TREATMENT OF CONTAMINATED LAND USING DIATOMITE: PROJECT SUMMARY REPORT

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Technical Report, March 1999
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Cover plate:
Left: Investigating diatomite deposits in Lampang Province, northern Thailand
Centre left: Collecting porewater samples from contaminated soil – diatomite field plots, Ron Phibun, Nakhon Si Thammarat Province, southern Thailand
Centre right: SEM photomicrograph of whole diatoms and coarse fragments enclosed in an illitic clay matrix. Sample SDJ1424 (D025S2/01)
Right: Mine waste – diatomite column leaching experiments set-up in DMR laboratories, Bangkok
EXECUTIVE SUMMARY

This Summary Report describes the outcome of project R6488 entitled “Treatment of contaminated land using diatomite”, funded by the British Department for International Development (DFID) under their Knowledge and Research (KAR) programme. This project involved collaboration between the Camborne School of Mines (CSM), the British Geological Survey (BGS) and the Thai Department of Mineral Resources (DMR) over a three-year period from April 1996 to March 1999. Other related DFID-KAR projects include the “Environmental impact of gold and complex sulphide mining”, (project number: R5553) and “Cost effective evaluation of potential hazards from metalliferous mine wastes”, (project number: R7118). In particular, the project examined the potential of diatomite (an industrial mineral) from Lampang Province, northern Thailand, for treatment of As-contaminated soil in the Ron Phibun District of Nakhon Si Thammarat Province, southern Thailand. Diatomite is a pale-coloured, soft, light-weight rock composed principally of the silica fossil remains of aquatic, unicellular algae known as diatoms. The main findings of the project are:

1. An inventory of diatomite deposits in the Lampang Basin, Changwat Lampang, northern Thailand was compiled. Sedimentary features observed in the field (clay content, Fe-staining, discrete clay beds, bedding lamination, clay- and Fe-filled burrows etc.) are responsible for marked variations in physical and chemical properties. Because of this heterogeneity, it was possible to classify intervals within the diatomite sequence as either “high quality” or “low quality” on the basis of defined physical and chemical criteria. From the inventory, a generic protocol for the field examination of diatomite deposits was developed. This approach could be adopted by Geological Surveys or Mines Departments in other countries for preliminary classification of their diatomite resources.

2. Mineralogical analysis of 14 diatomite samples collected from Changwat Lampang during the field inventory identified diatomaceous silica (Opal AN), quartz, goethite and clay minerals (smectite, kaolinite and illite) as the major constituents present. Three types of rock fabric were distinguished from petrographic analysis of these samples: (a) predominant well-preserved, whole diatoms, infrequently present as strand-like colonies, within a finely-comminuted matrix of diatom fragments; (b) alternating laminae of whole diatoms / diatom fragments and Fe-stained, K-rich clayey, irregular layers containing Fe- and/or Ti-oxide inclusions; and (c) finely-comminuted diatom fragments within a pervasive clay-rich matrix.

3. Laboratory sorption studies indicated that diatomite from the Lampang Basin, northern Thailand, provides an inert, rigid Opal AN substrate of high specific surface. It is probable that As (V) undergoes sorption onto Fe coatings bonded to this Opal AN substrate. Under certain conditions, the high Fe content of the diatomite may also initiate co-precipitation of As (V) by raising solute Fe concentration above saturation. For one sample examined, in the absence of competition, the sorption capacity of diatomite for As (V) was circa 224 mg/kg.

4. Approximately 42 solid and 24 water samples were collected from three mining areas in southern Thailand. These were subjected to detailed geochemical and mineralogical analysis to determine the nature of the arsenic and PTE contamination within them. The mine wastes from the three areas exhibited widely different geochemical and mineralogical characteristics. The Ron Phibun wastes (from Nakhon Si Thammarat Province) consisted of acidic waste rock with “hot-spots” of >1% arsenic and elevated concentrations of other PTEs. The To Mo mine wastes (from Narathiwat Province) consisted of almost pure silica sand with high concentrations of water soluble As. The Na Sua – Tham Thalu mine wastes (from Yala Province) consisted of highly sulphidic tailings currently generating acid rock drainage. Arsenic and other potentially toxic element (PTE) concentrations were high in both the wastes and the waters emanating from them. A field site near the village of Ron Phibun was chosen provisionally as the site for the long term field trials, however, owing to a change of DMR-policy towards the
disposal of As-rich mine wastes, this site was subsequently cleared. A second site was
chosen for the field trials after negotiations with DMR and local authorities in Ron
Phibun.

