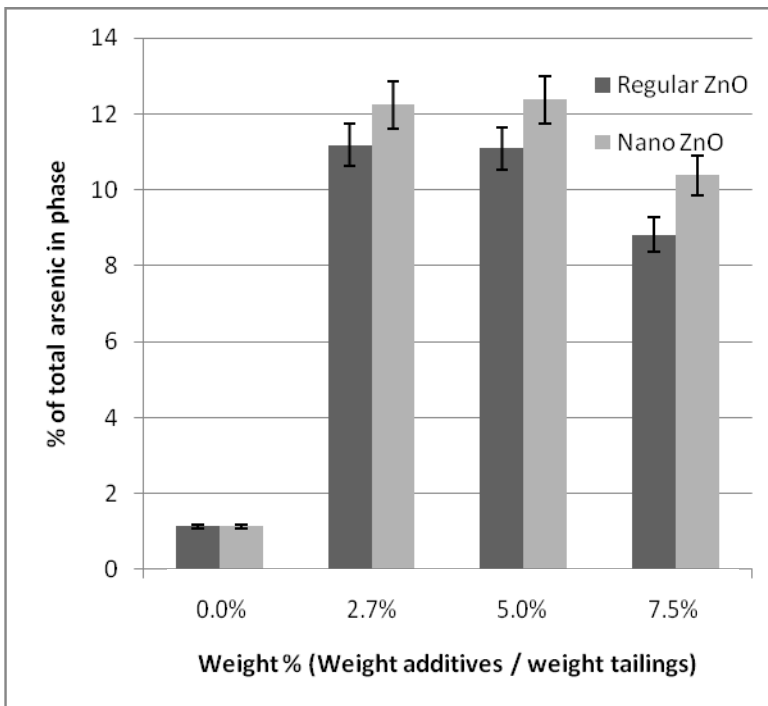


Figure 4-19 Effect of weight percentage of ZnO on the carbonate arsenic fraction in Golden Giant mine tailings following SSE tests.

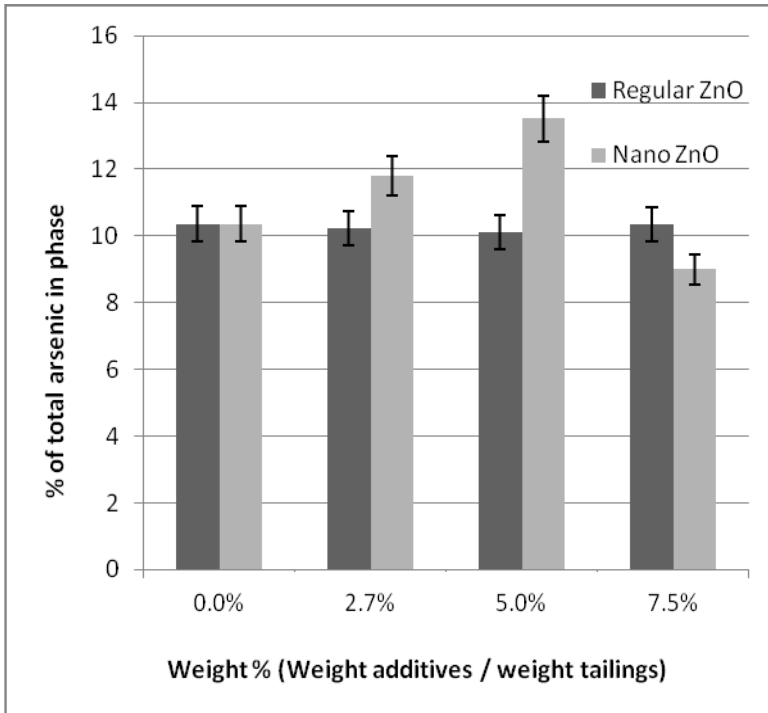


Figure 4-20 Effect of weight percentage of ZnO on the oxide/hydroxide arsenic fraction in Golden Giant mine tailings following SSE tests.

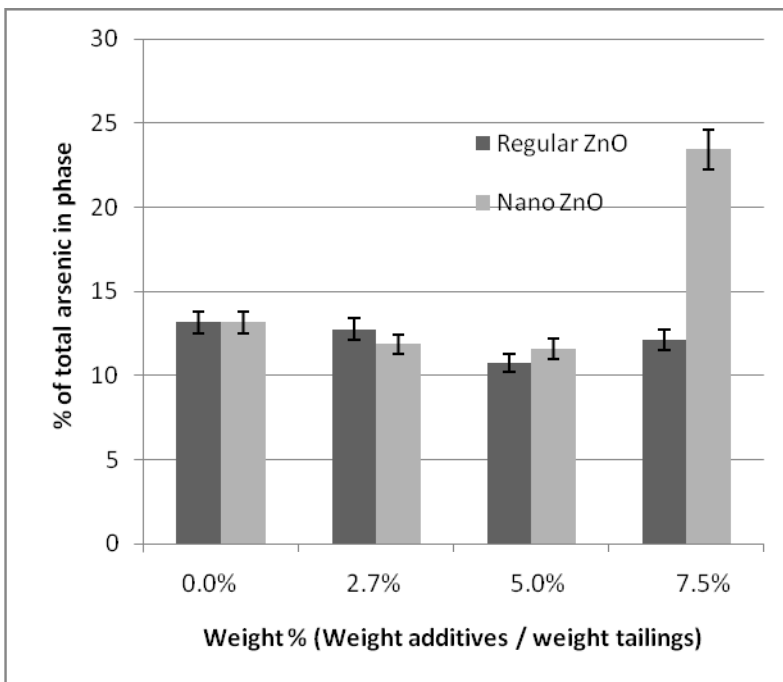


Figure 4-21 Effect of weight percentage of ZnO on the organic matter/sulfide arsenic fraction in Golden Giant mine tailings following SSE tests.

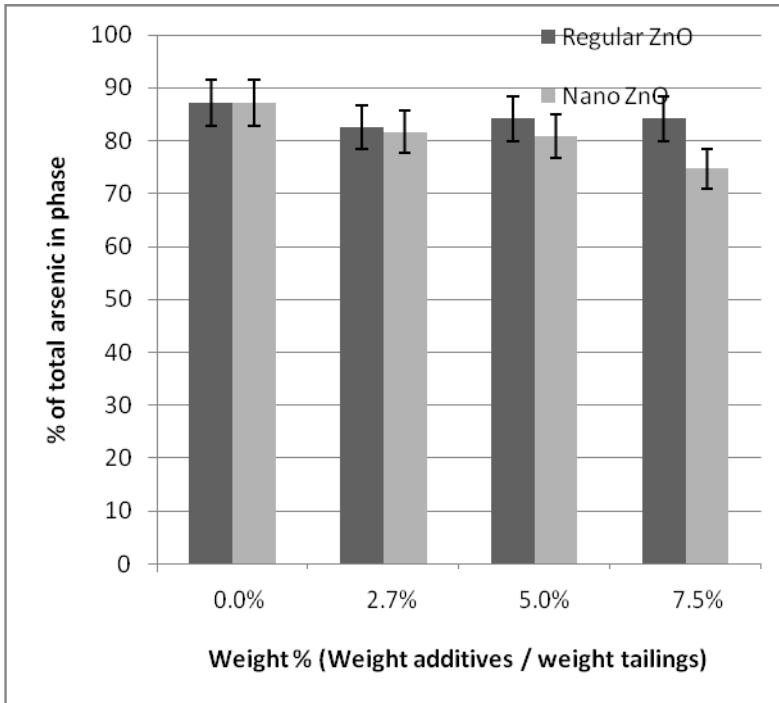


Figure 4-22 Effect of weight percentage of ZnO on the residual arsenic fraction in Golden Giant mine tailings following SSE tests.

