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WR08R002

COMBINATION OF CO-PRECIPITATION WITH ZEOLITE FILTRATION TO REMOVE ARSENIC FROM CONTAMINATED WATER

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Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water

Project Completion Report

By

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Project Summary

Title: Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water

Project ID: WR08R002

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Background/Need: Groundwater containing arsenic contamination imposes a great threat to people worldwide as well as to the residents of the state of Wisconsin. Developing new and cost-effective methods to remove arsenic from groundwater and drinking water becomes imminent. With several patents granted, using iron/aluminum hydroxide to remove arsenic from water is a proven technology. However, the key issue is the filtration media. Currently, the filtration media used were limited to sand, granular activated carbon, granular activated alumina, but not zeolite.

Objectives: In this research, zeolite was proposed to use as the filtration media to remove arsenic-containing iron hydroxide co-precipitates. The hypothesis was that zeolite had a larger surface area and higher cation exchange and sorption capacity, and the use of zeolite in lieu of sand media to filtrate the arsenic-containing iron hydroxide co-precipitates should be cost competitive to that of sand media while the performance would be much better than sand. Furthermore, due to an increase in capacity, less system faulting and less solid waste would be produced. In addition to removal of iron hydroxide co-precipitates, zeolite could also remove other undesired metal cations simultaneously.

Methods: Tests were conducted in batch, column as well as large 1-dimensional flow through system. Batch tests were focused Fe(II) and Fe(III) adsorption on zeolite, Fe(II) and Fe(III) removal by co-precipitation, initial Fe input on As removal, initial As input and As species on As removal by co-precipitation on iron hydroxide, the influence of solution pH on iron hydroxide co-precipitation formation. The column studies to were performed to investigate the efficiency of added Fe(III) to the removal of As in a continues flow system. Finally, a 1-dimensional large flow through system was used to test the As removal from syntehtic water, groundwater, as well as water from acid mine drainage to verify the batch and column test results. Aqueous concentrations of As, Fe^{TOT}, and solution pH were monitored with time for water quality.

Results and Discussion: Batch results showed that addition of $FeCl_3\cdot 6H_2O$ followed by addition of NaOH to elevate the solution pH to induce $Fe(OH)_3$ co-precipitation is an effective way to remove dissolved arsenic from water. Meanwhile, zeolite is a good sorbent for dissolved Fe(II) and Fe(III) with the calculated sorption capacity of 60 and 140 mmol/kg, respectively. Sorption of arsenic on Fe-modified zeolite was also strong with a sorption capacity of 100 and 50 mg/kg for As(III) and As(V) sorption on Fe-zeolite, respectively. Solution pH had a significant effect on arsenic sorption on Fe-zeolite. A drastic decrease in As sorption was found at pH 10 and above. On the contrary, the influence of solution pH on removal of As from water by co-precipitation of $Fe(OH)_3$ was different. When solution pH was lower than 6, removal of As was minimal due to minimal formation of $Fe(OH)_3$ precipitation. More over, when solution was above 10, arsenic becomes more mobile and will be less sorbed on $Fe(OH)_3$ precipitates. Thus, the optimal solution pH for As removal by co-precipitation was between 6 and 10. Efficiencies of As removal from water by $Fe(OH)_3$ co-precipitation was highly related to the amount of Fe added, thus, the amount of $Fe(OH)_3$ formed. On the contrary, the efficacy of the filtration system was reversely related to the amount of Fe added, i.e., system clogged more quickly as the amount of Fe added increased.

Large column tests using synthetic water and real water showed some interesting but also contradicting results. The co-precipitation followed by zeolite filtration method worked well for synthetic water with an initial As concentration of 1000 µg/L and Fe concentration of 1 mM with a 95% As removal up to 30 pore volumes (PVs). It also worked well for an acid mine drainage (AMD) water with an input As concentration of 147 µg/L and input Fe concentration of 101 mg/L with a non detectable effluent As concentration up to 20 PVs. On the other hand, the As removal was less effective for groundwater collected from Chia-Nan Plain that has an initial As concentration of 511 µg/L with minimal dissolved Fe. After addition of 0.2 mM Fe(III), the As removal was less than 40%, showing extremely inefficiency, possible due to the extremely reduced groundwater condition and the lower amount of Fe(III) added. Similar results were found for large column studies to remove As from water using Fe-zeolite as a sorbent.

Conclusions/ Implications/ Recommendations:

The research shows that addition of Fe(III) followed by raising solution pH to neutral and slightly alkaline conditions can effectively induce iron hydroxide precipitation. The precipitates could be removed by either sand filtration or zeolite filtration. The latter may cause some cloudiness for the water, i.e. an increased turbidity, in the beginning, due to large particle size, thus, large pore size, as well as the presence of fine particles. However, the system could maintain its long lasting filtration flow while the sand filtration system clogged quickly than the zeolite system, particularly for the removal of As from acid mine drainage after addition of NaOH to induce iron hydroxide precipitation. Although no clogging was found when zeolite was used, the cloudy water may impose a limitation to the method, particularly at the beginning of use. In addition, adding the correct amounts of Fe to produce minimal Fe precipitation with maximum As removal is also a challenge as it is affected by many factors such as solution pH and Eh, dissolved Fe and As concentration.

Related Publications:

Li,Z., Jean, J.-S., Koski*, A. J., Schulz*, L., Liu, C.-C., Reza, S., Merrill*, J. S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J., Reiley*, A. E., Fenske*, N., Ackley*, C. (2011) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *Environ. Earth Sci.*, under review after minor revision.

Key Words: Arsenic, Iron, co-precipitation, Sand, Filtration, Zeolite.

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Introduction

Arsenic (As) is a naturally occurring element present in soil and water. Three sulfide minerals, realgar, orpiment, and arsenopyrite, are the major contribution of As to soil and water. Known for centuries to be an effective poison, As is used in Chinese traditional medicines to cure several types of diseases. However, chronic uptake of As resulted in numerous As poisoning. Arsenic ingestion may result in internal malignancies, including cancers of the kidney, bladder, liver, lung, and other organs. Vascular system effects have also been observed, including peripheral vascular disease, which in its most severe form results in gangrene or Blackfoot Disease.

Arsenic poisoning is most common in developing countries such as Bangladesh and India, and some parts of China such as Inner Mongolia and Xinjiang. In just Bangladesh alone, it is estimated that drinking As-contaminated water could have harmed as many as 77 million people.