5. Results of column leaching experiments indicated that the addition of 10% by weight of
diatomite to contaminated mine wastes (from Ron Phibun and Pin Yo, Yala Province)
was capable of reducing the concentrations of As and other PTEs in column leachates.
In the Ron Phibun mine waste (the most contaminated), As was reduced by 41%, Cu by
37%, Fe by 38%, Mn by 29% and Zn by 24%. Effects were less marked for the Pin Yo
sample owing to its more weathered nature. Arsenic in the Pin Yo sample was intimately
associated with Fe oxides and hydroxides. Under saturated conditions, this As was
remobilised, even in the diatomite-treated samples, thus corroborating the hypothesis for
the sequestration of As by diatomite as described above.

6. Long term field trials were set-up in Ron Phibun towards the end of the project to
investigate the efficacy of different diatomite addition rates on the porewater chemistry of
a soil contaminated with elevated As, Cd, Mn and Pb concentrations. At the time of
writing, only one month of data is available which indicated no significant differences in
porewater element chemistry between any of the treatments. It is anticipated that
significant differences will emerge as unoxidised sulphides brought to the soil surface
during the preparation of the field trials begin to weather, mobilising the PTEs contained
within them.

7. A generic protocol was developed for examining the potential of industrial minerals as
amendments to contaminated soil.

The main recommendation arising from the project is that there is scope to examine a wider
range of industrial minerals as amendments to contaminated soil. This is warranted because
of the following factors:

1. The acute hazard posed to human populations by As and other PTEs in developing
countries, such as the well-documented water contamination crisis in Bangladesh
2. The need to achieve a lasting, positive development impact by progressing further the
existing findings
3. The desirability of continuing the strong institutional and professional links forged under
the current project
4. The success of the existing project partnership and its proven ability to deliver outputs
5. A further visit to Thailand in 99/00 to aid in the thorough interpretation of column-leach
and field trials data, and to help in the decommissioning of the former, would result in two
further reports and publications based on these data

It is the intention of CSM and BGS to pursue this matter through the next round of the DFID-
KAR programme.
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INTRODUCTION

Metalliferous mines are commonly associated with elevated concentrations of potentially toxic elements (PTEs) in both the wastes that they produce and in the soils surrounding them. PTEs are elements that may or may not be beneficial to organisms at very low concentrations, but are toxic at relatively low concentrations. The term "PTE" can include a variety of otherwise unrelated elements and is less etymologically ambiguous than the older term "heavy metal”. For the purposes of this report, the term PTE refers to the elements As, Cd, Cu, Mn, Pb and Zn, although Al, Ca, Fe, K and Mg were also investigated.

Tin mining and processing wastes in the vicinity of Ron Phibun village, Nakhon Si Thammarat Province, southern Thailand, are known to be enriched in As and other PTEs. This, coupled with the documented chronic arsenic-related health problems of the Ron Phibun area and the existence of nationally available diatomite deposits in northern Thailand, provided an opportunity to develop a long-term research programme into the novel aspect of ameliorating As-contaminated land with diatomite.

Camborne School of Mines (CSM), University of Exeter, has been at the forefront of research into reducing the environmental impact of mining and beneficiation wastes for over a decade. The main thrust of this research has been in the novel field of applying industrial minerals to contaminated land in order to reduce the PTE-availability. A variety of industrial minerals are potentially useful for this purpose and diatomite has been identified as one of the most promising. The British Geological Survey (BGS) possesses world-renowned expertise in the field of industrial minerals geology and state-of-the-art laboratory facilities.

Diatomite (also known as diatomaceous earth and kieselguhr) is a naturally occurring form of biogenic silica produced by phytoplanktonic organisms. It occurs as economically viable geological deposits in many parts of the world. Its primary commercial uses are as an industrial mineral, primarily as a filter aid in beer and wine processing and for clarifying edible oils. To a lesser extent, it is also used as a filler in paper, paint and plastics production, as an absorbent and as an abrasive. Competition from other industrial minerals has caused a decline in the importance of diatomite in its traditional fields, but potential new markets are now developing, particularly in the biotechnology and hazardous waste treatment industries.