4.3.3 SSE Tests on Fe₃O₄ Additives and Noranda Mine Tailings

As mentioned earlier, the samples with Fe₃O₄ additives were left to react for a period of 1 month before SSE tests were performed.

In contrast with the results obtained using the ZnO additives, Fe₃O₄ did not show promising results and although very safe, would not be an additive of choice to immobilize arsenic in mine tailings with similar composition to the ones studied. As seen from Figs. 4-25 – 4-30, the levels of arsenic in the water soluble phase vary tremendously and irregularly, increasing and decreasing with different weight percentages of Fe₃O₄. No detailed analysis of the results is necessary in this case since there is no observable effect of the additives on immobilization. Table 4-4 summarizes the factors by which the levels of arsenic have decreased in the Noranda tailings after treatment with 7.5% nanoscale Fe₃O₄.

Table 4-4 Decrease in the different chemical fractions of arsenic in Noranda mine tailings after the addition of 7.5% wt/ wt of nanoscale Fe₃O₄

Fraction	$C_{\text{Untreated tailings}} / C_{\text{Treated tailings}}$
Water Soluble	5.6
Exchangeable	1.2
Carbonate	1.3
Oxide/Hydroxide	1.4
Organic Matter/Sulfide	2.1
Residual Fraction	99.7×10^{-2}

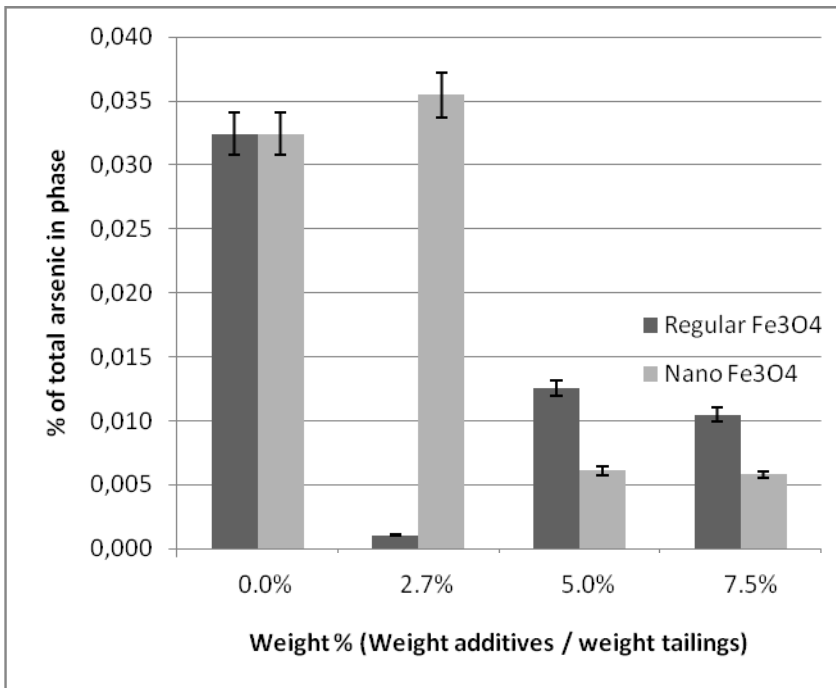


Figure 4-23 Effect of weight percentage of Fe₃O₄ on water soluble arsenic fraction in Noranda mine tailings as shown by SSE tests.

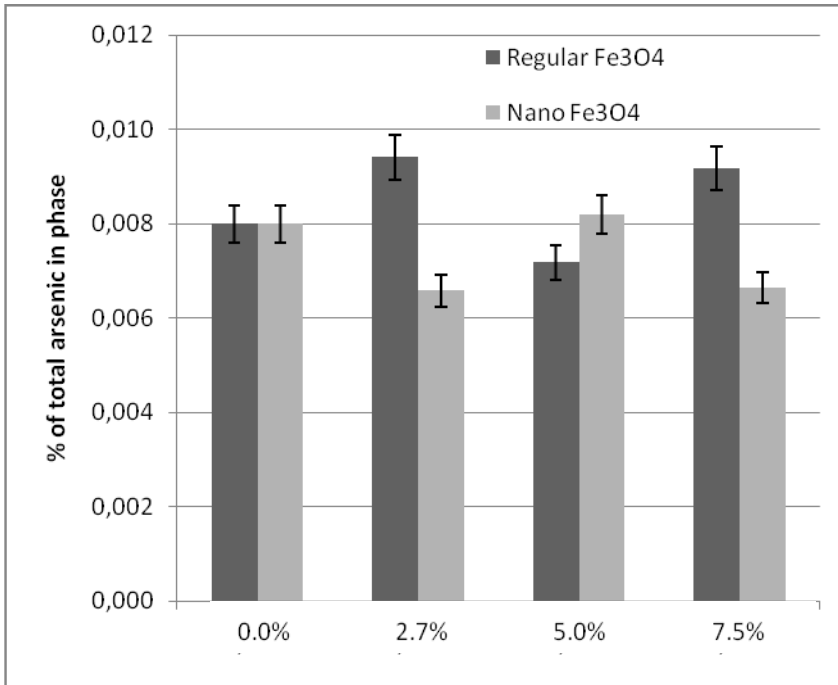


Figure 4-24 Effect of weight percentage of Fe₃O₄ on exchangeable arsenic fraction in Noranda mine tailings shown by SSE tests.

