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Immobilization of Arsenic in Mine Tailings using Standard and Nanoscale Metal Oxides

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ABSTRACT
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. 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. Both nanoscale and regular ZnO were found to significantly reduce arsenic leaching from Noranda mine tailings, whereas Fe_3O_4 had no significant effect.

RÉSUMÉ
Les niveaux élevés d'arsenic ont été trouvés dans des résidus miniers, sédiments et échantillons de sol. La lixiviation d'arsenic des résidus peut résulter dans la contamination des eaux de surface et souterraine. Dans cette étude, la performance des quelques types des oxydes métalliques comme des agents immobilisants ont été testés. Les tests de lixiviation et d'extraction séquentielle sélective ont été effectués avec des mélanges divers des résidus miniers et oxydes métalliques, en utilisant des ratios divers en poids, temps de réactions, et types d'oxydes. Les deux formes d'agents, nano échelle et régulier, d'oxyde de zinc, était capable de réduire la lixiviation d'arsenic des résidus miniers de Noranda, mais Fe_3O_4 n'est pas efficace.

1 INTRODUCTION

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).

The long term exposure to As 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).

Strategies for preventing arsenic from leaching into the environment are imperative, for the well-being of millions of people. Many technologies are available for the remediation of arsenic whether in soil, water, or air. Currently the method of treating 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).

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 attended to 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 the addition of nanoscale products as well as regular metal oxides and to explore their potential in immobilizing high levels of arsenic present in contaminated mine tailings. One additive, in particular, nanoscale magnetite (Fe_3O_4) was tested as it has been used successfully as an adsorbent of As in water filtration systems. It, along with zinc oxide (ZnO) were especially evaluated for their effectiveness on a short and long term basis. Nanoscale metal oxides were chosen 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.

2 MATERIALS AND METHODS

2.1 Materials

Mine tailings taken from four different areas in Canada were analyzed and scanned using an XRF analyzer (NITON XLP 700 series). These tailings are presented in Table 1.

Table 1. Mine tailings analyzed

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

Two of the four mine tailings with the highest arsenic weight content were retained for further tests (Noranda and Golden Giant). The additives used were oxides of aluminium, magnesium, calcium, zinc, titanium and iron. Their nanoscale and regular crystalline forms were both tested. They were manufactured by the company Nanoscale Corporation and the nanoscale magnetite (Fe_3O_4) was supplied by Sigma-Aldrich. Table 2 lists some properties of the nanoscale additives.

Table 2. Properties of nanoscale metal oxides

Additive	Specific Surface Area (m^2/g)	Crystallite Size (nm)
Nano Al_2O_3	≥ 275	Amorphous
Nano CaO	≥ 20	≤ 40
Nano MgO	≥ 230	≤ 8
Nano ZnO	≥ 70	≤ 10
Nano TiO_2	≥ 500	Amorphous
Nano Fe_3O_4	≥ 60	≤ 50

Source : (http://www.nanoscalecorp.com/)

2.2 Methods

2.2.1 Characterization of mine tailings

The XRF analyser used for this study is a Niton XLP 700 series. The samples measured were prepared in several steps. The mine tailings were first pulverised using a grinder. They were then air dried for 48h. The air dried mine tailings were then passed through a mesh #60 sieve to filter out the portion that is equal to or smaller than 250 µm. The fine powder was then placed in a small plastic holder, and then sealed at the top with a clear Mylar film. The prepared sample was inserted into the Niton XLP 700 holder and the XRF device was aimed at the sample and triggered. Measurements were taken this way for each individual mine tailing and the concentrations of arsenic were noted.

2.2.2 Leaching Tests

The mine tailings (Noranda and Golden Giant) were mixed with various metal oxides (listed in the previous section) at different weight ratios. They were left to react and at the end of the reaction period, they were subjected to leaching tests and SSE (Selective Sequential Extraction) tests.

The tests were meant to simulate the leaching of arsenic into ground and surface waters in acid rain conditions and are a modified version of the SPLP (Synthetic Precipitation Leaching Procedure, EPA Method 1312).