This report is the final output from a three-year collaborative project entitled “Treatment of contaminated land using diatomite” between CSM, University of Exeter, UK; BGS, UK and the Department of Mineral Resources (DMR) of the Government of Thailand. The work was funded by the Department for International Development (DFID) of the British Government under their Knowledge and Research (KAR) programme (project number: R6488). This report is also intended for use as a non-technical guide to investigating industrial minerals and other potential soil amendments for use in the amelioration of contaminated land. Some related DFID-KAR funded research includes Naden and Bland (1994), Fordyce et al. (1994), Williams and Breward (1995) (all from project number, R5553; "Environmental impact of gold and complex sulphide mining") and Metcalfe et al. (1998; project reference, R7118; "Cost effective evaluation of potential hazards from metalliferous mine wastes").

1.1 Overview and objectives

The three-year work project consisted of six distinct activities:

1. An inventory of diatomite deposits of the Lampang Basin, Changwat Lampang, northern Thailand. An inventory was compiled from a field study in August 1996 of diatomite...

2 A mineralogical and petrographic evaluation of diatomite from the Lampang Basin, Changwat Lampang, northern Thailand. Mineralogical and petrographic properties of diatomite were examined in the laboratory (Inglethorpe et al., 1999a).

3 An investigation of the sorption of arsenic by diatomite. The sorption of arsenic by diatomite was examined in the laboratory to identify the relevant process (or processes) involved (Inglethorpe et al., 1999b).

4 Preliminary field investigations of As-contaminated sites. Extensive sampling of mine sites of known or suspected As-contamination was made in several areas of southern Thailand. The PTE-geochemistry of these samples underwent intensive laboratory analysis. (Whitbread-Abrutat et al., 1997a, b).

5 Column leaching experiments. A diatomite identified from the sorption study was incorporated with contaminated mine wastes in laboratory-based based column leaching experiments (Whitbread-Abrutat et al., 1999a).

6 Preliminary field investigations. Long term field trials were established at Ron Phibun, southern Thailand (Whitbread-Abrutat et al., 1999b).

Each of these six activities is summarised in Section 2 below.

2 PROJECT ACTIVITIES

2.1 Inventory of diatomite deposits

The Lampang Basin is a post-Oligocene, intermontane basin occupying an area of approximately 1000 km². Between 25-28 m of diatomite of the Ko Kha Formation, Mae Moh Group, is underlain by cyclothems of mudstone, oil shale and lignite of the Mae Sot Formation. Overlying are Quaternary-to-Recent fluvial gravels, sands and clays, generally capped by laterite. Dominant Melosira granulata and rare Navicula and Fragilaria diatom species of post-Miocene age indicate a freshwater, eutrophic, stagnant lacustrine environment. Fieldwork was carried out by a team of DMR and BGS geologists in 1996 with the aim of compiling an inventory of diatomite deposits in Changwat Lampang. Detailed lithological logs of major quarry sections were prepared (figure 1). At each quarry, "spot" samples were collected at 0.5 m stratigraphic intervals and larger "laboratory" samples were also collected from the main diatomite beds. Diatomite quality was assessed mainly by physical analysis of the "spot" samples (block density, specific gravity, porosity, moisture content), supplemented by major-element chemical analysis of the larger "laboratory" samples. Results indicate that sedimentary features observed in the field (clay content, Fe-staining, discrete clay beds, bedding lamination, clay- and Fe-filled burrows etc.) are responsible for marked variations in physical and chemical properties. Because of this heterogeneity, it was possible to classify intervals within the diatomite sequence as either "high quality" or "low quality" based on defined physical and chemical criteria.

The main objective of the diatomite inventory was to identify sources of diatomite in Thailand for use in the treatment of contaminated land. However, it is emphasised that the approach to the assessment of diatomite resources outlined in this report is generic and could be adopted by Geological Surveys/Mines Departments in other countries for primary classification of their diatomite deposits.
<table>
<thead>
<tr>
<th>Graphic lithology</th>
<th>Lithological description</th>
<th>Specific gravity</th>
<th>Block density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Moisture content (%)</th>
<th>Munsell colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>DIATOMITE weakly laminated: Off-white to light grey to buff colour. Fe-STAINED strongly</td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td>DIATOMITE weakly laminated. Fe-STAINED</td>
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<tr>
<td>7</td>
<td>DIATOMITE laminated: Off-white to light grey to buff colour. Silty texture. Fe-STAINED strongly</td>
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<tr>
<td>8</td>
<td>DIATOMITE laminated: Off-white to light grey to buff colour. Silty texture. Fe-STAINED</td>
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</tr>
<tr>
<td>9</td>
<td>DIATOMITE laminated: Strongly laminated. Fe-STAINED</td>
<td></td>
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</table>

**Figure 1:** Graphical lithology and results for "section 3" (the accompanying field inventory photograph is displayed on the cover page).