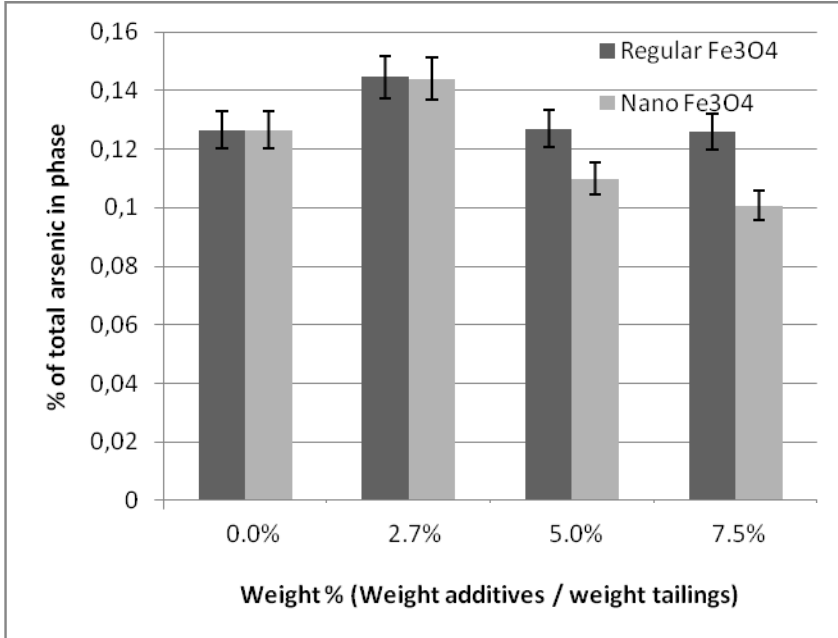


Figure 4-25 Effect of weight percentage of Fe₃O₄ on carbonate fraction of arsenic in Noranda mine tailings shown by SSE tests.

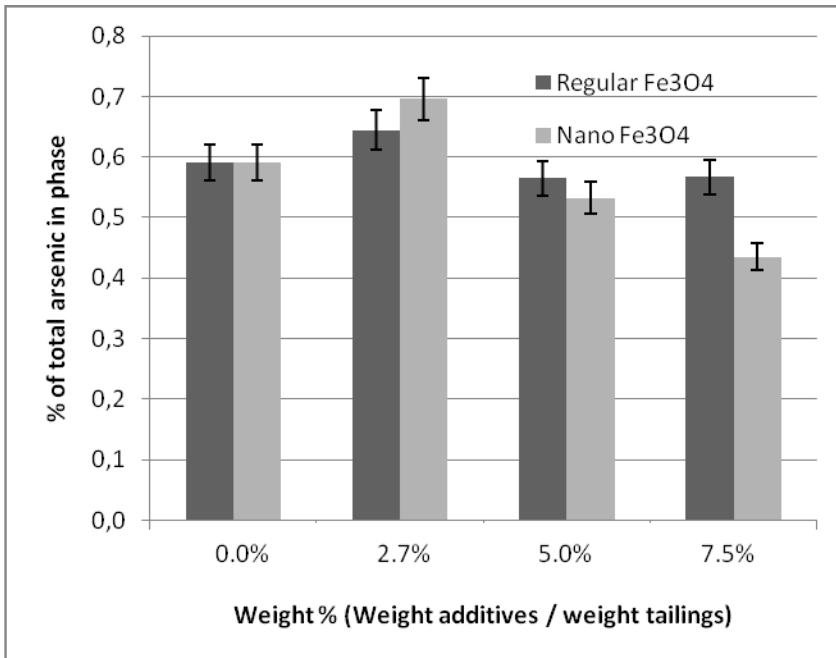


Figure 4-26 Effect of weight percentage of Fe₃O₄ on oxide/hydroxide arsenic fraction in Noranda mine tailings shown by SSE tests.

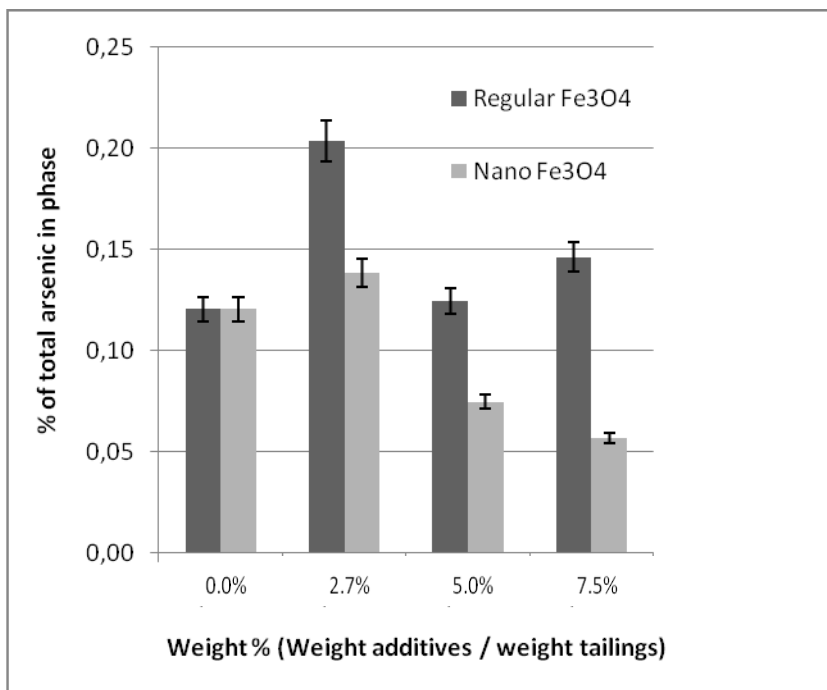


Figure 4-27 Effect of weight percentage of Fe₃O₄ on the organic/sulfide arsenic fraction in Noranda mine tailings shown by SSE tests.

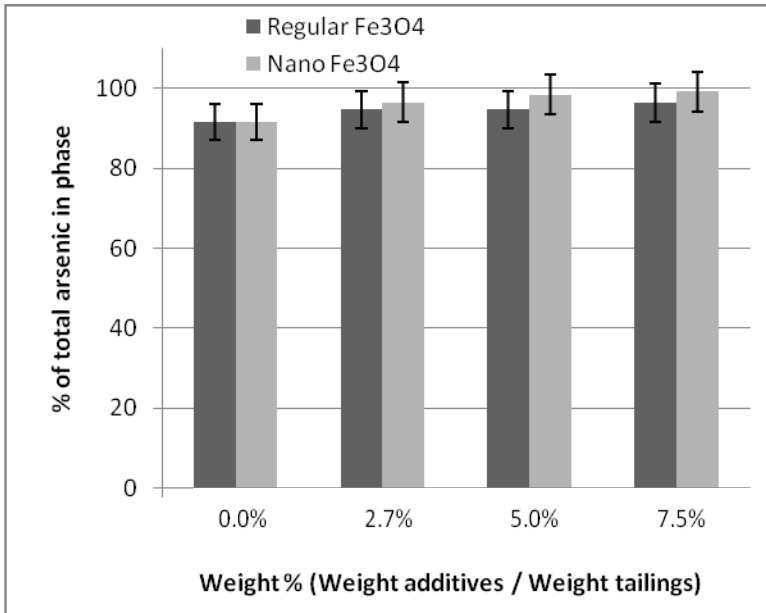


Figure 4-28: Effect of weight percentage of Fe₃O₄ on the residual arsenic fraction in Noranda mine tailings shown by SSE tests.

