An investigation of the sorption of arsenic by diatomite

S D J Inglethorpe, P H Whitbread-Abrutat & R Metcalfe
An investigation of the sorption of arsenic by diatomite

S D J Inglethorpe, P H Whitbread-Abrutat & R Metcalfe

A Report prepared for the Department for International Development under the Knowledge and Research Programme. The views expressed in this document are not necessarily those of the Department.

DFID Classification
Subsector: Geoscience
Theme: G2
Project Title: Treatment of contaminated land using diatomite
Reference number: R6488

Bibliographic reference:
An investigation of the sorption of arsenic by diatomite.

Keywords: Thailand, diatomite, sorption

Front cover illustration:

© NERC 1999

Keyworth, Nottingham, British Geological Survey, 1999
## EXECUTIVE SUMMARY

### 1. INTRODUCTION

1.1. Background

### 2. PREVIOUS STUDIES

2.1. Sorption
2.2. Sorption and minerals
2.3. Properties of silica
2.4. Arsenic speciation
2.5. Sorption of arsenic by minerals

### 3. RESULTS AND DISCUSSION

3.1. Arsenate jar tests
3.2. Silica dissolution experiments
3.3. Zeta potential
3.4. Arsenate sorption isotherm
3.5. Arsenate sorption vs. pH
3.6. Geochemical modelling

### 4. CONCLUSIONS

### 5. RECOMMENDATIONS FOR FURTHER WORK

### 6. REFERENCES

### APPENDIX 1:

**SAMPLES AND LABORATORY METHODS**

- A1.1. Materials
- A1.2. Arsenate jar tests
- A1.3. Silica dissolution experiments
- A1.4. Zeta potential
- A1.5. Arsenate sorption isotherm
- A1.6. Arsenate sorption vs. pH
- A1.7. Geochemical modelling

**Tables 1-5**

**Figures 1-19**
EXECUTIVE SUMMARY

Background

This report was produced for the Knowledge and Research (KAR) Programme project “Treatment of contaminated land using diatomite” (Project No R6488) managed by the Camborne School of Mines and funded by the UK Department for International Development (DFID). The main outcomes and achievements of this project are described by Whitbread-Abrutat et al. (1999a).

One of the key aims of the project was to examine how diatomite was able to sorb and remove arsenic. A proper understanding of the sorption process is necessary to enable:

- The long-term effectiveness and stability of diatomite added to contaminated land to be established
- Prediction of the ability of diatomite to sorb (or release) potentially toxic elements (PTEs) under different pH and redox conditions
- Full interpretation of column leach test and field trial results

Conclusions

The main conclusions regarding the sorption properties of diatomite are as follows:

- Diatomaceous silica (also known as opal-AN) is the principal constituent of diatomite. Diatomite appears to function by providing an inert, rigid substrate for other mineral phases involved in the sorption of arsenic.

- Diatomaceous silica was not directly implicated in the sorption of arsenic. An antipathetic trend was observed between arsenate sorption and the opal-AN content of samples. Opal-AN also possesses a negative surface potential between pH 12 and 1 which precludes the physical adsorption of negatively-charged arsenate species. Under acid conditions, co-precipitation of arsenic with silica is also considered unlikely as it was demonstrated that the solubility of opal-AN is minimal below pH 4.

- There is some evidence that arsenate undergoes physical adsorption onto iron oxide coatings bonded to the opal-AN substrate. Uptake of arsenate correlates with the iron oxide content of samples and also exhibits a pH-dependency characteristic of physical adsorption.

- The sorption of arsenate by iron oxide involves electrostatic attraction and the formation of weakly-bonded, outer-sphere complexes. Arsenate adsorbed onto iron oxide will be re-mobilised under anaerobic conditions. The iron oxide content of the diatomite may also initiate co-precipitation of arsenic by raising iron concentration of the solute above saturation.

- For diatomite sample D027, used in the project’s field trials, the sorption of arsenate closely-matched the Langmuir isotherm. This behaviour suggests that the sorption of arsenate involves a single type of surface functional group. From the Langmuir equation, an adsorption capacity for arsenate of 0.23 mg/g was derived for sample D027.
Recommendations

It is recommended that further studies to examine the use of industrial minerals in the treatment of contaminated land adopt the following approach:

1. Development of a surface complexation model. This would involve characterisation of mineral surfaces, sorption experiments and spectroscopic studies (e.g. EXAFS) to establish sorption mechanism(s) between surface functional groups and potentially toxic elements (PTEs).

2. Geochemical modelling. The surface complexation model developed should be incorporated within a geochemical thermodynamic database of aqueous species, complexes and mineral solubilities (e.g. EQ3/6 or PHREEQE). This would enable a realistic simulation of the interactions between industrial minerals and mine waste fluids.

3. Validation of the model. The validity of the surface complexation model should be tested by comparison of the results obtained from geochemical simulations with those from laboratory column leach experiments and/or field trials in which industrial minerals have been added to metalliferous waste.