A significant number of investigations have been conducted to develop cost effect remediation technologies to remove arsenic from contaminated water. A recent study indicated that co-precipitation/adsorption consists of 80% of full-scale, aboveground treatment technologies for arsenic removal (USEPA, 2002). Co-precipitation/adsorption technique involves in reaction of $FeCl_3$ with water or hydroxide to form $Fe(OH)_3$ precipitates, which than absorb arsenate due to surface complexation.

$$\equiv FeOH^0 + AsO_4^{3-} + 3\,H^+ \rightarrow \equiv FeH_2AsO_4 + H_2O \tag{1}$$

$$\equiv FeOH^0 + AsO_4^{3-} + 2\,H^+ \rightarrow \equiv FeHAsO_4^- + H_2O \tag{2}$$

The precipitates of iron hydroxide containing sorbed arsenate can be separated from water using sand filtrations (Meng et al. 2001). In addition, in using the co-precipitation/adsorption technology, it is necessary to convert As(III) in to As(V), as trivalent arsenic occurs in non-ionized form and is not subject to significant removal. Several approaches, including UV radiation, oxidation by hydrogen peroxide, and by permanganate, have been tested. In addition to co-precipitation/adsorption methods, iron coated sand has been proposed as sorbents to remove arsenate from water (Joshi and Chaudhury, 1996).

Zero valent iron (ZVI) is effective in removal of arsenic from water (Su et al., 2001; 2003; Farrell et al., 2001). In bench-scale experiments conducted at the University of Colorado-Denver, two different arsenic concentrations (200 and 2000 μg/L) were tested with 3 different loadings of ZVI: 2.5 g, 1.25 g and 0.625 g ZVI per liter of water. At the lowest loading of 0.625 g of zero valent iron, > 90% arsenic removal was achieved with a contact time of 3 hours. A similar technology, Arsenic Remediation Technology (AsRT) was developed at the University of Connecticut to achieve 90% of As removal for over 1000 pore volumes of water.

More practically, a technology called 3-Kalshi was developed to treat arsenic contaminated water in Bangladesh (Khan et al. 2000). A "kalshi" is the clay water pitcher used for collecting water throughout Bangladesh. The top kalshi is made of 3 kg (about 1/6 kalshi volume) iron filings and 2 kg coarse sand. The combined media fills about 1/3 kalshi volume. The rest of the space contains source water for treatment. The middle kalshi is made of 2 kg of fine sand and 1 kg of wood charcoal of a consistent size. The combined media fills about 1/6 kalshi volume. The bottom kalshi is for collecting treated water. A Three-Gagri filter was similar to that 3-Kalsi Filter use to treat arsenic contaminated water in Nepal (Pokhrel et al. 2009). It consists of three clay pots staggered vertically with a 1 cm in diameter hole in the bottom of the middle and top filters. The top and middle filters work as a reactor, and the bottom filter stores the treated water. The top filter contains the following, from bottom to top: a layer of polyester cloth, 3 kg of iron nails (3 cm depth), 2 kg of coarse sand (4 cm depth) and raw water. The middle filter contains the following from bottom to top: a layer of polyester cloth, about 50 kg of brickbats, 2 kg of fine sand (3.5 cm depth), 1 kg of charcoal (6 cm depth), 2 kg of brickbats (3 cm depth), and filtered water from the top filter. The Three-Gagri filters were initially introduced in a limited scale in Nepal for arsenic removal. Studies showed that these filters could remove 95–99% of arsenic (Pokhrel et al. 2009).

In most of these techniques, sand packs were used as filtration to separate precipitates from water. Compared to sand, zeolites have larger surface area, large interparticle and intraparticle pores, which will be ideal as filtration media to remove iron/aluminum hydroxide precipitates. In addition, zeolite can remove other undesired cations by cation exchange while sand cannot. However, using zeolite as the filtration media to remove arsenic containing iron/aluminum hydroxide was not reported.

Natural zeolitic rocks have been evaluated to remove arsenic from waters at a concentration of about 100 µg/L. The removal efficiency was 60–80% for chabazite-phillipsite raw materials and 40–60% for clinoptilolite-bearing ones (Ruggieri et al. 2008). A large zeolitic content in the chabazite-phillipsite raw materials increase the As removal. Instead, the inverse situation is observed in the clinoptilolite-bearing rocks (Ruggieri et al. 2008).

Procedures and Methods

Chemicals

The arsenate and arsenite used were $Na_2HAsO_4 \cdot 7H_2O$ and $NaAsO_2$, both from Fisher Scientific Pittsburg, PA). The $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ used were from Katayama Chemical (Osaka, Japan).

Batch Fe(II) and Fe(III) adsorption on zeolite and batch As (III) and As(V) sorption on Fe-zeolite

To each 50 mL centrifuge tube, 1.0 g of zeolite and 20.0 mL of Fe(II) or Fe(III) solution at concentrations from 0.1 to 10 mmol/L were combined. The mixture was shaken at 150 rpm for 24 hours at room temperature (25ºC). Then the mixture was centrifuged at 5000 rpm for 10 min and the supernatant was passed through a 0.45 µm syringe filter before being analyzed for equilibrium Fe concentrations. The amount of Fe adsorbed was calculated from the difference between the initial and equilibrium concentrations.

For As sorption, 1.0 g of Fe-zeolite was mixed with 50 mL of arsenic solutions in 50 mL centrifuge tubes. The initial As concentrations were 0.1 to 20 mg/L. The mixture was shaken at 150 rpm for 24 hours. The mixture was allowed to settle and the supernatant analyzed for equilibrium As solution concentration. For kinetic study on As sorption, 1.0 g of Fe-zeolite was mixed with 20 mL of 0.5 mg/L As solution in 50 mL centrifuge tubes for varying amounts of time. The samples were centrifuged for 5 min and the supernatant passed through a 0.45 µm syringe filter before being analyzed.

Batch study on influence of pH, initial Fe and As input on As removal and equilibrium Fe concentration

To study the influence of solution pH, 178 mL of DI water and 2 mL of 100 ppm As (V) solution were added to a 250 mL Erlenmeyer flask. After 20 mL of 10 mM $FeCl_3 \cdot 6H_2O$ were added, the pH dropped to 3.10. Then the pH of the solution was slowly raised by adding 1 M NaOH.

To determine the influence of added Fe to the removal of As from water, 196 mL of DI water and 2 mL of 100 mg/L As (V) solution were added to a 250 mL Erlenmeyer flask. Then 10 mM Fe solution was added in 2 mL increment. Each time after addition of Fe, the pH was adjusted to a value between 7 and 9 and samples were taken for As analysis.

To determine the influence of input Fe to the final concentration of Fe in water, 100 mL of DI water and 0.1 mL of 100 mg/L As (V) solution were added to a 250 mL Erlenmeyer flask. Then 10 mM Fe solution was added at 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mL. After addition of Fe, the pH was adjusted to a value between 7 and 9 and samples were taken for Fe analysis.