4.3.4 SSE Tests on Fe₃O₄ Additives and Golden Giant Tailings

Fe₃O₄ applied to Golden Giant tailings did not show more promising results than when applied to Noranda tailings. Figs. 4-31 – 4-35 show the different concentrations of arsenic obtained by the addition of various weights of this additive to Golden Giant mine tailings.

The levels of arsenic in all the phases vary tremendously and irregularly, increasing and decreasing with different weight percentages of Fe₃O₄. The only steady decrease that can be observed is in the organic matter/sulfide fraction of the mine tailings which decreases consistently as the weight of Fe₃O₄ increases. Another interesting observation is a steady increase in the residual fraction of arsenic in the tailings. This is an interesting phenomenon indicating that although the additive doesn't seem very effective in immobilizing arsenic in the loosely bound phases, it aids in the formation of stable complexes in the crystalline matrix of the tailings.

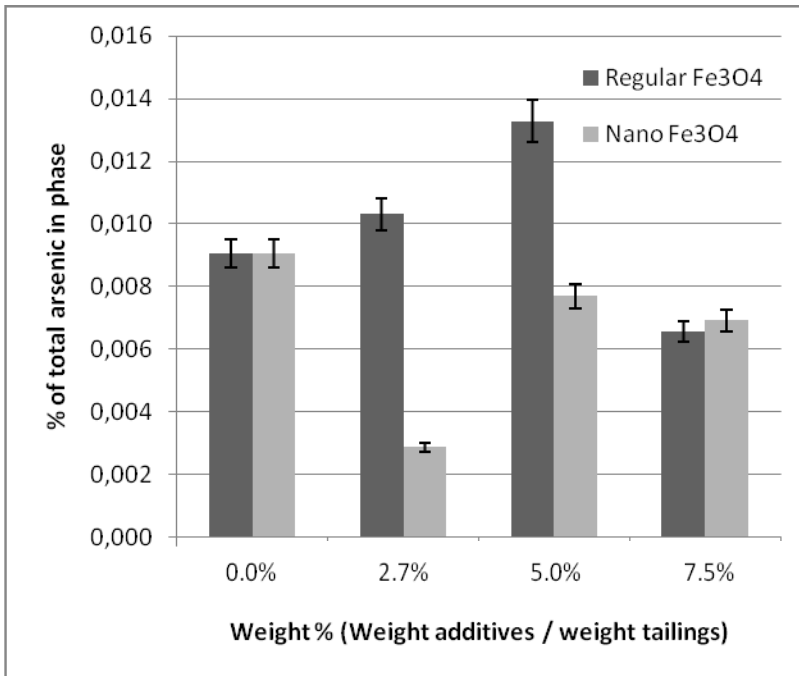


Figure 4-29 Effect of weight percentage of Fe₃O₄ on the water soluble fraction of arsenic in Golden Giant mine tailings shown by SSE tests.

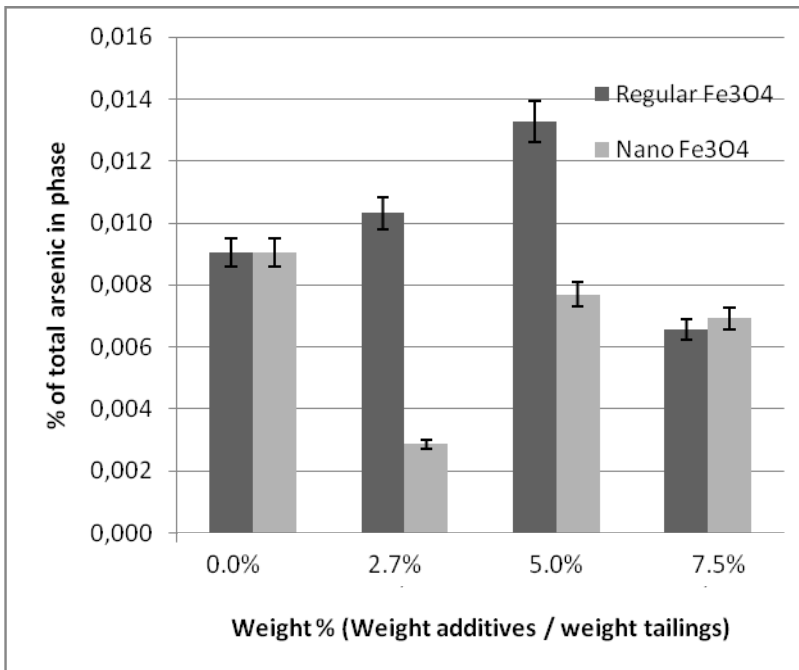


Figure 4-30 Effect of weight percentage of Fe₃O₄ on the exchangeable fraction of arsenic in Golden Giant mine tailings shown by SSE tests.

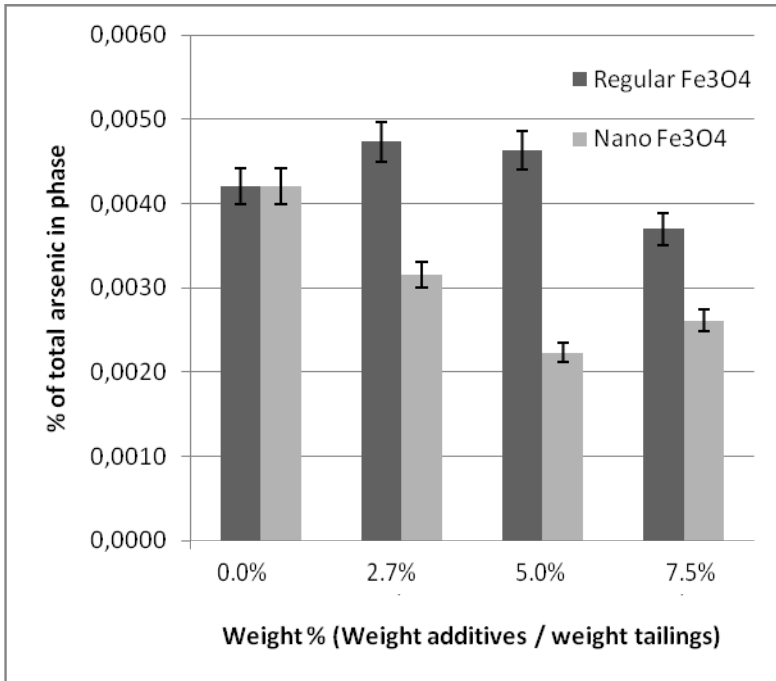


Figure 4-31 Effect of weight percentage of Fe₃O₄ on the carbonate fraction of arsenic in Golden Giant mine tailings shown by SSE tests.