Development of surface complexation models for industrial minerals used to treat contaminated land would complement other research on mine waste hazards currently being funded by DFID under the KAR programme, e.g. Environmental arsenic exposure: health risks and geochemical solutions (Project R6491), Cost-effective evaluation of hazards from mine waste (R7118).
INTRODUCTION

1.1. Background

This report was produced for the Knowledge and Research (KAR) Programme project "Treatment of contaminated land using diatomite" (Project No R6488) managed by the Camborne School of Mines and funded by the UK Department for International Development (DFID). The main outcomes and achievements of this project are described by Whitbread-Abrutat et al. (1999a).

An inventory report is available which describes the occurrence of diatomite within the Changwat Lampang region of northern Thailand and provides information on the geological setting (Inglethorpe et al., 1998). A report on the mineralogy and petrography of the diatomite samples studied here has also been produced (Inglethorpe & Pearce, 1999).

Between 1988 and 1993, research at the Camborne School of Mines examined the role of industrial minerals in the reclamation and revegetation of derelict mining land contaminated by metalliferous wastes (Atkinson et al., 1990; Mitchell, 1991; Mitchell & Atkinson, 1991; Mitchell & Atkinson, 1993; Mitchell et al., 1993). Natural zeolite, vermiculite, fuller's earth, diatomite and micaceous waste were among the amendments examined. Laboratory column leaching experiments indicated that diatomite was particularly effective at controlling acidity and the release of potentially toxic elements (PTEs) from metalliferous mine spoil.

When this project was initiated three years ago, there was little detailed understanding of how diatomite might function when added to contaminated mining land. The starting point was the mechanism proposed by Mitchell (1991) (see Figure 1):

- Diatom particles act as nucleation sites
- Dissolution of adjacent carbonate raises pH locally
- The high pH zone created around the nucleation site increases silica dissolution
- Potentially toxic elements (PTEs) enter this high pH zone
- PTEs are precipitated within the high pH zone as silicates and hydroxides
- Overall acidity of solute is reduced (diatomite acts as a buffer)

One of the key aims of the project was to examine how diatomite was able to sorb and remove arsenic. A proper understanding of the sorption process is necessary to enable:

- The long-term effectiveness and stability of diatomite added to contaminated land to be established
- Prediction of the ability of diatomite to sorb (or release) PTEs under different pH and redox conditions
- Full interpretation of column leach test and field trial results

To place findings in context, Section 2 of this report outlines the nature of the sorption process, describes pertinent properties of silica, examines the aqueous speciation of arsenic, and briefly reviews the sorption of arsenic by minerals. Following on from this, the results of a number of sorption experiments are summarised and the main findings of preliminary geochemical modelling are presented in Section 3. Sample information and laboratory methods are described in Appendix 1.
2. PREVIOUS STUDIES

2.1. Sorption

Essentially, sorption considers the distribution of a single chemical phase between a solute and a solid (Appelo & Postma, 1994). A distinction is made between adsorption (a surface process) and absorption (an internal process) as shown schematically in Figure 2. Sorption mechanisms include:

- Physical or non-specific adsorption
- Chemical or specific adsorption
- Precipitation
- Co-precipitation
- Ion-exchange
- Diffusion
- Hydrolysis
- Polymerization

Although ion-exchange does not fall within the strict definition of sorption - as a number of ions are considered and notions of competition also apply - for practical reasons ion-exchange is usually considered alongside other sorption reactions.

If the chemical species involved in adsorption is an ion, the term adion is used. Adsorption of an adion by functional groups on the surface of a solid is termed surface complexation. In aqueous geochemistry, any study of sorption also needs to consider the chemistry/speciation of aqueous phases and also the solubility behaviour of minerals. A number of software packages have been developed to model the distribution of aqueous species in geochemical fluids, e.g. PHREEQE, EQ3/6 etc. However, these geochemical models often do not incorporate codes for surface complexation reactions (Davis & Kent, 1990).

Physical or non-specific adsorption is usually recognised from the following characteristics (Parks, 1990):

- Sorption does not involve the formation of a chemical bond
- Sorption is essentially non-selective and mainly relates to the surface charge of the solid
- Sorption is governed by a pH-dependent electrostatic (coloumbic) attraction between the adion and the solid surface
- Adions only sorb when the solid surface is of opposite charge
- Sorption is low when the surface of the solid is neutral
- Adions are fixed within the diffuse layer forming outer-sphere complexes
- Adions involved usually do not hydrolyze significantly and do not form strong complexes in solution, e.g. Na, K, NO3 and ClO4

Chemical or specific adsorption is usually recognised from the following characteristics (Parks, 1990):

- Sorption does involve the formation of a chemical bond
- Sorption is specific and non-coloumbic
- Sorption is insensitive to surface charge and pH
Adions may sorb onto a solid surface of like charge
Adions may sorb when surface of solid is neutral
Adions are fixed within the Stern layer forming inner-sphere complexes
Adions involved are usually multivalent, hydrolyze well and form strong aqueous complexes