Column study on removal of As by filtrating iron hydroxide precipitates

Each 60 mL syringe sleeve was filled with 50 mL with zeolites (about 50 g as the bulk density of zeolite is about 1 g/cm^3). To each 1 L of 0.1 mg/L As solution, 1, 3, or 10 mL of 10 mM Fe stock was added to reach a final Fe concentration of 10, 30 and 100 μM. The solution pH was raised to between 7 and 9 by adding 1 M NaOH drop-wise before being passed through the column. Similarly, quantitative Fe was added to a final concentration of 10 mM in 1 L of 1.0 mg/L As solution. The solution pH was raised to between 7 and 9 by adding 1 M NaOH before being passed through the column.

Modification of zeolite by Fe(III)

To each 500 mL centrifuge bottle, 120 g of zeolite and 360 mL of 20 mM Fe(III) solution was combined. The mixture was shaken at 150 rpm for 20 hours at room temperature before pH was measured and 2 M NaOH solution was added to raise the pH. This procedure was repeated every 2 hours for a total of three times to bring the final solution pH to 9. The mixture was allowed to settle and the supernatant removed, followed by washing the zeolite with 360 mL DI water. The chloride concentration of supernatant was checked with $AgNO_3$ until no white precipitation was made, which was confirmed after the zeolite was washed with 6 portions of DI water. The modified zeolite was allowed to dry naturally. Test of Fe in the supernatant was 0.15 mg/L less than 0.3 mg/L for the secondary water standard.

Large column tests

The large columns had a diameter of 4.5 cm or 5.0 cm and 70 cm in length. To each column, 400 g of 8-14 mesh zeolite or Fe(III)-modified zeolite was packed. In one test, 10 L of 100 μg/L As (V) solution was made. Then 270 mg of $FeCl_3 \cdot 6H_2O$ was added to make a final Fe concentration of 5.6 mg/L followed by addition of 3.1 mL of 1 M NaOH to raise the pH to 9.1. The mixture was stirred vigorously to induce precipitation and then passed through the column at a flow rate about 300 mL/min. Samples were taken every liter. For real water collected from groundwater from Chia-Nan Plain aquifer, the added Fe(III) was equivalent to 0.2 mM, or 11.2 mg/L. While for a water collected from an acid mine drainage, Fe(III) was not added, as it contains 101 mg/L of dissolved Fe already. Only pH was raised by adding appropriate amounts of NaOH. The flow rate was between 125 and 150 mL/min.

Chemical analysis

The total dissolved iron (Fe^{TOT}) was determined using Loviband MutiDirect Photometric System (The Tintometer Ltd., Dortmund, Germany) with an analytical range of 0.02 to 1.0 mg/L. Proper dilution was made for higher solution Fe^{TOT} concentrations. The As analysis was made on either PE Optima 7000 DV ICP-OES with a detection limit of 1 μg/L or PSA Millennium System Excalibur (PS Analytical Ltd., UK) with a detection limit of 0.1 μg/L.

SEM observation and Fe determination on zeolite

Observation under scanning electron microscope (SEM) was performed on JEOL JSM-840A, Japan at a voltage of 15 kV and a current of 0.4 nA. The elements analysis was made with energy dispersion spectrum Bruker XFlash detector 5010. Samples were coated with Au for SEM image observation and C for EDS element analysis.

Results and Discussion

Sorption of Fe (II) and Fe(III) on zeolite is plotted in Fig. 1. The zeolite has a higher affinity for Fe(III) than Fe(II). The results were modeled with both Langmuir and Freundlich sorption isotherms. For the Fe(III) adsorption both models fit the experimental data equally well with a coefficient of determination r^2 = 0.99 and 0.98, respectively. The calculated Fe(III) sorption capacity was 144 mmol/kg. On the contrary, the Langmuir sorption isotherms fit the experimental data better than the Freundlich sorption isotherm for De(II) sorption on zeolite with r^2 = 0.99 and 0.95, respectively. The calculated Fe(II) sorption capacity was only 58 mmol/kg (Fig. 1).

Sorption of As (III) and As(V) on Fe-zeoliete can be seen in Fig. 2. As(III) had a higher sorption on Fe-zeolite than As(V). The experimental data were modeled with both Langmuir and Freundlich sorption isotherms. For both As(III) and As(V) sorption the Freundlich sorption isotherm fit the experimental data better than the Langmuir sorption isotherm with $r^2 = 0.99$ and 0.85, respectively. The calculated As (III) and As(V) sorption capacity on Fe-zeolite was 100 and 50 mg/kg, respectively (Fig. 2).

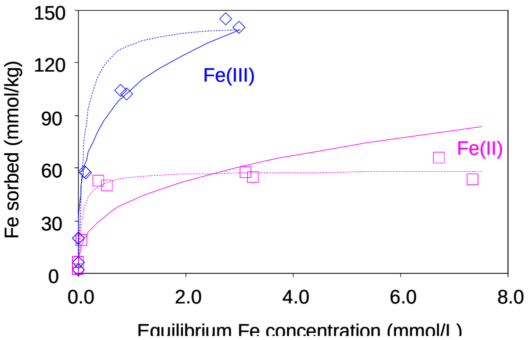

Fig. 1. Sorption of Fe(II) and Fe(III) on zeolite. The dashed lines are the Langmuir fits while the solid lines are the Freundlich fits to the experiment data.

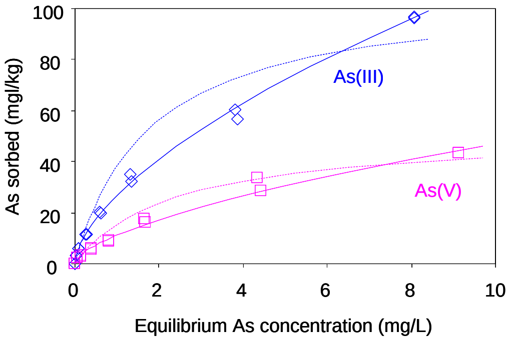

Fig. 2. Sorption of As(III) and As(V) on Fe-zeolite. The dashed lines are the Langmuir fits while the solid lines are the Freundlich fits to the experiment data.