### 2.2 Mineralogical and petrographic evaluation of diatomites

Quantitative mineralogical analysis of 14 diatomite samples collected from Changwat Lampang during the field inventory indicated 32-73% diatomaceous silica (Opal AN), 4-19% quartz, 1-31% goethite (extractable Fe₂O₃ basis) and 4-45% clay minerals (smectite, kaolinite and illite) as the major constituents present. Diatomaceous silica content ("grade") was determined both by chemical dissolution of amorphous silica and an X-ray diffraction (XRD) method. In all samples, chemical dissolution underestimated the proportion of diatomaceous silica relative to XRD. This may be due to incomplete chemical digestion, as Opal AN is at least partially ordered and not truly amorphous.

Three main types of rock fabric were distinguished from petrographic analysis by scanning electron microscopy (SEM) and transmission electron microscopy (TEM):

1. Predominant well-preserved, whole diatoms, infrequently present as strand-like colonies, within a finely-comminuted matrix of diatom fragments (plate 1)
2. Alternating laminae of whole diatoms/diatom fragments and Fe-stained, K-rich clayey, irregular layers containing Fe- and/or Ti-oxide inclusions
3. Finely-comminuted diatom fragments within a pervasive clay-rich matrix
In certain intervals within the diatomite sequence, the presence of rootlet structures (infilled by clay, Fe-oxide and abundant pollen grains and fungal hyphae), desiccation cracks and gypsum suggests periodic emergence from the lake and subaerial exposure of the sediment. In other parts of the diatomite sequence, pervasive Fe-staining and the presence of authigenic silica, sulphate phases (most likely jarosite and melanterite) and patchy zones of kaolinite and gibbsite are strong evidence of deep lateritic weathering.

Plate 1: SEM photomicrograph of abundant, well-preserved diatomite colonies (sample SDJI422 (D024S2/01))

2.3 The sorption of arsenic by diatomite

One of the principal objectives of this project was to establish how diatomite is likely to function as a soil amendment to contaminated land and predict how this mineral will perform under different geochemical regimes. During the course of the project, sorption mechanisms, the structure of diatomaceous silica (Opal AN), surface properties of silica and the sorption of As by minerals were investigated. In particular, a number of experimental findings and the use of a geochemical model (EQ36) are reviewed briefly below.

The sorption of As (V) by diatomite from Lampang Basin is consistent with physisorption by goethite. Experimental evidence indicates that the uptake of As (V) by diatomite correlates with extractable Fe content and exhibits a pH-dependency typical of physisorption. In contrast, the silica phase Opal AN, the principal constituent of diatomite, was not implicated in the sorption of As (V). An antipathetic trend was observed between As (V) sorption and Opal AN content of diatomite. In addition, the negative surface electric potential of Opal AN (indicated by zeta potential measurements between pH 2 to 12) precludes physisorption. Also, under the acidic conditions prevailing, co-precipitation of As (V) with silica is considered unlikely, given that it was demonstrated experimentally that the solubility of Opal AN falls with decreasing pH.

A more generic understanding of the function of diatomite was obtained using the geochemical model EQ36. This model enabled As speciation and the dissolution and precipitation of mineral phases to be predicted. Simulations were carried out for the interaction between amorphous silica and a typical Ron Phibun mine waste fluid composition. The model was run for oxidising conditions with both redox potential and pCO₂ in equilibrium with the atmosphere. Because carbonate minerals have been implicated in As sorption, EQ36 runs were carried out for amorphous silica both in the presence and absence of calcite. For the amorphous silica simulation in the absence of calcite, [H₂AsO₄]⁻ speciation
predominated with subordinate $[\text{H}_2\text{AsO}_4]$ and dissolution of Fe oxide and precipitation of minor smectite predicted. For the amorphous silica simulation in the presence of calcite, a transition in As (V) speciation was observed in response to rising pH. Dissolution of Fe oxide and precipitation of gypsum, minor kaolinite and minor smectite were predicted.