2.2. Sorption and minerals

All solid surfaces can act as sorbents. For a given geological material, sorption capacity is particularly influenced by (Appelo & Postma, 1994):

- Specific surface
- Particle-size, especially <2 μm content
- Clay mineralogy
- Free iron, manganese and aluminium oxide/hydroxide content
- Organic matter content

The surface charge of many oxide, silicate and aluminosilicate minerals (goethite, hematite, pyrolusite, gibbsite, quartz, kaolinite etc.) is derived from ionization of \(-\text{SOH}\) surface functional groups (Parks, 1990). The degree of ionization and the magnitude of the resulting surface charge is dependent on pH. Protonation of functional groups with decreasing pH proceeds as follows (Appelo & Postma, 1994):

\[
\equiv \text{SO}^- + 2\text{H}^+ \leftrightarrow \equiv \text{SOH} + \text{H}^+ \leftrightarrow \equiv \text{SOH}_2^+ 
\]

However, the surface charge of certain clay minerals (e.g. smectite, vermiculite and illite) is also partially derived from a structural charge deficit. Some typical cation exchange capacities (CECs) for minerals are listed in Table 1. Organic matter, vermiculite, smectite and iron and aluminium oxides have particularly large CECs.

In considering physical adsorption onto mineral surfaces, the concept of point of zero charge (PZC) is critical. Mineral surfaces are negatively-charged above their PZC and positively-charged below their PZC. Some example PZC values for minerals are listed in Table 2. Those minerals with a high PZC (e.g. calcite, hematite and goethite) act as anion exchangers over a large part of the pH range. Conversely, those minerals with a low pH of PZC (e.g. quartz) act as cation exchangers over a large part of the pH range. According to Iler (1979) and James & Parks (1982), amorphous silica surfaces are negatively-charged even at low pH and therefore will not exhibit a PZC.

As an example of the dependency of physical adsorption on pH and PZC, the uptake of Na and Cl onto the surface of tin oxide (PZC = 4.8) is shown in Figure 3. Above pH 4.8 the surface of the tin oxide is negatively-charged and Na cations are sorbed, while below pH 4.8 the surface of the tin oxide is positively-charged and the Cl anions are sorbed instead.

The sorption capacity of minerals in terms of the calculated density of surface functional groups is provided in Table 3. The densities of functional groups able to complex with anions (proton acceptor sites) and those functional groups able to complex with cations (proton donor sites) are also listed in Table 3. Davis & Kent (1990) suggest that amorphous silica lacks proton acceptor groups and is therefore unlikely to be able to sequester anions.
2.3. Properties of silica

Diatomite consists primarily of amorphous, hydrated opal silica of composition SiO$_2$.nH$_2$O, where n is between 0.5 and 2. In a recent review of natural forms of silica, Smith (1998) classed diatomaceous silica as opal-AN. This type of opal consists of a poorly-ordered, network-like arrangement of SiO$_4$ tetrahedra and silanol (Si-OH) groups.

Silica surfaces in contact with water exhibit a pH-dependent surface charge (Dove & Rimstidt, 1994). Silanol (>SiOH) groups are the predominant functional group on silica surfaces. An idealised triple-layer schematic of the surface interface between quartz and a saline fluid is shown in Figure 4.

Quartz is increasingly soluble above its PZC (pH 2); aqueous monomers and dimers form by dissolution as follows:

\[
\text{SiO}_2 (s) + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 (aq) \\
2\text{H}_4\text{SiO}_4 (aq) \rightarrow \text{H}_6\text{Si}_2\text{O}_7 (aq) + \text{H}_2\text{O}
\]

Amorphous silica is known to up to 10 times more soluble than quartz. The presence of aqueous aluminium and iron generally inhibits silica dissolution. Silica also acts as a buffer under alkaline conditions:

\[
\text{SiO}_2 (s) + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{SiO}_4^- + \text{H}^+
\]

Another important property of silica surfaces is their ability to bond strongly with iron. Experiments performed by Morris & Fletcher (1987) identified a number of reactions between quartz surfaces and iron. Micron-thick coatings of hydrous ferrous silicate and goethite were either accreted or underwent dissolution, in reducing and oxidising conditions, respectively (see schematic in Figure 5). Iron may also modify the reactivity of silica surfaces.

2.4. Arsenic speciation

According to Bhumbla & Keefer (1994), the mobility of arsenic in water is controlled by

- Speciation
- Redox conditions
- pH
- Biological activity
- Sorption onto solid phases

As (III) (arsenite) is the common soluble form of arsenic under reducing conditions. Forms of arsenite include H$_3$AsO$_3$, H$_2$AsO$_3^-$, HAsO$_3^{2-}$ and AsO$_3^{3-}$ species (Jekel, 1994). Transformations between arsenite and arsenate forms of arsenic are usually chemically- or microbially-mediated (Yan-Chu, 1994). Generally, it is not possible to remove arsenite from water efficiently. Therefore, arsenite is typically removed by firstly oxidising to arsenate, e.g. using permanganate, Cl$_2$/OCl$^-$ or H$_2$O$_2$/Fe$^{2+}$.