The results of As sorption kinetic study were plotted in Fig. 3. The observed data were fitted to pseudo-first order and pseudo-second order reaction and the latter fit the experimental data better. The rate constants were 0.01 and 0.06 g/mg-h for As(V) and As(III) sorption on Fe-zeolite. The initial rates were 1.4 and 3.6 mg/g-h for As(V) and As(III) sorption on Fe-zeolite, respectively. Influence of equilibrium solution pH on As sorption on Fe-zeolite is plotted in Fig. 4. As(V) sorption was more or less constant at 11 mg/kg when solution pH was between 3 and 6. Further increase in solution pH caused significant reduction in As sorption. At pH 10, the amount of As(V) sorbed was only 2 mg/kg (Fig. 4). Sorption of As(III) on Fe-zeolite was somehow slightly different. Higher As(III) sorption was found at pH 6 to 9, above which significant decrease in As(III) sorption was also found. However, the As(III) sorption was lower at solution pH 3 to 5 compared to 6–9 (Fig. 4).

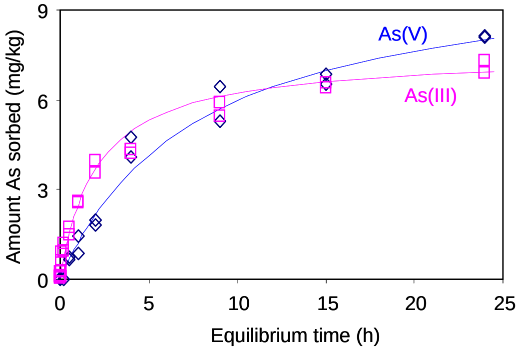

Fig. 3. Kinetics of As sorption on Fe-zeolite. The lines are pseudo-second order fits to the observed data.

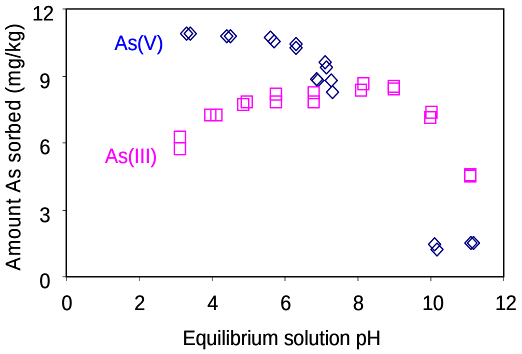

Fig. 4. Influence of equilibrium solution pH on As sorption on Fe-zeolite.

For As removal by $Fe(OH)_3$ co-precipitation, solution pH had strong influence on dissolved As concentration and Fe^{TOT}. When solution pH was 6.5–9.5, extensive precipitation of iron hydroxide occurred, which resulted in an Fe^{TOT} concentration much less than 0.3 mg/L (Fig. 5). Sorption of As(V) and As(III) on co-precipitated iron hydroxide is plotted in Fig. 6. The As sorption capacity is much higher than that on Fe-zeolite, with an initial Fe(III) concentration of 56 mg/L and the initial As concentration from 0.5 to 6 mg/L.

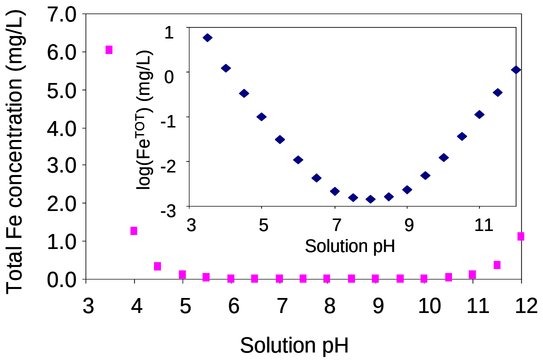

Fig. 5. Total Fe solution concentration as a function of solution pH. Fe removal was due to precipitation of iron hydroxide.

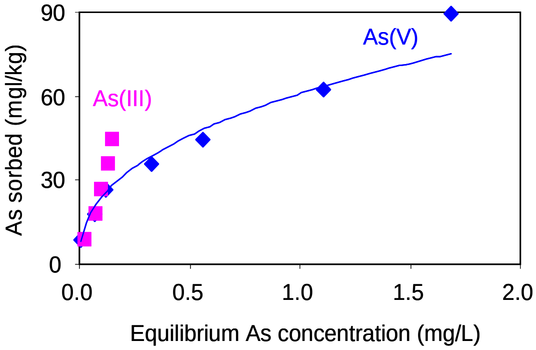

Fig. 6. As (III) and As(V) sorption on co-precipitated iron hydroxide.

The first test was to determine the amount of Fe needed at different initial As concentration. To 100 mL of 0.1 mg/L As solution, the amount of added Fe had an obvious effect on the equilibrium As concentration. However, the does of Fe used was not large enough to remove the As (Fig. 7a). Thus, a second trial with an initial As concentration of 1 mg/L and larger does of input Fe was made. It was anticipated that a minimum of 50 mg/L of Fe is needed to reduce an input As concentration from1 mg/L to 10 μg/L or below (Fig. 7b).

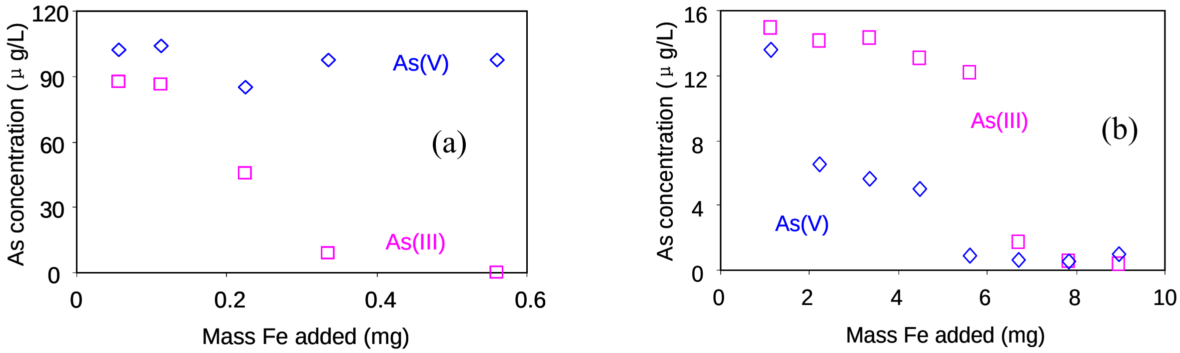

Fig. 7. Total Fe mass added per 100 mL of 0.1 mg/L (a) and 100 mL of 1.0 mg/L (b) As solution.

The solution As(V) and As(III) concentrations in batch co-precipitation tests were in the range of lower μg/L when the input As concentration was 1000 μg/L, a few hundreds, or even up to 1000 folds reduction in As concentration (Fig. 8). Again confirming that the maximum removal of As by co-precipitated iron hydroxide was in the pH 6.5 to 9 range.