Dry mine tailing samples weighing 2 g in total were mixed with 0.2 g (10% w/w) of the previously mentioned metal oxides. The mixture was then combined 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 samples were centrifuged at 4000 rpm for 15 min and the leachate was separated from the solid by decanting. The leachate was then analysed using Hach EZ Arsenic Test Kit strips (High Range and Low Range Models, Cat #282000 and 282000) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry, Agilent 7500ce). The detection range used for ICP-MS was from 0.1 ppb to 500 ppm. ICP-MS is one of the recommended methods (Method 6020A) for measuring arsenic concentrations in waste (EPA Online 2008).

A second round of leaching tests was conducted on the additives that appeared most promising at immobilizing arsenic. These tests were aimed at examining the effect of additive to mine tailing weight percentages on the efficiency of immobilization. The different weight ratios used were 0%, 5% and 7.5% and 10% of the total weight of the mine tailings (2 g).

2.2.3 SSE Tests

The goal of SSE 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). The procedure uses specific chemical reagents to release heavy-metal fractions in the soil once the binding phase is destroyed. The method gives a very good idea of 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 procedure used in this study was a modified version (Yong et al. 2003).

Table 3. Adapted SSE procedure

Seq #	Fraction	Chemical Reagents
1	Water soluble	8ml of distilled water shaking at room temperature for 30 min
2	Exchangeable	8ml of 1M $MgCl_2$ shaking at room temperature for 1 hour
3	Carbonate	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	8 ml of $NH_2OH.HCl$ in 25% v/v acetic acid in a water bath for 6 h at 96°C
5	Organic matter and sulphide	3ml of 0.02M HNO_3 and 5ml of 30% H_2O_2 adjusted to pH 2 with HNO_3 and then 5ml of 3.2M NH_4OH in 20% (v/v) HNO_3 diluted to 20ml 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) Ac denotes acetate

The adapted SSE procedure outlined in Table 3 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 the arsenic form bound to the soil particles.

Fourteen different samples were prepared for each mine tailing and additive using different additive to tailing weight ratios. Each individual 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 ×100%). The different weight ratios used were 0%, 2.7%, 5% and 7.5% of the total weight of the mine tailings (2 g).

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 unmixed 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, HG-AAS (Hydride Atomic Absorption Spectrometry), and FAAS (Flame Atomic Absorption Spectrometry).

The HG-AAS was composed of a Hydride Generator hooked up to Perkin Elmer AAnalyst 800 atomic absorption spectrometer and with a typical detection level around 2 ppb. It was used as an alternative when the ICP-MS device became unavailable, and is recommended by EPA Method 7061A (EPA Online 2008). The FAAS (Perkin Elmer AAnalyst 100 Flame atomic absorption spectrometer) was used for higher concentrations of arsenic such as those resulting from reverse aqua regia digestion to determine the residual fraction of arsenic.

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. 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 measured in the supernatant.

The total weight of arsenic was calculated by totalling the weight of arsenic in each of the phases:

$$W_T = W_1 + W_2 + W_3 + W_4 + W_5 + W_6 \qquad [1]$$

where $W_{1..6}$ represent the weight of arsenic in each of the six phases.

The percentage of arsenic in each of the phases was calculated using the following equation:

$$\%\text{ in phase } p = (W_p/W_T) \times 100\% \qquad [2]$$

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 the most promising.

3. RESULTS AND DISCUSSION

In this section we present the findings of leaching tests as well as the SSE tests, and determine the effectiveness of various additives that were tested. In this paper we have only included the findings related to one type of mine tailings (Noranda).

3.1 XRF Analysis

Using the XRF device, measurements were taken of the elements present in each of the four mine tailings. The results of two of the mine tailings, which have the highest concentrations of arsenic are presented in Tables 4 and 5. As can be seen, there are many other elements present in the mine tailings which have the potential to interfere with the effectiveness of the additives.

Table 4. XRF analysis results for Noranda and Golden Giant Tailings

Metal	Noranda Concentration (ppb)	Metal	Golden Giant Concentration (ppb)
Sr	178.2	Mo	1070
Pb	11k	Sr	987.6
As	2557	Rb	47.7
Zn	1208	As	273.3
Fe	384.5k	Hg	102.2
Ba	4662	Fe	52.2k
Ag	1044	Cr	2896
Ti	1276		
Ca	18.9k		

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

As explained in the materials section, leaching tests were conducted on mine tailings mixed with various additives. They were combined together in a 10% weight ratio (weight additive/weight mine tailing). After the completion of the tests, the different concentrations of arsenic in the leachate were measured using ICP-MS instrumentation. Each concentration was compared to a measurement taken from a plain sample with no additive. As can be seen from Fig 1, ZnO and Nanoscale ZnO showed very promising results with 7.4% and 6.8% of the original arsenic present or 92.6 % to 93.2% reduction respectively.