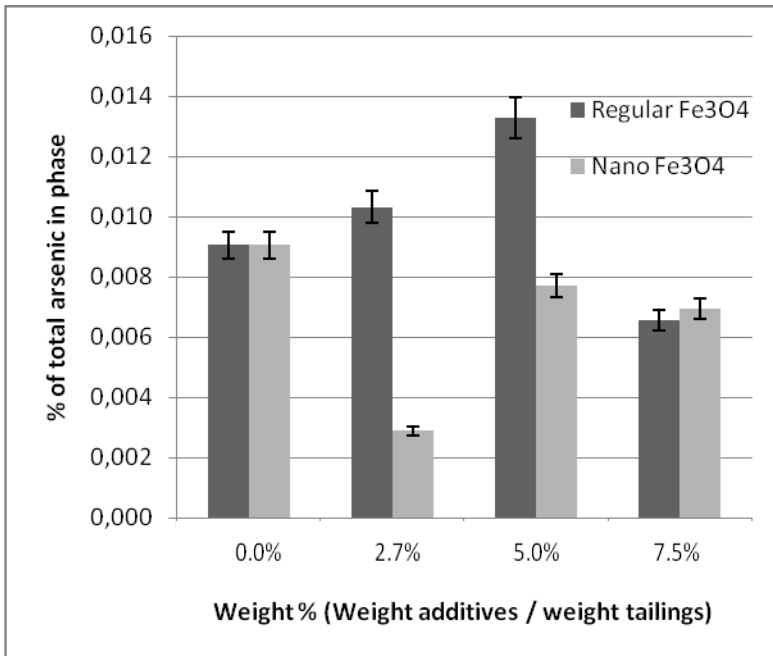


Figure 4-32 Effect of weight percentage of Fe₃O₄ on the oxide/hydroxide fraction of arsenic in Golden Giant mine tailings shown by SSE tests.

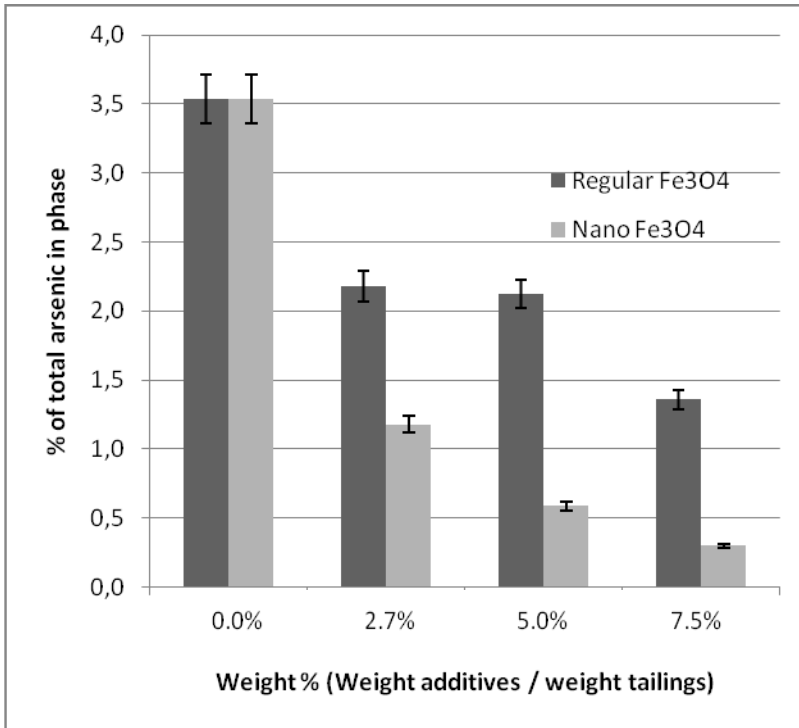


Figure 4-33 Effect of weight percentage of Fe₃O₄ on the organic matter/sulphide fraction of arsenic in Golden Giant mine tailings shown by SSE tests.

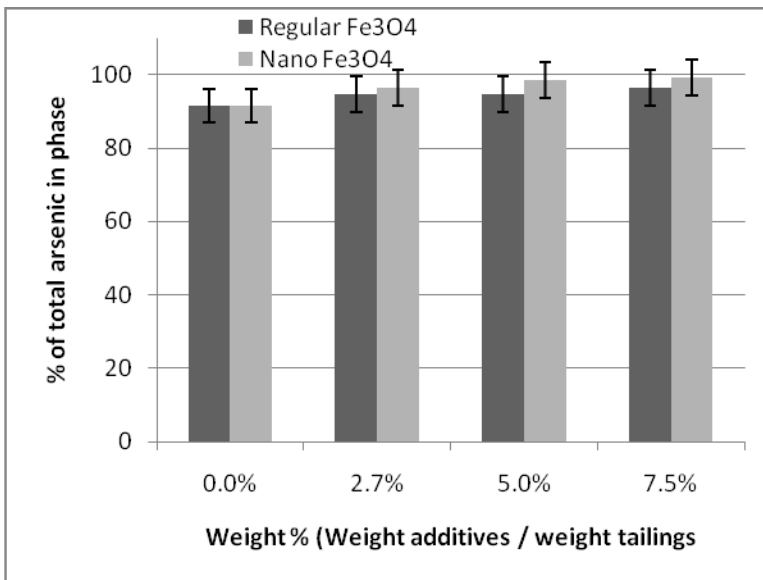


Figure 4-34 Effect of weight percentage of Fe₃O₄ on the residual fraction of arsenic in Golden Giant mine tailings shown by SSE tests.

Figs. 4-37 - 4-40 illustrate the distribution of the different chemical phases of arsenic in untreated mine tailings as well as tailings treated with 7.5% wt/wt of ZnO. It can be observed that the percentage of the residual fraction of arsenic increased in treated Noranda mine tailings as compared to untreated ones. However in the case of Golden Giant mine tailings, the addition of ZnO had the opposite effect and slightly increased the residual fraction. Figs. 4-37 - 4-38 show that a much higher percentage of arsenic is present in the residual form in untreated Noranda mine tailings as compared to Golden Giant mine tailings.