Under oxidising conditions, As (V) (arsenate) is the prevalent form of arsenic in acid mine drainage (AMD). Forms of arsenate include H$_3$AsO$_4$, H$_2$AsO$_4^-$, HAsO$_4^{2-}$ and AsO$_4^{3-}$ species (Jekel, 1994). Variation in the abundance of these species with respect to pH is shown schematically in Figure 6. It is evident from
Figure 6 that the charge of arsenate species increases as pH is elevated. On a commercial scale, arsenate has been effectively separated from potable water by a precipitation/coagulation process using Fe$^{3+}$ salts and also by filtration through beds of activated alumina granules (Jekel, 1994).

2.5. Sorption of arsenic by minerals

The effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals was examined by Frost & Griffin (1977). Uptake of arsenate by montmorillonite and kaolinite increased as pH was lowered with maximum adsorption around pH 5.

Xu et al. (1988) measured the adsorption of arsenate by hematite, kaolinite, quartz and alumina, as a function of pH and arsenic concentration (see Figure 7). Uptake of arsenate was by a pH-dependent coloumbic attraction consistent with physical adsorption. For hematite, kaolinite and alumina, adsorption was at a maximum under weakly-acidic conditions (pH 4-6) below their PZC. The drop in adsorption of arsenic below pH 4 was attributed to increasing speciation of arsenate as neutral H$^+_3$AsO$_4$ and the dissolution of iron and aluminium from the surfaces of mineral substrates. Possible complexation/precipitation of arsenate with dissolved aluminium and iron was also discussed. The negligible adsorption of arsenate by quartz was attributed to the negative surface charge of this mineral due to its low PZC (pH 2).

Prasad (1994) examined controls on the removal of arsenate from aqueous systems by hematite and feldspar adsorbents. The antipathetic trend between removal of arsenate and pH suggested a process based on electrostatic attraction. The amount of arsenate removed was at a maximum at pH 4.2 for hematite and at pH 6.2 for feldspar. Results obtained were consistent with physical adsorption of arsenate onto mineral surfaces in the form of weakly-bonded, outer-sphere complexes, analogous to the selenate complexes identified on the surface of goethite by EXAFS. Dissolution of minerals was thought to be responsible for the marked decrease in arsenate adsorption exhibited by both minerals at very low pH.

Generally, the mobility of arsenic in soils is governed by the presence of aluminium and iron oxides. Iron oxides and hydroxides strongly adsorb arsenic (Leckie et al., 1980) and act as a major sink for arsenic in aerobic soils (Bhumbla & Keefer, 1994). Arsenic is also adsorbed by manganese oxides (Oscarson et al., 1983) and aluminium oxides (Gupta & Chen, 1978). In weathered sulphide-rich soils, arsenic can also co-precipitate with jarosite and natrojarosite (Bhumbla & Keefer, 1994) and aluminium, manganese and iron oxides (Moore et al., 1988).

3. RESULTS AND DISCUSSION

3.1. Arsenate jar tests

A summary of the results obtained from the arsenate jar tests are listed in Table 4. Of the 14 samples examined, it is evident that the three “high quality” diatomite samples from Section No 2 (D025), Section No 4 (D030) and Section No 6 (D034) exhibit the lowest sorption capacity for arsenate (114-180 mg/kg). Opal-AN predominates in these three samples (63-73%) which are only moderately clayey (27-28% clay minerals) and low in free iron oxide (<2%).

To examine the influence of the mineralogy of the 14 diatomite samples on sorption, arsenate sorption capacity values from Table 4 were plotted against opal-AN content, clay mineral content, cation exchange capacity (CEC) and free iron oxide in Figures 8-11, respectively. Antipathetic trends are evident between
arsenate sorption and both opal-AN and clay mineral content, suggesting that these phases act as diluents and are not involved in sorption of arsenate. No clear relationship is apparent between arsenate sorption and CEC, implying that cation exchange is not a sorption mechanism. This is not surprising given the anionic speciation of arsenate. Norimoto & Osamu (1982) also reported no correlation between arsenic sorption and CEC.

There is a correlation between free iron oxide and arsenate sorption capacity. This suggests that iron oxide present in the diatomite (goethite) is acting as a sorbent for arsenate. Previously, Jacobs (1970) also found that adsorption of arsenic correlated with free iron oxide content. Arsenic sorbed by iron oxide is likely to be released under anaerobic conditions (Fordham & Norrish, 1979).