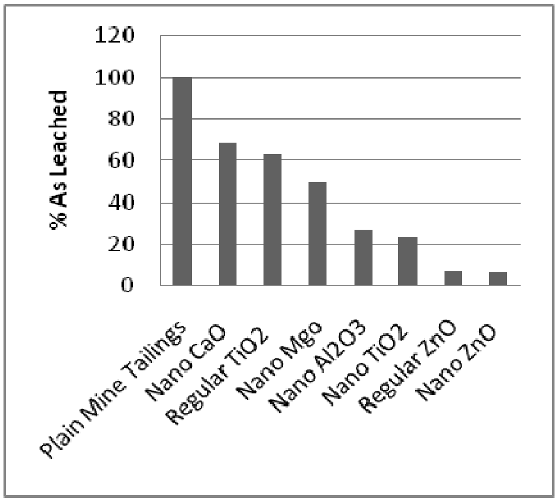

Figure 1. Arsenic % leached according to type of metal oxide additive, in comparison to plain Noranda mine tailings

3.3 Effect of Weight Additive/ Weight Tailing ratio on Arsenic Immobilization for 2 metal oxide additives

Leaching tests were repeated on ZnO alone using different weight ratios. As can be seen from Fig 2, it was found that the effectiveness of the mine tailings increased with weight, with a maximum reduction of 97.4% at a weight ratio of 7.5%. There was a slight decrease in efficiency after that. This could be due to several factors: either due to experimental error or to complex interactions between the other metals in the tailings. Further experiments would be needed to determine this aspect. Fe_3O_4, was also introduced in the study, as nanoscale magnetite has shown very promising results in arsenic water filters and has been relatively less explored for its immobilization potential. Fe_3O_4 was also selected for its low toxicity in comparison to ZnO.

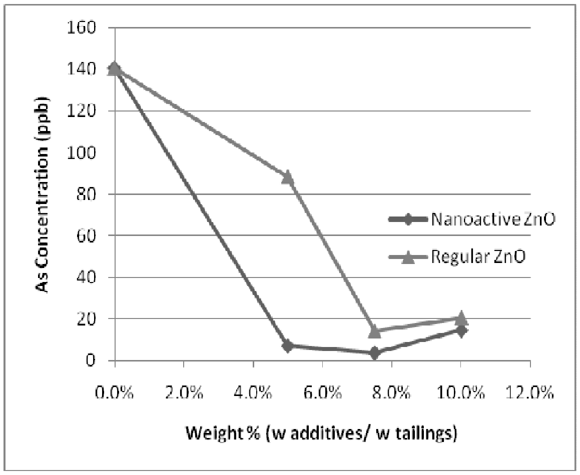

Figure 2. Arsenic concentration (ppb) leached from Noranda mone tailings according to weight percentage of nanoscale and regular zinc oxide after 24 hours.

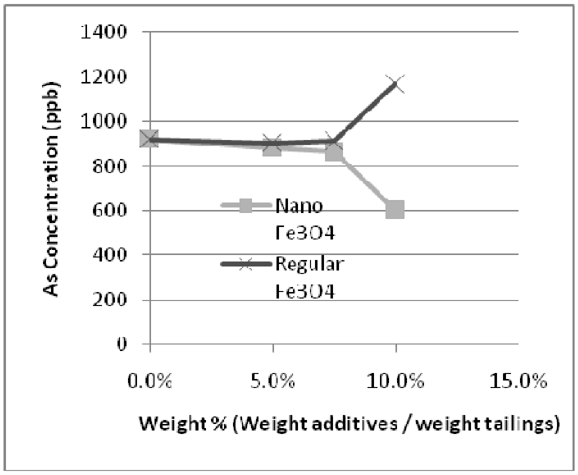

Figure 3. Arsenic concentration (ppb) leached from Noranda mine tailings after 24 hours as a function of weight percentage of nanoscale and regular Fe_3O_4

As can be observed in Fig 3, nanoscale Fe_3O_4 reduced arsenic concentration in the leachate by 40%, whereas regular Fe_3O_4 strangely increased the degree of leaching. The reasons for an increase in leaching are unclear, but could be due to unknown interactions with the other metals present in the tailings.