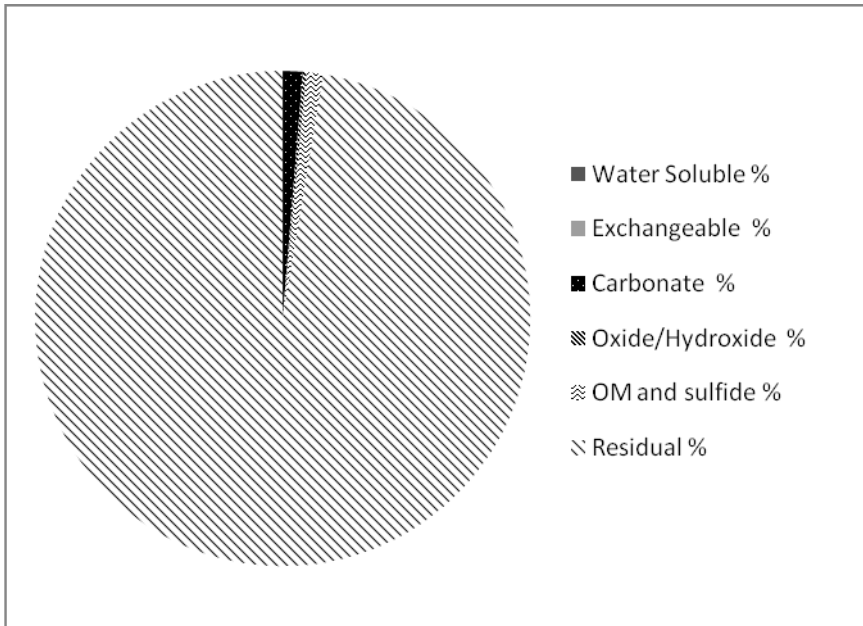


Figure 4-35 Distribution of phases in untreated Noranda tailings

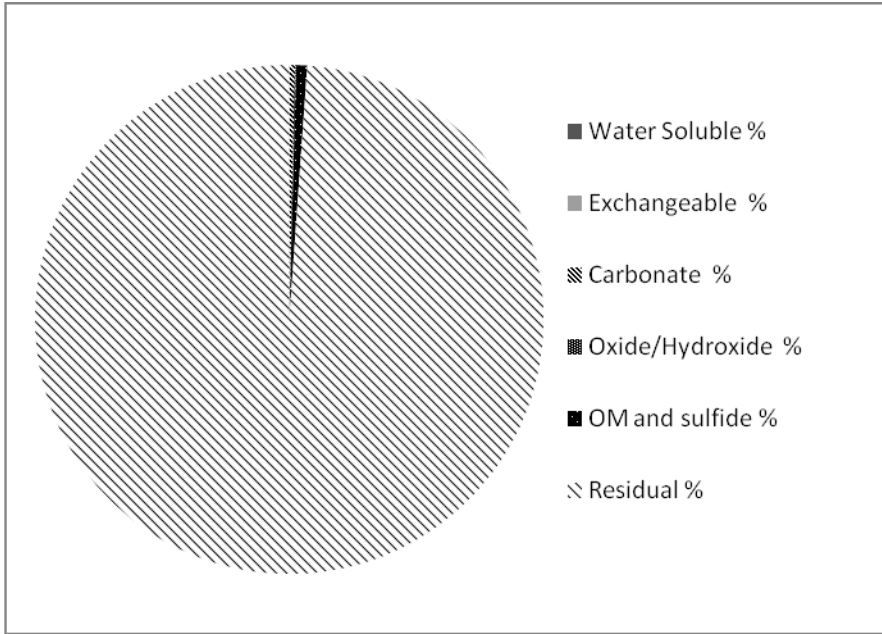


Figure 4-36 Distribution of phases in Noranda tailings treated with 7.5% in weight of ZnO additives

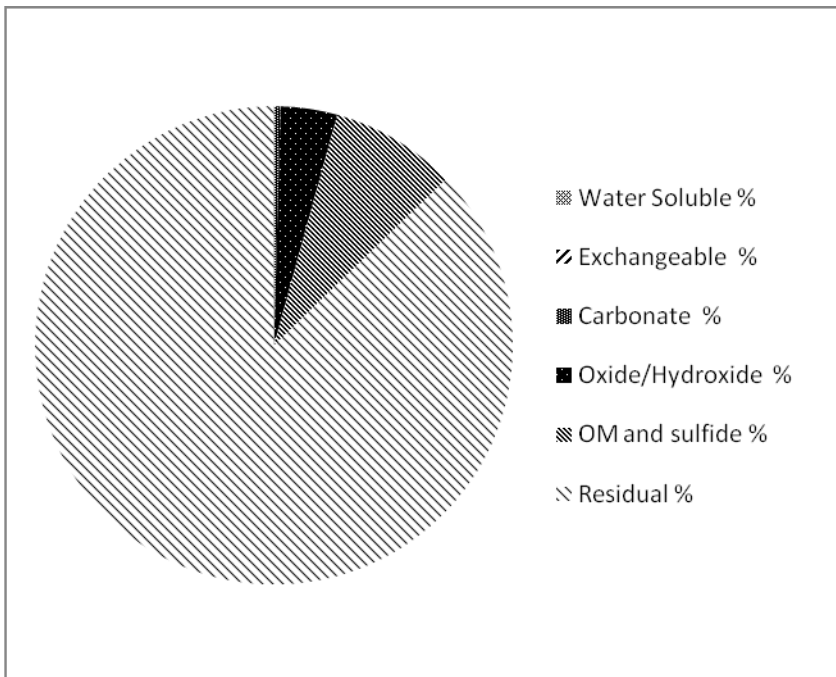


Figure 4-37 Distribution of phases in untreated Golden Giant tailings

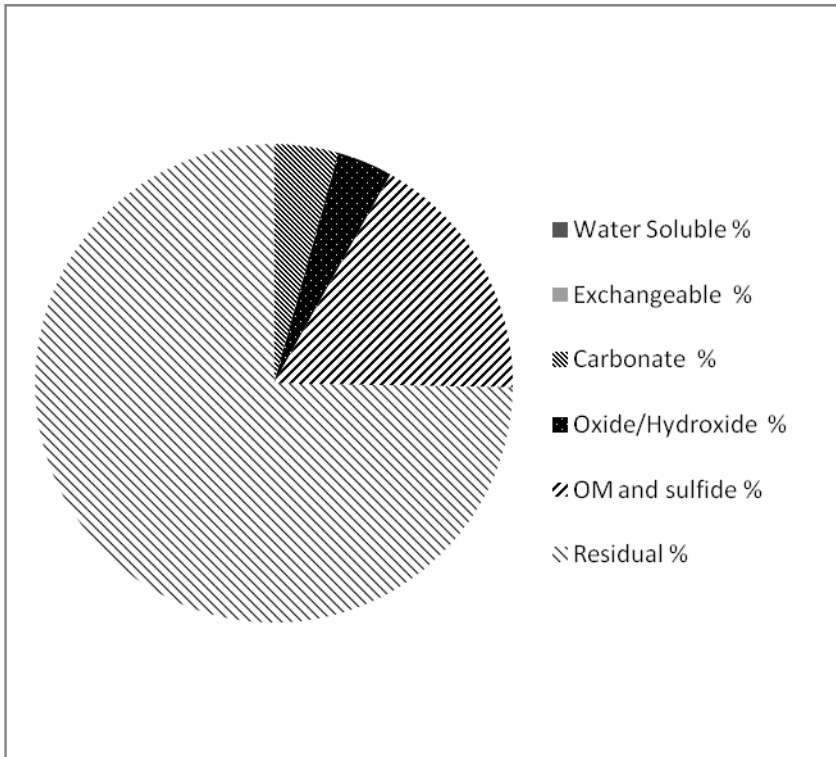


Figure 4-38 Distribution of phases in Golden Giant tailings treated by 7.5% in weight of ZnO additives

Discussion on the immobilization mechanisms of ZnO additives

It is not known what the exact mechanism is by which ZnO additives immobilize arsenic. One hypothesis is that it takes place through adsorption and coprecipitation on the ZnO particles which would themselves also bind to the tailings. This is similar to the hypothesis of immobilization proposed by the study conducted done by Boisson et al., 1999 on zero valent iron. Another possibility would be the formation of stable crystalline compounds between the arsenic in the tailings and the ZnO in an aqueous environment.