It is concluded that the function of diatomite in the As-sorption process is to provide an inert, rigid Opal AN substrate of high specific surface area. It is probable that As (V) undergoes sorption onto Fe coatings bonded to this Opal AN substrate. Under certain conditions, the high Fe content of the diatomite may also initiate co-precipitation of As (V) by raising solute Fe concentration above saturation. For one sample examined, in the absence of competition, the sorption capacity of diatomite for As (V) was \textit{circa} 224 mg kg$^{-1}$.

2.4 Field investigations of arsenic-contaminated sites

The first stage of this project was to identify As-contaminated sites in Thailand that were suitable for the establishment of long-term field plots involving the application of locally-available diatomite to As-contaminated land.

Samples of mining and processing wastes and the waters in their vicinity were collected from three mining areas of known or suspected As-contamination in southern Thailand. Ron Phibun District, Nakhon Si Thammarat Province has been the focus of much research into the causes of chronic arsenism recorded in the local population. Previous research concerned with As-contamination in Ron Phibun District has focussed primarily on identifying the source of the As-contamination causing the health problems. The second area investigated was To Mo gold-mine in Narathiwat Province on the border with Malaysia. It was known that arsenopyrite is associated with the gold-bearing ore so a potential As-pollution problem around this mine was suspected. The Tham Thalu Subdistrict of Yala Province was the third area investigated. This area contains many lead and tin-mines which have been shown to be the main cause of potentially toxic element input into the Pattani River system (plate 2). The cassiterite from these mines is closely associated with a wide variety of sulphide minerals. On exposure to the atmosphere, these weather to produce acid rock drainage (ARD) containing elevated concentrations of PTEs (often including As). The pH, conductivity and oxidation-reduction potential (ORP) of the water samples were recorded as soon as possible after collection. These samples were later analysed in the laboratory by ICP-AES to determine the concentrations of Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn. The waste samples were first analysed for their As concentrations after a modified \textit{aqua regia} digestion to identify those samples containing less than 1000 μg As g$^{-1}$ which were then excluded from further analyses. Those samples containing above this concentration underwent further analysis, including pH, conductivity and sequential analysis for the above elements. The methodology for the sequential analysis was developed during this project as a generic tool for the analysis of As geochemistry in mine wastes. Selected samples were examined by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) techniques. The two samples containing the highest As concentrations from the Ron Phibun and Na Sua-Tham Thalu sites were subjected to froth flotation and analysed further by XRD and SEM.
Plate 2: The derelict Tham Thalu processing plant showing the opencast mine (background), derelict plant buildings (middleground) and flotation waste impoundment (foreground)

Results from XRD, SEM and sequential extraction analyses indicated that the chemical characteristics of the sites differed considerably with respect to the geochemistry of As (and other PTEs). The two mine sites at Ron Phibun contained elevated As concentrations, despite the removal of the high grade wastes from one site. Cd and Zn were also present at highly elevated concentrations (up to 179 and 2074 µg g⁻¹ respectively). Arsenic was present mainly as weathered arsenopyrite grains exhibiting scorodite rims and was of generally low availability. The To Mo Mine wastes consisted primarily of high purity silica sand. They contained less than 1000 µg As g⁻¹. These wastes showed a low potential for impinging on environmental and human health. The Na Sua and Tham Thalu mine wastes exhibited the typical ARD characteristics of acidic pH values and high concentrations of soluble Fe and PTEs. For example, As concentrations varied widely between 2946 and 14715 µg g⁻¹. The wastes were dominated by pyrrhotite, although one waste pile at Na Sua Mine was enriched in secondary cerussite and anglesite. The waste dumps showed evidence of surface
weathering with a high content of secondary minerals such as gypsum, jarosite and goethite. Both arsenopyrite and pyrite were found in these wastes. The water soluble As concentrations were generally higher in these wastes than for either the Ron Phibun or To Mo wastes. Mine wastes from this area had been implicated previously as a major source of contamination of local soils and surface waters although the effects on groundwaters were negligible.

2.5 Amelioration of acidic leachates from metalliferous mine wastes by diatomite: Column leaching experiments

A series of pilot scale laboratory-based column-leaching experiments were set-up to investigate the effects of different diatomite application rates and drainage regimes on the leachate properties of two different types of mine waste. The main objectives were to: define optimal diatomite application rates for the field trials; investigate the efficacy of diatomite in reducing PTE mobility; compare the efficacy of diatomite in mine wastes of different properties; study the effects of saturation and evaluate the long-term stability of PTE sequestration.