3.4 Results of SSE analysis for Zinc Oxide additives at different weight ratios

After leaving the mine tailings mixed with various weight ratios of either ZnO or Fe_3O_4 for a period of 1-2 months, SSE extraction tests were performed. The samples had been left to react for a period of 1 month for Fe_3O_4 and 2 months for ZnO.

In Figures 4 and 5, we can see the effect of the additives on the different fractions of arsenic in Noranda mine tailings. There is an overall decrease in the water soluble arsenic fraction after the addition of the ZnO. However, a clear correlation is not apparent between the weight ratio of the additives and the concentration of arsenic. This could be due partly to the lack of precision of the SSE method, but could also be caused by complex interactions which would need to be further investigated. 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 100 000 for 7.5% nanoscale ZnO. The large scale reduction calculated for 7.5% nanoscale ZnO could be partly attributed to instrument error, and would have to be verified by further experiments.

As for the exchangeable fraction of arsenic, the decrease in arsenic varies from factor of 2.2 for 2.7% nanoscale ZnO, to 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 decrease of arsenic in the carbonate phase varies from a factor of 2.1 for 2.7% nanoscale ZnO, to 11.5 for 5% regular ZnO. 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. The effect of the additives on the remaining fractions is presented in Table 6.

Table 6. Decrease in the different chemical fractions of arsenic in Noranda mine tailings after the addition of ZnO.

Fraction	Ratio initial As concentration to final concentration in each phase
Water Soluble	50.00×10^3
Exchangeable	17.10
Carbonate	6.78
Oxide/Hydroxide	3.62
Organic Matter/Sulfide	1.52
Residual Fraction	0.96

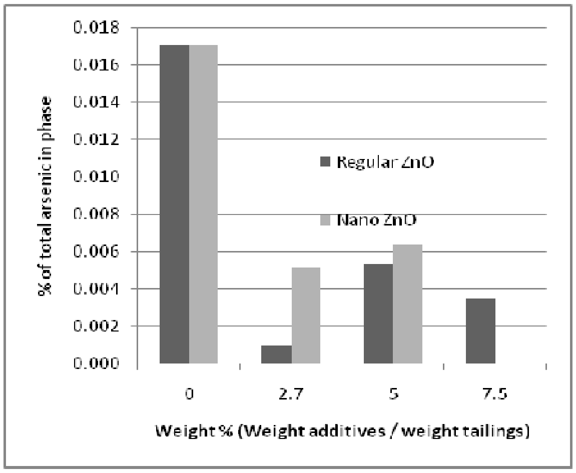

Figure 4. Effect of weight percentage of ZnO on water soluble arsenic fraction in Noranda mine tailings in SSE tests.

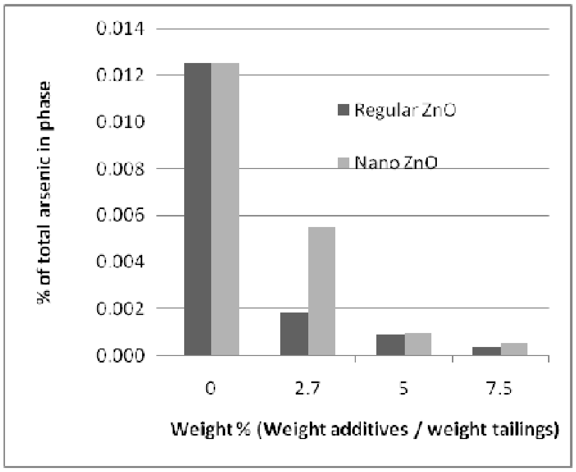

Figure 5. Effect of weight percentage of ZnO on exchangeable arsenic fraction in Noranda mine tailings following SSE tests.