A study has been done on ZnO nanoparticles ability to adsorb arsenic in drinking water (Kuriyavar et al., 2005). The study investigated the use of spherical aggregates of nanoparticulate ZnO and commercial ZnO for the removal of arsenic from water. The results found are very interesting. Commercial ZnO with a surface area of 0.13 m²/mg was not found to be effective at all in the removal of arsenic from groundwater. However spherical nanoparticulate ZnO with a surface area of 30 m²/g, nearly 300 times bigger

than the commercial grade, was found in one experiment to reduce the concentration of arsenic from an initial value of 3 ppm to 40 ppb, or by a factor of 75.

The above could shed light on the current study. It points strongly to the hypothesis that ZnO could be immobilizing the arsenic through sorption.

One other discrepancy in the current study was the fact that both regular commercial ZnO and nanoactive ZnO from Nanoscale Corporation seemed to show equivalent performance. If the observations from the study from Kuriyavar et al. (2005) hold true in this case, then there should be a definite difference between both forms of ZnO. To investigate the cause of this discrepancy, we performed a particle size analysis, using the Horiba Particle Size Analyzer: results are shown in Table 4-5. It was found that the regular commercial grade of ZnO from Fisher Scientific, showed a mean particle size in the order of 3.67 μ m. The ZnO nanoactive particles from Nanoscale Corporation, seemed to have slightly larger particle sizes than the commercial grade ZnO, a very surprising fact, but due to the conglomeration of smaller sized nanoparticles into larger micro sized conglomerates. The mean particle size found for the ZnO nanoactive particles was about 12.45 μ m. This could explain the similarity in efficiency between both ZnO products. On one hand the nanoparticle conglomerates have a larger overall particle size and high porosity, on the other hand the regular ZnO from Fisher Scientific have a smaller particle size but a lower porosity.

Table 4-5 Particle size analysis of nanoscale ZnO and commercial grade ZnO

	NanoActive ZnO from Nanoscale Corporation (μm)	Commercial grade ZnO from Fisher Scientific (μm)
Median Size	10.88 μ m	3.50 μ m
Mean Size	12.45 μ m	3.67 μ m
Variance	53.00 μ m ²	1.91 μ m ²
Std	7.28 μ m	1.38 μ m

4.4 Discussion on the performance of Fe₃O₄

The fact that Fe₃O₄ is very efficient at adsorbing arsenic in water but doesn't seem to show any promising results in immobilizing the tailings in the current study shows that it may act as an effective adsorbent of the high concentrations of competing metals in the mine tailings first, making its sites unavailable for arsenic.

One research paper by Giménez et al. (2007) showed that the adsorption capacity of natural Fe₃O₄ for arsenate varied negligibly when the pH was increased from 2 to 10, and by 50% in the case of arsenite (As (V)) when the pH was increased from 3 to 9. The initial concentration in solution used in the above study was 2×10^{-5} M and the amount of Fe₃O₄ used was 0.1g (Giménez et al., 2007). The adsorption capacity for natural Fe₃O₄ as determined in the study was approximately 0.89 m²/g. The concentrations of arsenic in solution in this current study are much lower than used by Giménez et al. (2007). This information helps to rule out the pH of the solution as a possible factor in explaining the ineffectiveness of Fe₃O₄ at immobilizing arsenic.

Based on the XRF measurements, the metals present in decreasing order of concentration are: iron (52.2 mg/kg), chromium (2.896 mg/kg), molybdenum (1.07 mg/kg) and strontium (987.6 mg/kg). Arsenic comes fifth with a concentration of 237 mg/kg. Since one of the main oxidation states of chromium is +3, it is possible that there is a competitive sorption with As (III) on the adsorption sites of Fe₃O₄. Since the pH of the solution is below 8, the dominant species of arsenic in solution is As (III). Since the concentration of chromium is at least 10 times higher than arsenic in the Golden Giant ores, it is likely that Cr ions could have occupied adsorption sites in Fe₃O₄.

Another study tested the effect of starch stabilized nanoparticles of magnetite (Fe₃O₄), iron sulphide (FeS) and zero valent iron on immobilizing arsenic in two different arsenic contaminated soils. One of the samples was a sandy soil, with an arsenic concentration of 315 mg/kg collected from an orchard contaminated by pesticides in Washington, USA. The soil had an iron content of 52.4 g/kg and a pH of 6.75. The other soil was collected

near a police fire range in Alabama. It had an iron content of 122 g/kg and a pH of 4.83. After a 3 day treatment, the PBET bioaccessability of arsenic decreased from an initial value of 71.3 ± 3.1 % to 29.8 ± 3.1 %. The Fe/As ratio used was 100:1. The TCLP based leachability showed a decrease in the level of arsenic from an initial value of (0.51 ± 0.11) % to (0.17 ± 0.04) %. The study also revealed that the treatment was more effective on the soil with a lower iron content and higher leachability than on the soil with a higher iron content and lower leachability (Zhang et al., 2010).

Because nanoparticles tend to agglomerate into large microscale particles, reducing their reactivity and mobility, the nanoparticles in the study were stabilized with starch and cellulose to prevent agglomeration. This resulted in the performance previously outlined.

The findings in the above study suggest that one of the reasons for a poor performance of Fe_3O_4 in the current study could be the result of particle agglomeration. It has been proven in many studies that regular grade Fe_3O_4 is not an effective arsenic sorbent, and that only the nanoscale Fe_3O_4 is effective. However, since the particles in the current study were not stabilized to prevent agglomeration, they behaved like larger sized ineffective particles.

It is also possible that the high content of iron in the mine tailings interferes with the efficiency of Fe_3O_4 . Both mine tailings have very high contents of iron. Fe_3O_4 could be a more general adsorbent, and a larger variety of metals in the tailings could have an affinity for the surface area of Fe_3O_4 , resulting in its selective inefficiency for arsenic.

No specific tests were done to assess the bioavailable portion of arsenic in the tailings. However it was found that in the case of ZnO applied to Noranda mine tailings a large decrease in the degree of arsenic in the water and exchangeable fraction would significantly reduce the dissolution of arsenic into ground and pore water and therefore its availability to plants. A study on bioavailability would have to be done to determine the availability of arsenic to plant life and other organisms which feed on plants.

4.5 Summary of Results

Eight different metal oxide additives were tested in this study and it was found that both nanoscale and regular ZnO showed the best performance. It was also found that the effectiveness of these additives was mine tailing specific, giving overall good results only when applied to Noranda tailings. Both leaching and SSE tests were in agreement as to the effectiveness of ZnO on Noranda mine tailings.