The two mine wastes were intensively characterised by a variety of chemical, physical and mineralogical tests prior to setting-up the column-leaching experiments. These tests included: total element analysis, maximum leachability assay, particle size analysis and chemical analysis of the size fractions, chemical analysis of the heavy mineral components, and mineralogical investigations.

These investigations identified major differences between the two samples. The Ron Phibun waste was a highly complex, heterogeneous mixture of sulphides, silicates and oxides with high total concentrations of As and Cd. A large proportion of the PTEs was also present in highly soluble forms. Evidence of weathering was relatively limited. By contrast, the Pin Yo waste was a relatively simple silica dominated substrate with high concentrations of some PTEs, especially Cu, Mn and Zn. The non-silica mineralogy was dominated by secondary minerals thus indicating a high degree of weathering.

Duplicate sets of column experiments were set-up: one at CSM in the UK and one at DMR in Bangkok (plate 3). The CSM-based experiment was used to test the effects of adding a microbial inhibitor (1 mM sodium dodecyl sulphate) after an eight-month period had elapsed of concurrent results between the CSM- and DMR-based experiments. Each experiment consisted of two kinds of mine waste (Ron Phibun and Pin Yo), three diatomite concentrations (1%, 5% and 10%) and a control (0%), and two drainage regimes (saturated and free-draining). The UK columns were leached monthly for ten months before the experiment was ended. The DMR experiment was intended to be of a longer time scale. Monthly additions of column-specific pore volumes of leachant were applied to each column. The leachant consisted of demineralised water at pH 5.5 to simulate unpolluted rainwater.

Leachates were collected from each column and analysed for: volume collected, pH, conductivity and the concentrations of Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn and Zn. Ron Phibun waste leachate concentrations of Fe and Mn were decreased by 5% diatomite. 10% diatomite decreased the concentrations of Al, As, Ca, Cu, Fe, Mn, and Zn, while increasing the pH and the concentration of Mg. The Pin Yo waste leachate Ca concentration was decreased by 1% diatomite, although Mg concentrations increased; 5% diatomite decreased Ca and Mn concentrations and conductivity, but increased K and Mg. 10% diatomite decreased Pin Yo leachate concentrations of Ca, Mn and Zn concentrations and conductivity, but increased K and Mg concentrations and pH. Increased leachate K and Mg concentrations resulted from the leaching of these elements from the diatomite itself which was enriched in these elements relative to the mine wastes.
Plate 3: The DMR-based column experiment set-up in the Mineral Analysis Division Laboratory, DMR, Bangkok, Thailand, with associated DMR personnel

Saturation decreased PTE concentrations in Ron Phibun leachates and increased pH substantially. However, when interacting with the Pin Yo mine waste, saturation increased leachate concentrations of As, Fe and Mn. This provided independent verification of the hypothesis developed during this project concerning the mechanism of As-sorption by Fe oxides and hydroxides on diatomite particle surfaces (Inglethorpe et al., 1999b).

2.6 Amelioration of arsenic-contaminated soils using diatomite: Field trials set-up

An area of land known to be contaminated with As and other PTEs, adjacent to an abandoned ore-dressing plant in Ron Phibun village, Nakhon Si Thammarat Province, southern Thailand, was chosen as the field site. Before setting-up the experiment, the site was cleared of vegetation and refuse. Twenty 1.5 m × 1.5 m plots were laid out. Each plot was then homogenised by hand to reduce variation in soil chemical and physical properties. The experiment was designed as a fully randomised block with three application rates of diatomite plus a control, each replicated five times. Application rates were calculated from rates previously calculated for the column leaching experiments and adapted to a soil depth of 30 cm (the maximum depth to which diatomite was incorporated). The diatomite was applied by hand at rates (including the corresponding mass applied in each case) of: 0% (control), 2.5% (20.6 kg), 5% (41.2 kg) and 10% (82.5 kg) (plate 4).