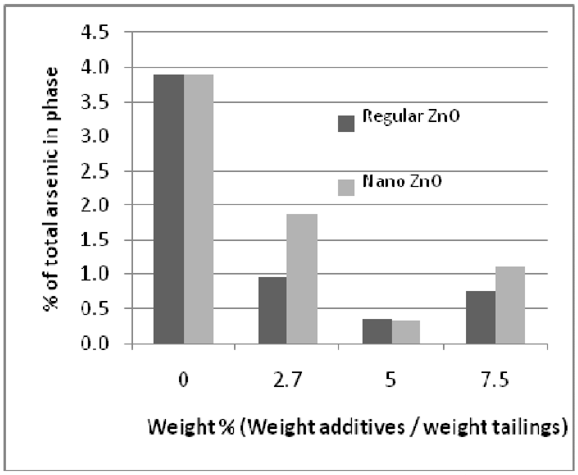

Figure 6. Effect of weight percentage of ZnO on carbonate bound arsenic fraction in Noranda tailings following SSE tests.

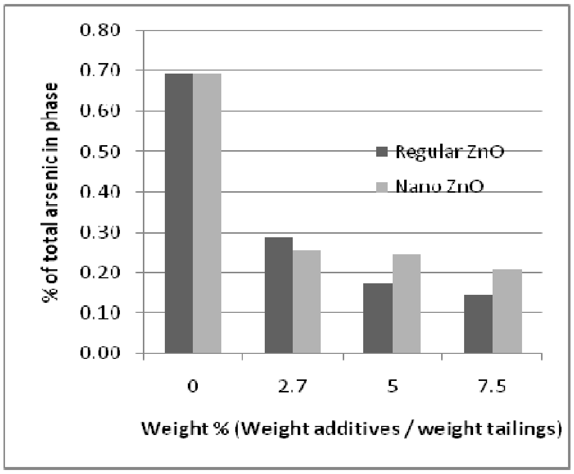

Figure 7. Effect of weight percentage of ZnO on oxide/hydroxide arsenic fraction in Noranda mine tailings following SSE tests.

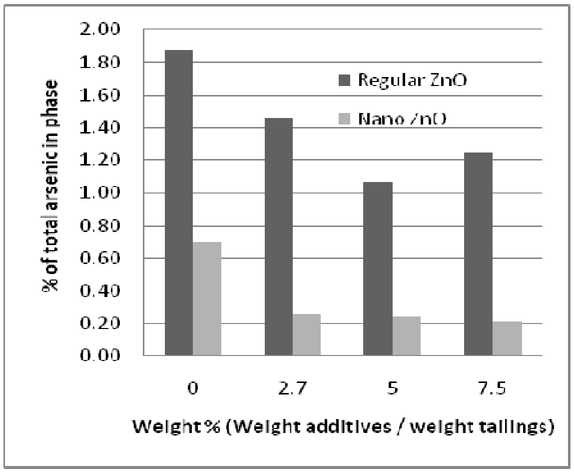

Figure 8. Effect of weight percentage of ZnO on sulphide/organic matter arsenic fraction in Noranda mine tailings following SSE tests.

3.5 Results of SSE analysis for Iron Oxide (Fe_3O_4) additives at different weight ratios

As mentioned earlier, the samples with Fe_3O_4 additives had been left to react for a period of 1 month before SSE tests were performed on them.

In contrast with the results obtained using the ZnO additives, Fe_3O_4 did not show as promising results and although very safe, would not be an additive of choice to immobilize arsenic. Figures 9 – 13 show the different concentrations of arsenic obtained by the addition of various weights of this additive and Table 7 summarizes the minimum and maximum factors by which the levels of arsenic have decreased. A value smaller than 1 indicates that the additive has increased rather than decreased the concentration.

Table 7. Decrease in the different chemical fractions of arsenic in Noranda mine tailings after the addition of Fe_3O_4

Fraction	Ratio initial As concentration to final concentration in each phase
Water Soluble	15.70
Exchangeable	1.04
Carbonate	2.13
Oxide/Hydroxide	1.10
Organic Matter/Sulfide	1.36
Residual Fraction	0.10