3.2. Silica dissolution experiments

Mitchell & Atkinson (1993) proposed precipitation with dissolved silica as a mechanism for arsenic sorption. Therefore, a simple indicator test was carried out to measure the dissolution of silica with respect to pH for diatomite samples D027, D034 and BD1. Results obtained are plotted in Figure 12. It is evident that, for all three diatomite samples, very little silica enters solution below pH 4. However, the solubility of silica does increase markedly between pH 4 and 12. These results are generally in accord with the published data.

3.3. Zeta potential

Zeta potential is a measure of the electrostatic charge which exists at the solid-liquid interface. It is the magnitude and polarity of this electric charge which controls the physical adsorption of adions onto the surface of a solid. Graphs of zeta potential vs. pH for the three diatomite samples are plotted in Figure 13. For all three samples, results indicate that diatomite surfaces possess a net negative electrostatic charge from pH 1 to 12. Although the magnitude of zeta potential decreases as pH is lowered, it does not fall to zero and the PZC is not reached. The negative zeta potential values obtained confirm that proton donator sites are prevalent, regardless of pH. It is concluded that physical adsorption of arsenate onto the surface of diatomite is unlikely as both arsenate ions and zeta potential are of like charge between pH 1-12.

3.4. Arsenate sorption isotherm

The sorption of arsenate by sample D027 is plotted as a Langmuir isotherm in Figure 14. The correlation coefficient of 0.98 obtained for this straight line plot indicates that the sorption process closely-matches the Langmuir equation. Luo et al. (1991) and Livesey & Huang (1981) also found that arsenate adsorption by soils followed the Langmuir model. A close approximation to ideal Langmuir behaviour is consistent with sorption of arsenate involving a single type of surface functional group (Parks, 1990). From the Langmuir equation, an arsenate adsorption capacity (Qmax) of 0.23 mg/g and an energy of adsorption (b) of 0.6988 L/mg were derived for sample D027.

3.5. Arsenate sorption vs. pH

The influence of pH on the sorption of arsenate by diatomite sample D027 was also measured (Figure 15). Sorption of arsenate increases as pH is lowered from pH 6 and pH 2. This type of pH-dependent response is considered typical of a physical adsorption mechanism. Usually, the adsorption of arsenate onto minerals is at a maximum under slightly acid conditions and decreases at very low pH due to an increase in speciation of arsenate as neutral H3AsO4 and the dissolution of mineral substrates. However, the increased sorption of arsenate at pH 2 observed in these
experiments may due to either complexation or precipitation of arsenate with dissolved aluminium and iron, as discussed by Xu et al. (1988).

3.6. Preliminary geochemical modelling

The model EQ3/6 was used to obtain generic information on how diatomite was likely to interact with an arsenic-bearing fluid. EQ3/6 is a useful tool for prediction of the aqueous speciation of arsenic and the likely dissolution and precipitation of minerals. The EQ3/6 simulations were performed for an oxidising environment in which both redox and partial pressure of CO2 were assumed to be in equilibrium with the atmosphere. Because carbonate has been implicated as a key phase involved in arsenic sorption (Mitchell, 1991), EQ3/6 simulations were carried out for: (1) an “amorphous silica” composition; and (2) an “amorphous silica + calcite” composition. For all EQ3/6 simulations, fluid composition was that of Ron Phibun mine waste leachate (see Whithbread-Abrutat et. al., 1999b).

The speciation and dissolution/precipitation outputs for “amorphous silica” obtained from EQ3/6 are shown graphically in Figures 15 and 16. For the “amorphous silica” simulation, the H2AsO4− form of arsenate predominated in the solute although the subordinate H3AsO4 form did increase during the simulation. The “amorphous silica” simulation also predicted that oxidising conditions would promote the dissolution of iron and manganese oxides (hematite, pyrolusite) and precipitation of smectite (Ca-nontronite).

The speciation and dissolution/precipitation outputs for “amorphous silica + calcite” obtained from EQ3/6 are shown graphically in Figures 17 and 18. For the “amorphous silica + calcite” simulation, the presence of carbonate raised pH as the simulation progressed. The significant changes in arsenate speciation during the course of the EQ3/6 simulation reflect this pH transition. The “amorphous silica + calcite” simulation also predicted that saturation conditions would allow dissolution of iron oxide (hematite) and precipitation of gypsum, clay minerals (Ca-nontronite, kaolinite, illite), zeolite (scolecite), copper oxide (tenorite) and arsenic-bearing phases (Zn3[AsO4]2).

4. CONCLUSIONS

• Diatomaceous silica (also known as opal-AN) is the principal constituent of diatomite. Diatomite appears to function by providing an inert, rigid substrate for other mineral phases involved in the sorption of arsenic.

• Diatomaceous silica was not directly implicated in the sorption of arsenic. An antipathetic trend was observed between arsenate sorption and the opal-AN content of samples. Opal-AN also possesses a negative surface potential between pH 12 and 1 which precludes the physical adsorption of negatively-charged arsenate species. Under acid conditions, co-precipitation of arsenic with silica is also considered unlikely as it was demonstrated that the solubility of opal-AN is minimal below pH 4.