Soil samples were taken from each plot before and after the addition of diatomite for subsequent chemical analysis. The samples taken before the addition of diatomite were digested by modified aqua regia and analysed by atomic absorption spectrophotometry to determine the "total" concentration for each element. Both pre- and post-diatomite soil samples were analysed for their water soluble concentrations of As, Cd, Cu, Fe, Mn, Pb and Zn. Samplers were uniquely designed and constructed for use in this project to sample in situ soil porewaters. One soil porewater sampler was installed in the centre of each plot. Soil porewaters were sampled the day after the installation of the porewater samplers.
Plate 4: Incorporation of diatomite into contaminated soil in one of the trial plots during the preparation of the long-term field experiment in Ron Phibun village

The field site was shown to be geochemically heterogeneous with a hot-spot of high PTE concentrations running through the site producing very high PTE concentrations in the corresponding field plots. Statistical comparisons (using the Kruskal-Wallis non-parametric method) showed no significant differences between treatments. These results were mirrored in the analysis of the soil porewaters taken the day after the installation of the samplers. The differences between treatments in soil porewater element concentrations were much less marked than for the soil "total" element results.

To date (March 1999), only one complete set of porewater results has been received. Consequently, it is too early to derive firm conclusions regarding the efficacy of the diatomite application in the field trials. However, the soil porewater sampling technology is a cheap and easy to construct and operate technology that could and should be used more widely for the sampling of soil porewaters, e.g. in agricultural and ecological contexts. Similarly, this design of field experiment is a simple and statistically rigorous means of investigating the actions of a wide variety of soil amendments, including other industrial minerals, fertilisers and organic soil improvers.

3  DISSEMINATION

Two papers based on work done in relation to this project were presented at the International Conference on Stratigraphy and Tectonic Evolution of Southeast Asia and the South Pacific (GEOTHAI '97) held in Bangkok in August 1997, and were published in the conference proceedings (Inglethorpe et al., 1997; Whitbread-Abrutat et al., 1997b). At least two more publications are anticipated from work relating to this project.
As part of the dissemination process, a one day workshop entitled *Industrial minerals and the environment*, was held at DMR in Bangkok on 26 February 1999 (plate 5). The workshop was attended by 87 delegates from a variety of countries, namely Belgium, Hong Kong, Japan, UK and Thailand, and covering a wide range of expertise and institutions (see the *Industrial minerals and the environment* proceedings for a list of delegates).

The workshop was officially opened by Mr. Nopadon Mantajit, the Director General of DMR. The morning session was devoted to wide-ranging presentations on the geology and environmental applications of industrial minerals. The first presentation discussed the broad-ranging environmental applications of industrial minerals. Following this was a review of previous work on the use of industrial minerals in the amelioration of contaminated land. The final two presentations of the morning session were devoted to the detailed geology of the diatomite deposits of Lampang Province.

![Plate 5: The workshop panel fielding delegates' questions from the floor](image)

The afternoon session emphasised the related environmental issues. The Director of Environment Division, DMR, presented an introduction to the major environmental issues in Thailand and the role of the DMR. This was followed by two case studies based on this project. The first involved the dissemination of intensive work investigating the sorption of As by diatomite (section 2.3) followed by a more applied presentation of work investigating the interactions between diatomite and contaminated substrates (sections 2.5 and 2.6). An hour of group discussion ended the day (plate 5). The bilingual (English and Thai) nature of the workshop encouraged audience participation with many questions and interesting debate. The main points raised from the discussion session were:

- If desired, the potential of a wider range of industrial minerals for treatment of contaminated land could be examined by DMR using the capability for column leaching experiments established under the current project.
An estimate of the costs of using diatomite to treat contaminated land – in comparison to other methods of remediation – would be valuable.

Generic conclusions about the use of diatomite for the treatment of contaminated land – including statements on how diatomite is likely to function under different geological conditions – should be highlighted in project outputs.

The methodology developed as part of the project to examine As-sorption (characterisation of industrial minerals, sorption experiments, identification of surface complexation mechanisms, use of geochemical models) should also be given prominence in the project outputs.

The workshop was formally brought to a close by the Director of Environment Division, DMR. A detailed proceedings was produced by DMR staff (see Whitbread-Abrutat et al., 1999c).

4 CONCLUSIONS

1 During work on the inventory of diatomite deposits in the Lampang Basin, a generic protocol for the field examination of diatomite deposits was developed. The protocol identifies “high quality” and “low quality” diatomites on the basis of defined physical and chemical criteria. The protocol could be adopted by Geological Surveys or Mines Departments in other countries for preliminary classification of their diatomite resources.