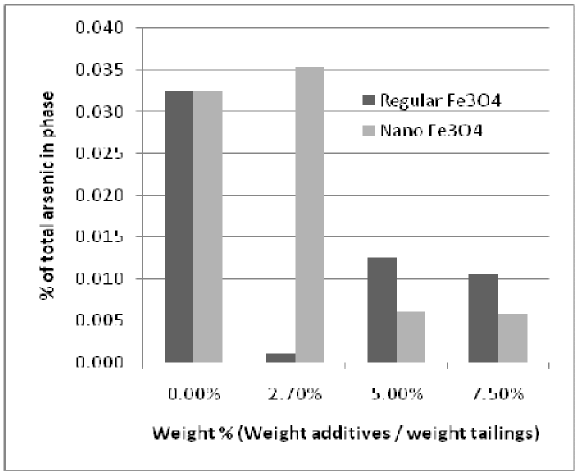

Figure 9. Effect of weight percentage of Fe_3O_4 on water soluble arsenic fraction in Noranda mine tailings following SSE tests.

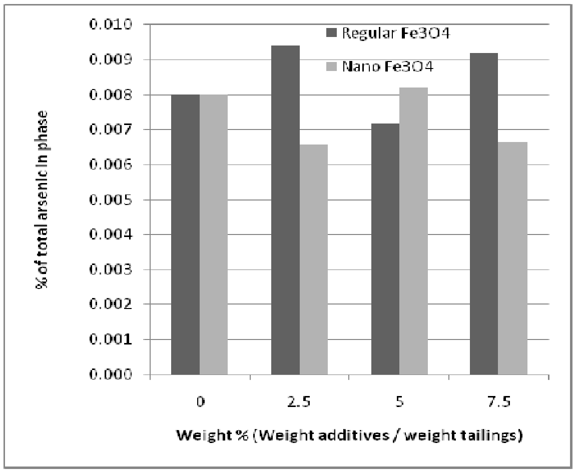

Figure 10. Effect of weight percentage of Fe_3O_4 on exchangeable arsenic fraction in Noranda mine tailings following SSE tests.

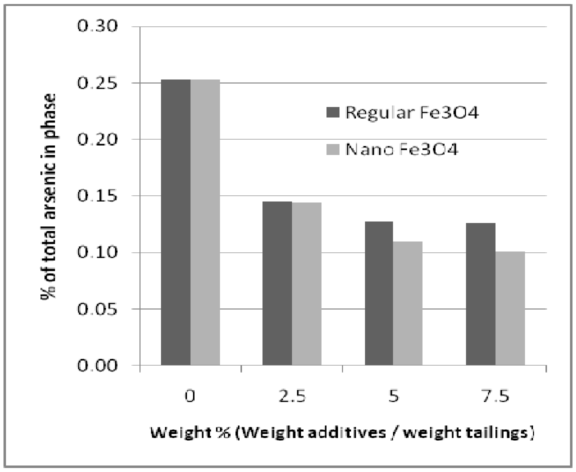

Figure 11. Effect of weight percentage of Fe_3O_4 on carbonate fraction of arsenic in Noranda mine tailings following SSE tests.

CONCLUSIONS

From the above results, it is apparent that the addition of regular and nanoscale ZnO to Noranda mine tailings significantly reduces the amount of arsenic leached. Results were effective for weight ratios of 2.7%, 5% and 7.5% without a particular weight ratio showing better performance overall. Table 6 summarizes the findings. It would be beneficial to perform more experiments with lower weight ratios as similar performance might be found, while reducing the cost and toxicity of the additives.

Regular and nanoscale magnetite (Fe_3O_4), although significantly less toxic than ZnO, did not show overall promising results whether in the preliminary leaching tests or the SSE tests. They do not appear to be additives of choice.

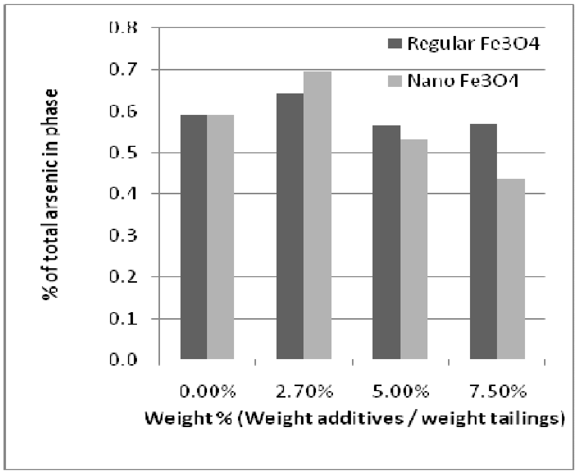

Figure 12. Effect of weight percentage of Fe_3O_4 on oxide/hydroxide arsenic fraction in Noranda mine tailings following SSE tests.