• There is some evidence that arsenate undergoes physical adsorption onto iron oxide coatings bonded to the opal-AN substrate. Uptake of arsenate correlates with the iron oxide content of samples and also exhibits a pH-dependency characteristic of physical adsorption.

• The sorption of arsenate by iron oxide involves electrostatic attraction and the formation of weakly-bonded, outer-sphere complexes. Arsenate adsorbed onto iron oxide will be re-mobilised under anaerobic conditions. The iron oxide
content of the diatomite may also initiate co-precipitation of arsenic by raising iron concentration of the solute above saturation.

- For diatomite sample D027, used in the project's field trials, the sorption of arsenate closely matched the Langmuir isotherm. This behaviour suggests that the sorption of arsenate involves a single type of surface functional group. From the Langmuir equation, an adsorption capacity for arsenate of 0.23 mg/g was derived for sample D027.

5. RECOMMENDATIONS FOR FURTHER WORK

It is recommended that further studies to examine the use of industrial minerals in the treatment of contaminated land adopt the following approach:

1. Development of a surface complexation model. This would involve characterisation of mineral surfaces, sorption experiments and spectroscopic studies (e.g. EXAFS) to establish sorption mechanism(s) between surface functional groups and potentially toxic elements (PTEs).

2. Geochemical modelling. The surface complexation model developed should be incorporated within a geochemical thermodynamic database of aqueous species, complexes and mineral solubilities (e.g. EQ3/6 or PHREEQE). This would enable a realistic simulation of the interactions between industrial minerals and mine waste fluids.

3. Validation of the model. The validity of the surface complexation model should be tested by comparison of the results obtained from geochemical simulations with those from laboratory column leach experiments and/or field trials in which industrial minerals have been added to metalliferous waste.

Development of surface complexation models for industrial minerals used to treat contaminated land would complement other research on mine waste hazards currently being funded by DFID under the KAR programme, e.g. Environmental arsenic exposure: health risks and geochemical solutions (Project R6491), Cost-effective evaluation of hazards from mine waste (R7118).

6. REFERENCES


APPENDIX 1: SAMPLES AND LABORATORY METHODS

A1.1. Materials

A suite of 14 diatomite samples was collected from the Lampang Basin, Changwat, Lampang, northern Thailand (see Inglethorpe et al., 1998). The chemistry, mineralogy and petrology of these samples was described by Inglethorpe & Pearce (1999). Initially, a simple indicator test was carried out to measure the sorption capacity of these 14 diatomite samples for Arsenate (see Sections 3.1. and A1.2). On the basis of the results obtained, two of these 14 samples were then selected for further investigation: sample D027, a "low quality" diatomite from Section No 3,
5.80 m; and sample D034, a "high quality" diatomite from Section No 6, 1.99 m. The mineralogy of these two samples is summarised in Table 5. In addition, for comparison purposes, an "XRD pure" diatomite from Burney, Lake Britton, Shasta County, California (BD1) was also examined. This sample contains around 91 % amorphous SiO2.

A1.2. Arsenate jar tests

A simple indicator test was carried out to measure arsenate sorption by diatomite. 1 g of diatomite (<150 mesh) was shaken for 12 days in an end-over-end shaker with 50 ml of 10 mg/l Arsenate solution. After 12 days had elapsed the solute was filtered through a nitrocellulose filter of 0.45 μm pore size and analysed for arsenic by graphite furnace atomic absorption spectrophotometry. For each sample, four replicate tests were carried out and the results obtained averaged. Result are reported both in terms of mg of arsenic sorbed per kg of solid and as percentage arsenic removed from solution.

A1.3. Silica dissolution experiments

A simple indicator test was carried out to measure the solubility of diatomaceous silica with respect to pH. 0.5 g portions of diatomite (<150 mesh) were shaken with the following six 50 ml buffer solutions: pH 2.01 (K, Cl buffer), pH 4.03 (K, Na, phthalate buffer), pH 6.13 (K, Na, phthalate buffer), pH 8.10 (K, Na, phosphate buffer), pH 10.55 (K, Na, phosphate buffer) and pH 12.20 (K, Cl, borate buffer). Dissolved silica was then determined by inductively-coupled plasma optical emission spectrophotometry.

A1.4. Zeta potential

A small amount of each sample was wetted by stirring with approximately 5 ml of deionised water. Each sample was dispersed by adding 150 ml of surfactant solution and placing in an ultrasonic bath for 5 minutes. Zeta potential was then measured at whole pH unit increments between pH 1 and pH 12 using a Malvern Instruments Zetasizer. Initially, pH was adjusted to pH 1 using 1 M HCl solution. Subsequent pH adjustment was carried out using either 1 M or 0.01 M NaOH solution. At each pH increment, three replicate zeta potential measurements were carried out and averaged.