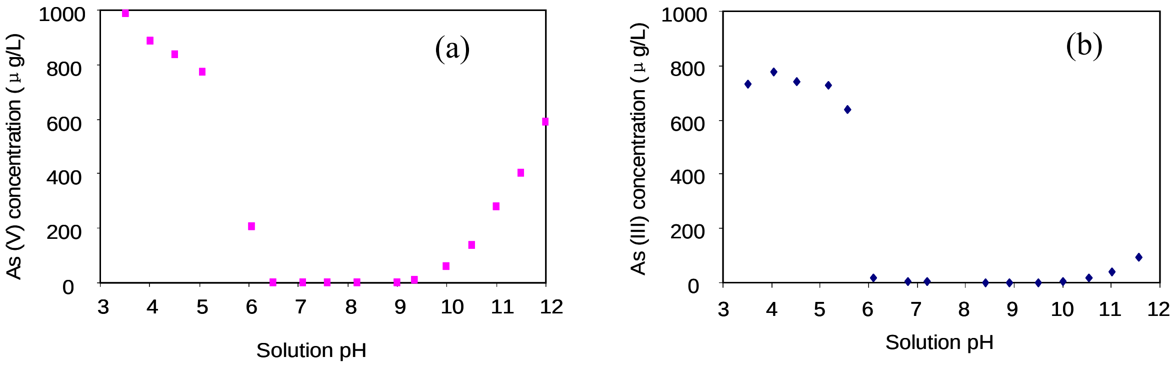

Fig. 8. As(V) (a) and As(III) (b) solution concentration as a function of solution pH. Arsenic removal was due to sorption onto iron hydroxide precipitation.

Small column tests were made to investigate the input Fe on As removal at an initial As concentration of 100 µg/L. The results showed that a minimum of 100 µM is needed to reduce the input concentration to 10 µg/L (Fig. 9). Better removal of As(V) was achieved compared to As(III).

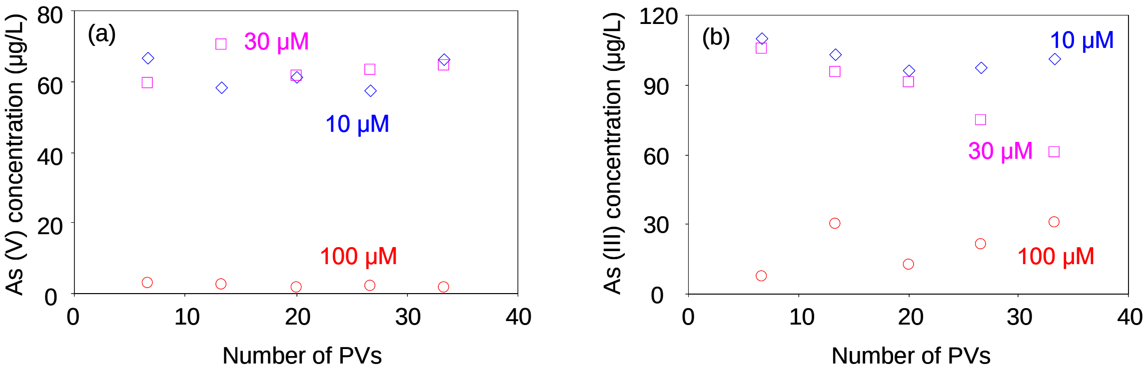

Fig. 9. Influence of added Fe^{TOT} on effluent As(V) (a) and As(III) (b) concentrations after iron co-precipitation followed by zeolite filtration. The initial As concentration was 100 µg/L.

Small column tests on As removal showed that at an initial concentration of 1000 µg/L, significant reduction in effluent As concentration could be achieved after addition of Fe(III) equivalent to 1 mM followed by inducing precipitation and then zeolite filtration (Fig. 10). The increase in As concentrations at 7 and 12 PVs in Fig. 9 was due to dry out of the columns. The effluent iron concentration was around 0.03 mg/L for all samples. Separately, at an initial As concentration of 100 µg/L, and an initial Fe concentration of 0.1 mM, after inducing iron hydroxide co-precipitation followed by infiltration through the zeolite column, the effluent As was below 10 µg/L up to 35 PVs (Fig. 10). The rise in effluent As concentration at 42 PV was due to column dry out. The effluent Fe concentration was below 0.3 mg/L up to 42 PVs (Fig. 11).

In comparison to Fig. 9, a column packed with course Ottawa sand was tested for As(V) removal at an initial concentration of 100 µg/L and different Fe(III) doses. A minimum of 30 µM of Fe(III) is needed to reduce the As(V) concentration to below 10 µg/L (Fig. 12). Separately, a sand column flushed with 1000 µg/L mixed with 1 mM of Fe(III) followed by inducing iron hydroxide precipitation is plotted in Fig. 13. A lower effluent As concentration could be achieve. However, due to the smaller pore size the system clogged quickly.

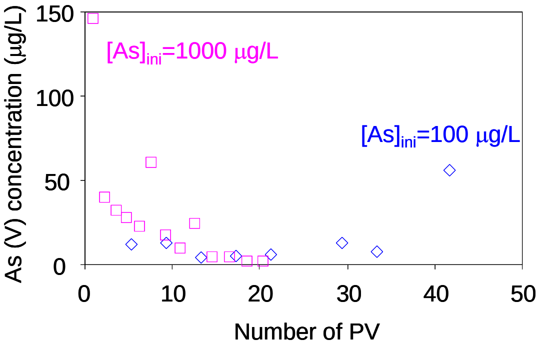

Fig. 10. Effluent As concentration from a zeolite column with input As and Fe concentrations of 1000 µg/L and 1 mM and 100 µg/L and 0.1 mM.

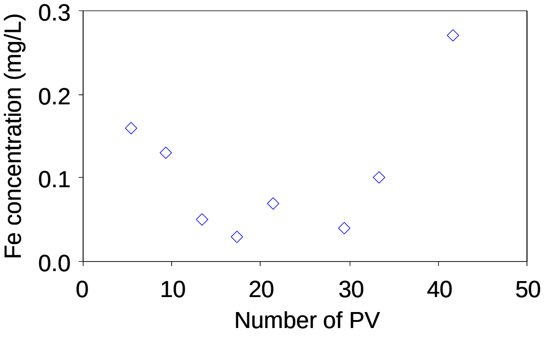

Fig. 11. Effluent Fe^{TOT} concentration from a zeolite column with input As and Fe concentrations of 100 µg/L and 0.1 mM.