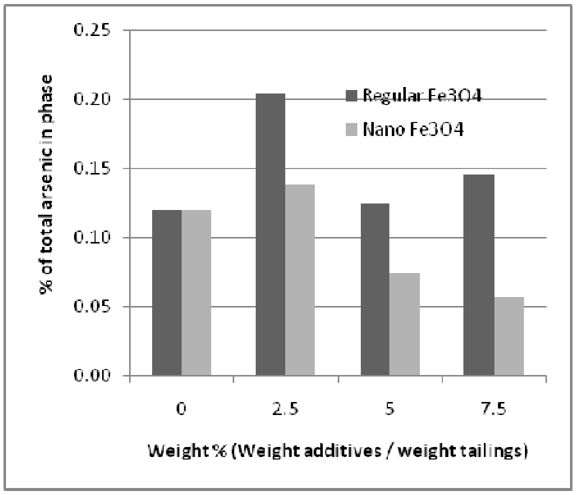

Figure 13. Effect of weight percentage of Fe_3O_4 on the Organic/Sulfide arsenic fraction in Noranda mine tailings following SSE tests.

Experiments were also conducted on Golden Giant mine tailings, although the results were not presented in this paper. Nanoscale and regular ZnO were not as effective in immobilizing arsenic in these mine tailings as they were found in the case of Noranda tailings. This could be due to the different variety and quantity of metals present in the tailings, perhaps interfering with the reactions responsible for immobilizing arsenic. It is recommended that the study be repeated with a larger variety of tailings to see whether it is effective in a majority of cases. It could then be used as a strategy for large scale and long term remediation.

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REFERENCES

Ahmad, K., 2001. Report highlights widespread arsenic contamination in Bangladesh, *The Lancet,* 358: 133.

Chakraborti, D., Basu, G.K., Biswas, B.K., Chowdhury, U.K., Rahman, M.M., Paul, K., Chowdhury, T.R., Chanda, C.R.,Lodh, D., and Ray, S.L., 2001. Characterisation of arsenic bearing sediments in Gangetic Delta of West Bengal, India, Arsenic Exposure and Health Effects, Elsevier: 27–52.

Gupta, S.K., and Chen K.Y., 1978. Arsenic removal by adsorption, *Journal of the Water Pollution Control Federation,* 50:493–506.

IARC, 1987. Arsenic and arsenic compounds (Group 1), *IARC monographs on the evaluation of the carcinogenic risks to humans,* Supplement 7, date accessed: 6 February 2003. Available from <http://193.51.164.11/htdocs/monographs/suppl7/arsenic.html>.

Jekel, M.R., 1994. *Removal of arsenic in drinking water treatment,* Nriagu Ed., *Arsenic in the Environment. Part I. Cycling and Characterizatio*n, John Wiley & Sons, Inc., New York, NY.

Kartinen E.O. Jr., and Martin, C.J. 1995. An overview of arsenic removal processes, *Desalination*, 103 (1–2): 79 –88.

Korngold, E., Belayev, N., and Aronov, L., 2001. Removal of arsenic from drinking water by anion exchangers, *Desalination*,141: 81–84.

Seidel, H., Gorsch K., Amstattera, K., and Mattusch, J., 2005. Immobilization of arsenic in a tailings material by ferrous iron treatment., *Water Research*, 39: 4073–4082.

Tessier, A., Campbell, P.G.C., and Bisson, M.,1979. Sequential extraction procedure for the speciation of particulate trace metals., *Analytical Chemistry*, 51: 844–850.

US EPA Online, http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/chap2.pdf.

World Health Organization - WHO, 2001. *Arsenic in drinking water*. Facts Sheet Number 210, http://www.who.int/mediacentre/factsheets/fs210/en/index.html.

Yong, R. N., Galvez-Cloutier, R., and Phadingchewit, Y., 1993. Selective Extraction Analysis of Heavy-Metal Retention in Soil, *Can. Geotech. J.*, 30(5): 834–847.

Yong, R.N., and Mulligan, C.N., 2004. Natural attenuation of contaminants in soils, CRC Press, Boca Raton.