A1.5. Arsenate sorption isotherm

A number of solutions were prepared containing 1, 3, 6, 12, 15 and 18 mg/l arsenate solution. For each arsenate concentration, 1 g of diatomite (<150 mesh) was shaken for 12 days in an end-over-end shaker with 50 ml of solution. After 12 days had elapsed the solute was filtered through a nitrocellulose filter of 0.45 μm pore size and analysed for arsenic by graphite furnace atomic absorption spectrophotometry. For each sample, duplicate tests were carried out and the results obtained averaged.

The Langmuir equation describes the theoretical adsorption of a phase onto a solid surface:

\[
\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b}\right) + \left(\frac{C_e}{Q^0}\right)
\]

Where

\(C_e = \) equilibrium concentration of arsenate in solution (mg/L)
\(q_e = \) amount of arsenate adsorbed by the solid at equilibrium (mg/g)
Q° = adsorption capacity of diatomite for Arsenate (mg/g)

b = energy of the adsorption process (L/mg)

To examine whether results obtained closely-matched the Langmuir isotherm, a graph of \( C_e \) vs. \( C_e/Q° \) was plotted. Values of \( Q° \) and \( b \) were then derived from the slope of this graph and the Y-axis intercept.

A1.6. Arsenate sorption vs. pH

Three batches of 10 mg/l arsenate solutions were prepared and their pH adjusted to pH 2.13, 4.18 and 6.40, respectively, with dilute sulphuric acid. For each pH solution, 1 g of diatomite (<150 mesh) was shaken for 12 days in an end-over-end shaker with 50 ml of 10 mg/l arsenate solution. After 12 days had elapsed the solute was filtered through a nitrocellulose filter of 0.45 μm pore size and analysed for arsenic by graphite furnace atomic absorption spectrophotometry. For each sample, duplicate tests were carried out and the results obtained averaged. Result are reported both in terms of mg of arsenic sorbed per kg of solid and as percentage arsenic removed from solution.

A1.7. Geochemical modelling

EQ3/6 is a set of computer codes and associated databases for use in modelling the complex geochemical processes that occur when aqueous solutions (e.g. groundwaters, saline waters, effluent streams) react with soil, rock, or solid waste materials. Some of the processes of interest that can be modelled using EQ3/6 include mineral dissolution, mineral precipitation, wasteform leaching, and incorporation of heavy metals and other inorganic toxic components into secondary minerals. The software allows the user to create and evaluate models that include the effects of chemical equilibrium, disequilibrium, and kinetics. The software can handle both dilute waters and high-ionic-strength brines. The database is the most comprehensive of its kind, and includes data for both inorganic and organic species of interest.

EQ3/6 was originally developed to model rock/water interactions in hydrothermal and geothermal systems over the temperature range of 0 to 300 degrees Celsius. The software later underwent extensive further development for use in modelling geochemical processes pertinent to the geologic disposal of high-level nuclear waste. EQ3/6 can also be applied to waste treatment, assessment of contaminated sites, assessment of the effects of natural remediation processes, and the design and assessment of engineered remediation processes.
Table 1. Cation exchange capacity (CEC) values for selected minerals and organic matter (Appelo & Postma, 1990).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halloysite</td>
<td>5-10</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3-15</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10-40</td>
</tr>
<tr>
<td>Glaucnite</td>
<td>5-40</td>
</tr>
<tr>
<td>Illite</td>
<td>20-50</td>
</tr>
<tr>
<td>Goethite, Hematite, Allophane</td>
<td>up to 100</td>
</tr>
<tr>
<td>Smectite (montmorillonite)</td>
<td>80-120</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>100-200</td>
</tr>
<tr>
<td>Organic matter</td>
<td>150-400</td>
</tr>
</tbody>
</table>

Table 2. The pH of point of zero charge (PZC) for selected mineral phases (Appelo & Postma, 1990).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>9.5</td>
</tr>
<tr>
<td>Corundum</td>
<td>9.1</td>
</tr>
<tr>
<td>Hematite</td>
<td>8.5</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>7.6</td>
</tr>
<tr>
<td>Goethite</td>
<td>7.3</td>
</tr>
<tr>
<td>Rutile</td>
<td>5.8</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>5.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>4.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 3. The calculated density of surface functional groups for selected minerals (Davis & Kent, 1990).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Total site density (sites/nm²)</th>
<th>Below PZC</th>
<th>Above PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Proton acceptor groups able to complex anions (sites/nm²)</td>
<td>Proton donor groups able to complex cations (sites/nm²)</td>
</tr>
<tr>
<td>Hematite</td>
<td>5-22</td>
<td>Not available</td>
<td>Not available</td>
</tr>
<tr>
<td>Goethite</td>
<td>2.6-16.8</td>
<td>4.4</td>
<td>6.7</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.2</td>
<td>2.6</td>
<td>4.2</td>
</tr>
<tr>
<td>Amorphous Silica</td>
<td>4.5-12</td>
<td>None</td>
<td>All</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>2-12</td>
<td>2.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.3-3.4</td>
<td>0.35</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 4. Results of arsenate jar tests.