2 Mineralogical analysis of diatomite samples collected during the field inventory identified diatomaceous silica (Opal AN), quartz, goethite and clay minerals (smectite, kaolinite and illite) as the major constituents. Three types of rock fabric were distinguished from petrographic analysis of these samples: (a) predominant well-preserved, whole diatoms, infrequently present as strand-like colonies, within a finely-comminuted matrix of diatom fragments; (b) alternating laminae of whole diatoms / diatom fragments and Fe-stained, K-rich clayey, irregular layers containing Fe- and/or Ti-oxide inclusions; and (c) finely-comminuted diatom fragments within a pervasive clay-rich matrix.

3 Laboratory sorption studies indicated that diatomite provides an inert, rigid Opal AN substrate of high specific surface. It is probable that As (V) undergoes sorption onto Fe coatings bonded to this Opal AN substrate. Under certain conditions, the high Fe content of the diatomite may also initiate co-precipitation of As (V) by raising solute Fe concentration above saturation.

4 Mine wastes from Ron Phibun and Pin Yo mine were chosen for further investigations into their interactions with diatomite in the subsequent column-leaching experiments. A field site near the village of Ron Phibun was chosen provisionally as the site for the long term field trials, however, owing to a change of policy by DMR towards the disposal of As-rich wastes, this site was subsequently cleared. A second site was chosen for the field trials after negotiations with DMR and local authorities in Ron Phibun.

5 Diatomite, applied at a rate of 10%, proved effective in substantially reducing the leachate concentrations of As and other PTEs emanating from columns of mine waste and diatomite. Effects were less marked for the Pin Yo sample owing to its more weathered nature and lower PTE content. Waste saturation was the most useful in reducing leachate PTE concentrations, in general. However, As in the Pin
Yo sample was intimately associated with Fe oxides and hydroxides. Under saturated conditions, this As was remobilised, even in the diatomite-treated samples, thus supporting the hypothesis for the sequestration of As by diatomite as described above. This unexpected result has implications for the application of diatomite to control As mobility in contaminated soils prone to waterlogging.

Long term field trials were set-up in Ron Phibun near the end of the project to investigate the efficacy of different diatomite addition rates on the porewater chemistry of a soil contaminated with elevated As, Cd, Mn and Pb concentrations. At the time of writing, only one month of data is available which indicated no significant differences in porewater element chemistry between any of the treatments. It is anticipated that significant differences will emerge as unoxidised sulphides brought to the soil surface during the preparation of the field trials begin to weather, mobilising the PTEs contained within them.

A generic protocol was developed for examining the potential of industrial minerals for use as amendments to contaminated soil (see figure A1). This protocol is flexible enough to allow the investigation of other potential, non-mineral soil amendments, for example, organic materials.

5 RECOMMENDATIONS

The main recommendation arising from the project is that there is scope to examine a wider range of industrial minerals as amendments to contaminated soil using the protocol developed in this project. This is warranted because of the following factors:

1 The acute hazard posed to human populations by arsenic and other PTEs in developing countries, e.g. the well-documented water contamination crisis in Bangladesh

2 The need to achieve a lasting, positive development impact by progressing further the existing findings, including the social and economic aspects of contaminated land amelioration with diatomite

3 The desirability of continuing the strong institutional and professional links forged under the current project

4 The success of the existing project partnership and its proven ability to deliver outputs

It is the intention of CSM and BGS to pursue this matter through the next round of the DFID KAR programme.

Despite the attainment of all the initial objectives at the end of the project, there remain two ongoing experiments at DMR related to this project. The column experiments are currently in their fourteenth month and the field trials are in their fourth month. A further visit to Thailand in 99/00 by CSM personnel to aid in the thorough interpretation of column-leach and field trials data, and to help in the decommissioning of the former, would result in two further reports and related publications based on the resulting data.
REFERENCES


6 APPENDIX: PROJECT OUTPUTS

The main outputs identified in the original proposal were achieved as were several unexpected outputs. The total outputs were:

1. Six technical reports

2. Project summary report:

3. Three annual reports and one final report

4. Presentation of results at a major international conference resulting in two published papers:

5. Workshop proceedings:

6. Long term column experiment set-up in DMR laboratory including donation of column-leaching equipment

7. Long term field set-up including donation of soil porewater samplers
8. Generic protocol for the production of diatomite inventory
9. A generic protocol for the analysis of minerals as potential soil amendments for ameliorating contaminated land (figure A1).

Figure A1: Generic protocol flow chart for investigating minerals as soil amendments