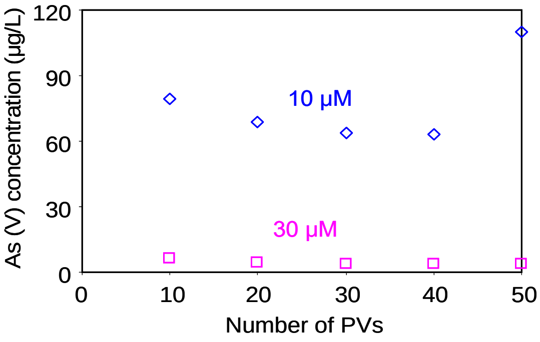

Fig. 12. Influence of added Fe(III) on effluent As(V) concentrations after iron co-precipitation followed by sand filtration. The initial As concentration was 100 µg/L.

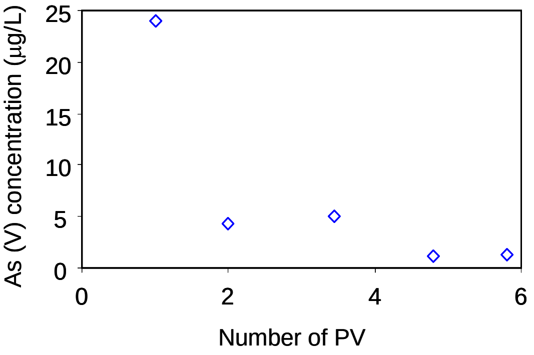

Fig. 13. Effluent As concentration from a sand column with input As and Fe concentrations of 1000 µg/L and 1 mM and 100 µg/L and 0.1 mM.

Based on the small column tests, large column tests were made for synthetic water, water from an acid mine drainage (AMD), and groundwater from Chia-Nan Plain. The As concentration in the AMD water was 147 µg/L while that of well water was 511 µg/L. Fig. 14 is the plot of effluent As and Fe from a synthetic water with an initial As(V) concentration of 1000 µg/L mixed with 0.1 mM Fe(III). Fig. 15 is the plot of effluent As concentrations after Fe co-precipitation followed by zeolite filtration for AMD and Well water. The effluent As concentration was all non detectable for AMD water. This could be attributed to the water containing significant amount of dissolved iron. The Fe(II) and Fe^{TOT} concentrations were 91 and 101 mg/L, respectively. Therefore, after addition of 55 to 70 mL of 1 M NaOH, significant amount of precipitation with black color was seen. This large amount of Fe precipitation may completely sorb the As from the water as its concentration was only 147 µg/L. On the other hand, removal of As from well water was not successful for the following reasons. The As concentration was as high as 511 µg/L. The water was under extremely reduced environment and the As species might be As(III). The amount of Fe(III) added may not be enough to remove significant amount of As from water or not enough to induce significant amount of $Fe(OH)_3$ precipitation.

Compared to co-precipitation followed by infiltration, the effluent As concentration leaching from the large Fe-zeolite column using AMD water and well water is plotted Fig. 16. The flow rate was between 125 and 150 mL/min. A similar observation was found, i.e. effluent of AMD water showed zero As concentration while that of well water showed substantial As concentration.

For the control of a large sand column, 800 g of coarse Ottawa sand was used. With a porosity of 0.3, the PV is about 250 mL, too. Thus, only 6 PVs were flushed before significant reduction in flow rate occurred. The effluent As concentration from the control column was zero.

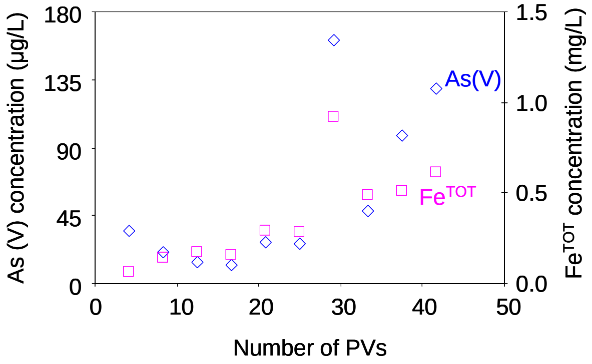

Fig. 14. Effluent As and Fe concentrations from a large zeolite column with input As and Fe concentrations of 1000 µg/L and 1 mM.

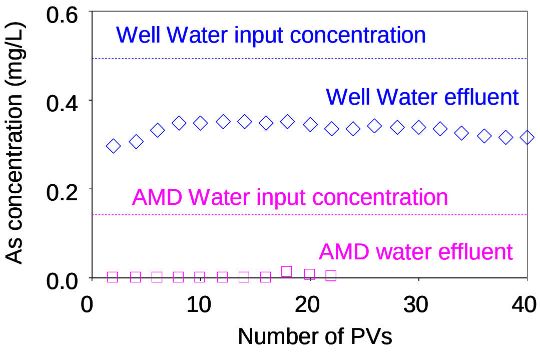

Fig. 15. Effluent As concentrations from a large zeolite column with input AMD and well water. Fe(III) added was equivalent to 0.2 mM for the well water.

SEM observation showed that the zeolite had euhedral crystals with particle size in the range of 10 µm (Fig. 17). The crystal morphology did not change after Fe modification (Fig. 17) or after As sorption (Fig. 18). However, fibrous minerals were formed after co-precipitation followed by zeolite filtration for the AMD water (Fig. 19). The $Fe(OH)_3$ precipitates were essential amorphous fine very fine particle size (Fig. 20). Its EDS spectrum showed the presence of As peak, confirming the adsorption of As on $Fe(OH)_3$ precipitates (Fig. 21)

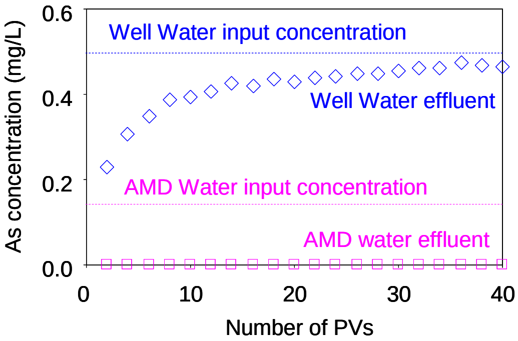

Fig. 16. Effluent As concentrations from a large Fe-zeolite column with input AMD and well water.

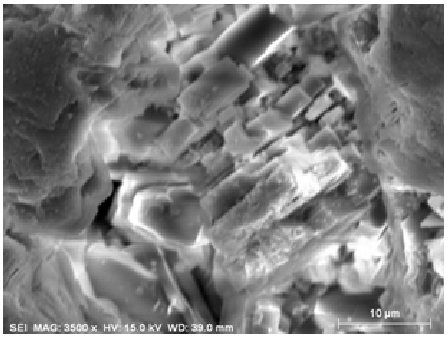

Fig. 17. SEM photo showing the euhedral clinoptilolite crystals.