<table>
<thead>
<tr>
<th>Section (A)</th>
<th>Arsenate sorption (mg/kg)</th>
<th>(B) Arsenate sorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D022, 8.09 m</td>
<td>441</td>
<td>90.15</td>
</tr>
<tr>
<td>D023, 5.59 m</td>
<td>366</td>
<td>74.74</td>
</tr>
<tr>
<td>D024, 3.09 m</td>
<td>478</td>
<td>97.47</td>
</tr>
<tr>
<td>D025, 1.49 m</td>
<td>180</td>
<td>36.73</td>
</tr>
<tr>
<td>D026, 0.28 m</td>
<td>376</td>
<td>76.79</td>
</tr>
<tr>
<td>D027, 5.80 m</td>
<td>440</td>
<td>90.26</td>
</tr>
<tr>
<td>D028, 4.85 m</td>
<td>290</td>
<td>59.18</td>
</tr>
<tr>
<td>D029, 4.40 m</td>
<td>300</td>
<td>43.96</td>
</tr>
<tr>
<td>D030, 4.15 m</td>
<td>114</td>
<td>25.00</td>
</tr>
<tr>
<td>D031, 6.55 m</td>
<td>447</td>
<td>97.99</td>
</tr>
<tr>
<td>D032, 3.00 m</td>
<td>219</td>
<td>48.08</td>
</tr>
<tr>
<td>D033, 3.30 m</td>
<td>321</td>
<td>70.60</td>
</tr>
<tr>
<td>D034, 1.99 m</td>
<td>127</td>
<td>28.02</td>
</tr>
<tr>
<td>D035, 2.62 m</td>
<td>178</td>
<td>39.01</td>
</tr>
</tbody>
</table>

Table 5. Mineralogy of two diatomite samples examined from the Lampang Basin, Changwat Lampang, northern Thailand. Note that data are estimates.

<table>
<thead>
<tr>
<th>Estimated mineralogy</th>
<th>&quot;Low quality&quot; diatomite D027, Section (3), 5.80 m</th>
<th>&quot;High quality&quot; diatomite D034, Section (6), 1.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opal-AN (%)</td>
<td>53</td>
<td>63</td>
</tr>
<tr>
<td>Quartz (%)</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Smectite (%)</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>Illite (%)</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Kaolinite (%)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Total clay minerals (%)</td>
<td>38</td>
<td>27</td>
</tr>
<tr>
<td>Free Fe2O3 (%)</td>
<td>8</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Total (%)</td>
<td>113</td>
<td>104</td>
</tr>
</tbody>
</table>
Figure 1. Removal of potentially toxic elements (PTEs) from solution by diatomite, as proposed by Mitchell (1991).
Figure 2. Summary of the three main types of sorption process.
Figure 3. pH-dependent physical adsorption of Cl (solid line) and Na (dashed line) onto the surface of tin oxide (PZC = 4.8) (after Apollo & Postma, 1994).
Figure 4. Idealised schematic of a triple-layer model of the surface of quartz in contact with a saline fluid.
In groundwater, ferrous iron reacts with surface of a silica particle to form a microlayer of hydrous ferrous silicate.

Dissolution of silica and iron as ferric hydroxyoxide and H4SiO4

New layer of goethite forms

H4SiO4

Oxidising Conditions

Reducing Conditions

FeO.OH

New goethite precursor layer forms

Figure 5. Reactions between iron and silica surfaces (after Morris & Fletcher, 1987).
Figure 6. Schematic representation of the variation in the abundance of arsenate species with respect to pH.
Figure 7. Adsorption of As(V) onto kaolinite (solid line), hematite (long dashes) and quartz (short dashes) as a function of pH (after Xu et al., 1988).
Figure 8. Plot of As (V) sorption by diatomite vs. opal-AN (diatomaceous silica) content.

Figure 9. Plot of As (V) sorption by diatomite vs. clay mineral content.
Figure 10. Plot of As (V) sorption by diatomite vs. cation exchange capacity (CEC).

Figure 11. Plot of As (V) sorption by diatomite vs. free Fe₂O₃ content.
Figure 12. Solubility of silica vs. pH for three diatomite samples.

Figure 13. Zeta potential vs. pH for three diatomite samples.
Figure 14. Langmuir isotherm for sorption of As (V) by diatomite sample D027.

Figure 15. Sorption of As (V) by diatomite sample D027 vs. pH.
Figure 16. EQ3/6 speciation output for “amorphous silica” in contact with Ron Phibun mine waste leachate.

Figure 17. EQ3/6 dissolution/precipitation output for “amorphous silica” in contact with Ron Phibun mine waste leachate.
Figure 18. EQ3/6 speciation output for “amorphous silica + calcite” in contact with Ron Phibun mine waste leachate.

Figure 19. EQ3/6 dissolution/precipitation output for “amorphous silica + calcite” in contact with Ron Phibun mine waste leachate.