Table 4-6 summarizes the results of the leaching tests performed on ZnO. In all but two cases, there is a decrease in efficiency of the additives over a 1 month period as compared to 24 hours. It was hypothesized that this could be the result of reaching a more stable form of immobilization over time after a rapid initial reaction that appears to be more efficient.

Leaching tests showed ZnO to be efficient when applied to Golden Giant mine tailings which is in disagreement with the results of the SSE tests. This could be due to the different components that were measured by each of the tests, and the different types of solvents used. It is therefore clear that Golden Giant mine tailings treated with ZnO are not chemically stable as shown by SSE tests. Therefore, using ZnO to immobilize arsenic is not recommended for this mine tailing.

Table 4-6 Percentage of arsenic concentration in leachate following immobilization of mine tailings with different weights of ZnO additives. Results are compared to the mine tailings with no additives.

Noranda Mine Tailings			Golden Giant Mine Tailings		
Sample	24 hour tests	1 month tests	Sample	24 hour tests	1 month tests
No additive	100%	100%	No additive	100%	100%
5% nano ZnO	4.9%	10%	5% nano ZnO	12.5%	27.9%
7.5% nano ZnO	2.6%	9.5%	7.5% nano ZnO	5.7%	7.9%
5% regular ZnO	63%	15.4%	5% regular ZnO	19.1%	4.9%
7.5% regular ZnO	10%	20.6%	7.5% regular ZnO	4.6%	12.3%

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and concluding remarks

The effectiveness of a variety of different metal oxides on arsenic immobilization was tested using two different mine tailings and various leaching tests. The two mine tailings used were Noranda tailings originating from a copper and gold mine in Rouyn-Noranda, and Golden Giant tailings originating from a gold mine near Thunder Bay Ontario.

The following metal oxides were subjected to preliminary leaching tests: nanoscale MgO, nanoscale CaO, nanoscale TiO₂, commercial grade TiO₂, nanoscale CaO, nanoscale Al₂O₃, commercial grade ZnO, nanoscale ZnO. Measurements were taken using ICP-MS and Hach EZ Arsenic Test strips. Both nanoscale ZnO and regular commercial grade ZnO showed the best performance of all of the above additives, and along with regular grade Fe₃O₄ nanoscale Fe₃O₄ were subjected to a more thorough analysis using further leaching tests and SSE.

Further leaching tests were performed over a period of 24 hours with different additive to mine tailing weight ratios on nanoscale ZnO, commercial grade ZnO and nanoscale and commercial grade Fe₃O₄. The results showed that both forms of ZnO were very effective in immobilizing arsenic, whereas the efficiency of Fe₃O₄ was questionable.

The same leaching tests were repeated over a period of one month with several additive to mine tailing weight ratios. It was found that there was a very slight decrease in arsenic immobilization efficiency for all types of additives. This suggests that a more stable form of immobilization could have been reached after a rapid initial reaction.

SSE procedures of long term tests were conducted on both forms of ZnO. It was found that ZnO additives were very efficient at immobilizing arsenic in all of the 5 chemical phases in Noranda mine tailings. It was found that the most efficient weight ratios were 5% and 7.5%. The results were not as positive as on Golden Giant mine tailings, where

the additives showed erratic and unstable behaviour for each of the phases. It was hypothesized that the cause of these results could be the preferential affinity of other metals in Golden Giant mine tailings for adsorption sites on ZnO.

Long term SSE procedures were conducted on Fe₃O₄. It was found that Fe₃O₄ additives were not efficient at immobilizing arsenic in all 5 chemical phases of arsenic in either Noranda or Golden Giant mine tailings. There have been several reasons hypothesized for this lack of efficiency, including the agglomeration of nanoactive particles into larger sized micron sized particles. Many studies have shown that Fe₃O₄ is only effective at adsorbing arsenic if the particles size remains small. Another hypothesis was that other metals present in the mine tailings had more affinity than arsenic in adsorbing onto Fe₃O₄ thereby limiting the arsenic sorption. A third possibility could be that the high content of iron in both the tailings could be interfering with the relatively small amount of Fe₃O₄ and preventing the formation of solid bonds with arsenic.

The zinc concentration was measured in different solutions of mine tailings after leaching tests. It was found that lower pH values increased the solubility of the ZnO additive and therefore increased the zinc ions in solution. The effectiveness of ZnO in immobilizing arsenic was found to be independent of pH in the leaching tests. It was proposed to add a basic salt to increase the pH of ZnO additives when mixed with the soil, thereby reducing the amount of zinc leached into the soil.

No significant difference in reactivity was found between nanoscale ZnO and regular commercial grade ZnO. A particle size analysis determined that the commercial grade of ZnO from Fisher scientific had a smaller average particle size than the nanoscale ZnO from Nanoscale Corporation. The larger particle size of the nanoscale ZnO was due to particle agglomeration into micron-sized conglomerates. This explains the similar results of both forms of ZnO: on one hand the commercial grade of ZnO had smaller particle sizes and the nanoscale had larger overall particle sizes but higher porosities.

Economically the cost of using nanoscale ZnO at a 5% weight ratio to remedy one ton of mine tailings would be 43.50 USD, and the cost of regular commercial ZnO would be 60.00 USD. This is a reasonable price to pay on a small scale but could become unaffordable for larger scale remediation, especially in developing countries with smaller budgets. It is necessary to improve the cost effectiveness of this method, and one such suggestion can be found in the section below.

5.2 Recommendations for future work

This study attempted to find a suitable agent to immobilize arsenic in mine tailings. Zinc oxide (ZnO) was identified as an effective additive on Noranda mine tailings. Further studies would have to be done to improve the efficiency, cost and versatility of this additive.

One recommendation would be to find a method of improving the selective efficiency of ZnO at immobilizing arsenic, so that it could be used on any mine tailings even when concentrations of other metals are high. Experiments could be performed by mixing ZnO with other additives or synthetic substances to see if its selectivity towards arsenic could be improved.

Another suggestion would be to perform studies using the same additives on natural soil and minerals that do not have the high concentrations of other metals that are found in mine tailings. The additives may prove to be many times more efficient at immobilizing arsenic in these soils.

It would be useful to do toxicity studies in the same soils and measure how much of the arsenic has been made non hazardous to living organisms. For example, tests that measure enzyme activity can be a useful predictor of how much arsenic is taken up by plants, as the enzymatic activity decreases with the toxicity of the soil (Tyler et al., 1989; Nannipieri, 1995).

To reduce the cost of treatment an alternative method of producing ZnO which is more cost effective should be investigated. One idea is to use minerals that have naturally occurring ZnO instead of investing on commercial grade ZnO. It would be beneficial to evaluate the use of nanoscale ZnO in solution with added dispersants that would prevent agglomeration of the nanoparticles particles and to measure if there has been a change in efficiency.

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