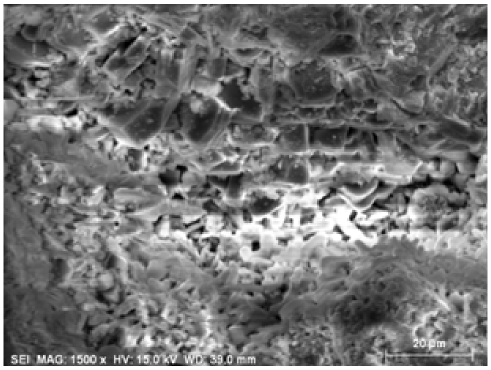

Fig. 18. SEM photo showing the euhedral clinoptilolite crystals in spent Fe-zeolite after As sorption.

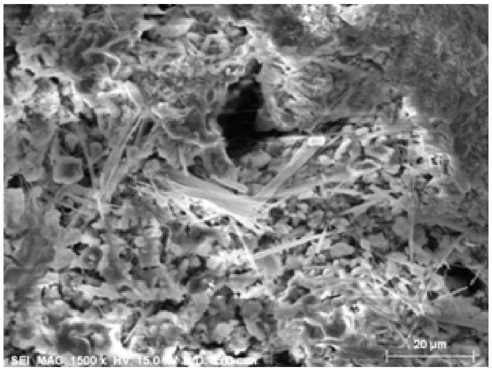

Fig. 19. SEM photo showing the euhedral clinoptilolite crystals and fibrous minerals in spent zeolite after As and Fe co-precipitation and filtration.

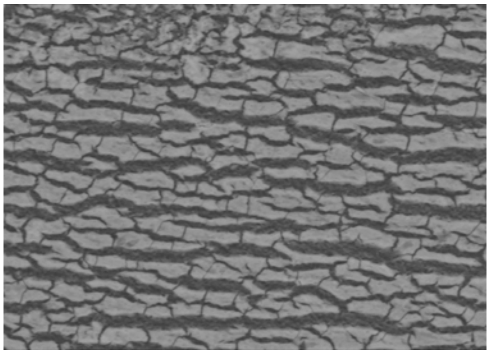

Fig. 20. SEM photo showing the fine particle size and dehydrated texture of $Fe(OH)_3$ precipitates.

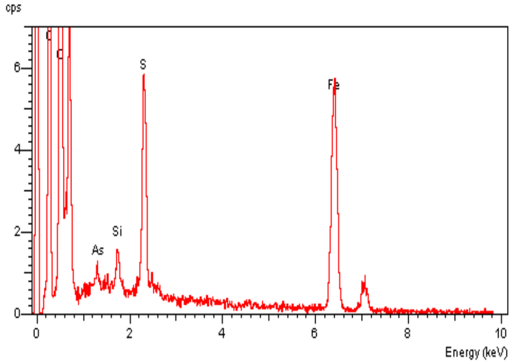

Fig. 21. EDS spectrum of Fe(OH)3 precipitates showing the presence of adsorbed As..

Conclusions and Recommendations

Removal of Arsenic from water can be achieved fairly effectively using Fe co-precipitation followed by zeolite filtration. This method works well if the water contains significant amount of dissolved iron and the water is not under extremely reduced condition. The precipitation of $Fe(OH)_3$ not only decreased the concentration of As in water, but also that of Fe, provided a good filtration system was maintained. However excess dissolved Fe would generation more precipitates once the pH of the water was adjusted between 6 and 9. More precipitation means that the system will get clogged quickly. Thus, optimizing the amount of Fe added to maximize As removal with minimal $Fe(OH)_3$ precipitation is more specific to each individual water. It requires preliminary measurement of a few field parameters such as pH, Eh, dissolved Fe (concentration), and maybe other chemical species that serve as Eh buffer to affect $Fe(OH)_3$ precipitation. A second issue is the cloudiness of the water after filtration with 4-14 mesh zeolite aggregates due to the fine particle size of each individual crystal of zeolite. More pilot tests are needed in order to assess the technology at a even larger scale. Nevertheless, this study provided preliminary data from batch and column tests to support the initial idea. And the simple and yet somehow effective technique may find its way to remove arsenic from water in a low cost manner in developing countries.

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Appendix A:

Journal Publications:

Li, Z., Hong, H., Jean, J.-S., Koski*, A. J., Liu, C.-C., Reza, S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J. (2011) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *Environ. Earth Sci.*, **64**, 823-831. http://dx.doi.org/10.1007/s12665-011-0938-7

Liu, C.-C. Maity, J. P., Jean, J.-J., Sracek, O., Kar, S., Li, Z., Bundschuh, J., Chen, C.-Y., Li, H.-Y. (2011) Biogeochemical interactions among arsenic, iron, humic substances, and microbes in mud volcanoes in southern Taiwan, *J. Environ. Sci. Health Part A*, **46**, 1218-1230. http://dx.doi.org/10.1080/10934529.2011.598793

Kar, S., Maity, J. P., Jean, J.-S., Liu, C.-C., Nath, B., Lee, Y.-C., Bundschuh, J., Chen, C.-Y., Li, Z. (2011) Role of organic matter and humic substances in the binding and mobility of arsenic in a Gangetic aquifer, *J. Environ. Sci. Health Part A*, **46**, 1231-1238. http://dx.doi.org/10.1080/10934529.2011.598796

Liu, C.-C., Maity, J. P., Jean, J.-S., Li, Z., Nath, N., Lee, M.-K., Reza, A.H.M. S., Lin, K.-H., Bhattacharya, P. (2011) Geochemical characteristics of the mud volcano Fluids in southwestern Taiwan and their possible linkage to elevated arsenic concentration in Chianan plain groundwater, *Environ. Earth Sci.*, re-revision in review.

Lv, G., Li, Z., Jiang, W.-T., Jean, J.-S., Hong, H., Liao, L., Lv, G. (2011) Combination of hydrous iron oxide precipitation with zeolite filtration to remove arsenic from contaminated water, *Desalination.*, **280**, 203-207. http://dx.doi.org/10.1016/j.desal.2011.07.009

Li, Z., Jean, J.-S., Jiang, W.-T., Chang, P.-H., Chen, C.-J., Liao, L. (2011) Removal of arsenic from water using Fe-exchanged zeolite, *J. Hazard. Mater.*, **187**, 318-323. http://dx.doi.org/10.1016/j.jhazmat.2011.01.030

Li, Z., Koski*, A. J., Merrill*, J. S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J., Reiley*, A. E., Ackley*, C. J., Fenske*, N. A., Schulz*, L. A., Jean, J.-S., Liu, C.-C., Reza, A. H. M. S. (2010) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *In* Jean, Bundschuh, Bhattacharya (eds.) *Arsenic in Geosphere and Human Diseases*, Taylor & Francis Group, London, p 553-555.

Hong, H., Yin, K., Lai, X., Du, Y., Li, Z., Jean, J.-S. (2010) Occurrence of Arsenic in Mudstone of the Endemic Blackfoot Disease Region, Taiwan, *In* Jean, Bundschuh, Bhattacharya (eds.) *Arsenic in Geosphere and Human Diseases*, Taylor & Francis Group, London, p 556-557.

Conference Presentation: (Both presentations are invited)

Li, Z., Koski*, A. J., Merrill*, J. S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J., Reiley*, A. E., Ackley*, C. J., Fenske*, N. A., Schulz*, L. A., Jean, J.-S., Liu, C.-C., Reza, A. H. M. S. (2010) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *Arsenic in Geosphere and Human Diseases*, The Third International Congress on Arsenic in the Environment, May 12 – 17, 2010, Tainan, Taiwan.

Li, Z. (2008) Sorption of arsenic by surfactant-modified zeolite and kaolinite, 2008 International Workshop on Arsenic and Humic Substances in Groundwater and Their Health Effects, May, 2008, Tainan, Taiwan.

Other Funding:

A grant award at the amount of 700,000 New Taiwan Dollar (equivalent to $22,000) was awarded to the collaboration among myself, Prof. Min-Kuo Lee from Auburn University and Prof. Jiin-Shuh Jean from National Cheng Kung University between Oct. 1, 2008 and Sept. 30, 2009. See attachment for email notice from the PI and the award letter (in Chinese) from the funding agency.

* Denotes undergraduate students from University of Wisconsin – Parkside.

Fw: 國立成功大學邁向頂尖大學計畫推動總中心函：國際合作計畫補助(案號：P97001)(不另送紙本)

簡錦樹 [jiinshuh@mail.ncku.edu.tw]

Sent: Sunday, December 28, 2008 10:51 PM
To: Ming-kuo Lee [leeming@auburn.edu]; Li, Zhaohui
Attachments: OriginalMsg.htm (19 KB) ; 國立成功大學邁向頂尖大學計畫推動總中心函113-P9~1.pdf (84 KB)

Dear Ming-Kuo and Zhaohui,

I am pleased to tell you that our application for the financial support for our international collaboration research program has been approved by NCKU as attached. However, only NT$700,000 of grant is allocated to this program, in which NT$140,000 should be used in personnel, NT$420,000 in inviting visiting professors to NCKU, and NT$140,000 used for me in travel expense to attend any conference abroad. These expenses must be fulfilled no later than September 15, 2009. The collaborative report should also be submitted to NCKU at that time.

Both of you can use NT$420,000 for a research at NCKU before September 15, 2009. I kindly invite both of you to attend the International Workshop on Arsenic and Humic Substances on May 11-12, 2009 at NCKU as we had in May 2008. At that time, I will also drill a well (~200m deep) along with 10 different depths of piezometers at Yichu where the groundwater in this area contains high arsenic concentration but without the incidence of any Blackfoot disease (BFD) cases before. This can lead us to compare the difference in groundwater quality between the Budai drilling sites with BFD cases before) and the Yichu drilling site without any BFD cases before. Each of you will share this much money, NT$210,000 each, whcih includes the round-trip flight ticket (economic-class) and living allowances (NT$8175/day for full professor and NT$6540/day for associate professor). Unfortunately, NCKU only pays the round-trip ticket to a graduate student, exclusive of living allowances. I would like to know how long you will stay at NCKU.

I look forward to hearing from you.

Happy New Year!

with best wishes,
Jiin-Shuh

----- Original Message -----
From: 陸美蓉
To: 龔慧貞 ; 饒瑞鈞 ; 羅尚德 ; 簡錦樹 ; 蔡金郎 ; 劉正千 ; 楊懷仁 ; 黃奇瑜 ; 游鎮烽 ; 陳燕華 ; 袁彼得 ; 翁偉嘵 ; 孫鎮球 ; 林慶偉 ; 李紅春 ; 吳銘志 ; 江威德 ; jennifer kung ; 楊耿明
Cc: 賴美婷
Sent: Thursday, December 25, 2008 5:27 PM
Subject: Fw: 國立成功大學邁向頂尖大學計畫推動總中心函：國際合作計畫補助(案號：P97001)(不另送紙本)

> Subject: 國立成功大學邁向頂尖大學計畫推動總中心函：國際合作計畫補助(案號：P97001)(不另
> 送紙本)
>

國立成功大學邁向頂尖大學計畫推動總中心 函

承辦單位：邁向頂尖大學推動總中心國際化組
聯絡方式：蘇郁雅 (06)2757575 轉 50995
電子信箱：yuya@mail.ncku.edu.tw

受文者：如正副本單位

發文日期：中華民國 97 年 12 月 17 日
發文字號：(97) 頂 國 字第 113 號
速別：
附件：

主旨：有關教授申請簽訂國際合作計畫補助乙案，審查結果詳如說明，請　查照。

說明：

一、 本案已依「發展國際一流大學及頂尖研究中心計畫簽訂國際合作計畫補助要點」，於 97 年 12 月 15 日完成審查。

二、 本案簽約之國際合作計畫三方皆含有經費，合作總經費總計 NTD$10,500,008 元，年平均經費 NTD$5,250,004 元

三、 依本校「發展國際一流大學及頂尖研究中心計畫簽訂國際合作計畫補助要點」，本案擬予以補助新台幣 70 萬元，本項經費限使用於一般業務費用(如邀請國外學者來訪及舉辦國際研討會)，不可用於執行計畫。另，人事費用僅可支應工讀金及獎助金，且人事費之額度不得超過補助金額之 20%、業務費不得超過補助金額之 60%、差旅費不得超過補助金額之 20%。

四、 本案之補助經費將儘速核撥至　貴單位之分配經費項下(D97-3200)，並同時函知　貴單位及相關行政單位，以便經費之使用及核銷。

五、 本組將保留補助經費之 25%，待 98 年 9 月 15 日前繳交中英文成果報告書(含電子檔)及經費使用明細，於確認無誤後，剩餘經費再行撥款。

六、 依教育部規定，一案不得由同一部會的不同經費來源共同補助。故凡已獲教育部部分補助之申請案，原則上不得再由本計畫予以補助。如獲本計畫之補助，且同時獲得其他政府部會補助者(如國科會、經濟部、農委會等)，於經費核銷時，亦須明列各不同經費來源之詳細經費分攤。

正本：地球科學系簡錦樹教授

副本：理學院、地科系、邁向頂尖大學計畫推動總中心國際化組