DTI SMART AWARD

USE OF WASTE & LOW VALUE CLAYS TO REMOVE METALS FROM POLLUTED STREAMS AND DISCHARGES.

SUMMARY REPORT

AQUATONICS LTD
Glenthorne, Searle Street, Crediton, Devon, EX17 2DB, UK
Tel 01363 776456 e-mail earth@online.rednet.co.uk

PHILIP R J SMITH, BSc, PhD, MCIWEM, MRSC, CChem.

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EXECUTIVE SUMMARY

This SMART feasibility study has shown that dredged clays and other clays with low economic value have considerable commercial potential for removing metals from effluents and contaminated streams. Novel methods of treating effluents and polluted streams have been devised, including "in-stream treatment" of watercourses which has many advantages over conventional treatment methods.

The most important findings are:

- Although all clays and silts remove metals such as copper and zinc, there are significant differences between the clays, which we attribute to the cation exchange capacity of the clay and its ability to raise the pH of the test solution.
- One of the best-performing clays that we tested was a glauconitic clay from Eling, in Southampton Water. This clay is very similar to the material that would be dredged from the Dibden area in Southampton Water if a proposed container terminal obtains planning permission.
- A significant beneficial use could be found for clays from capital dredging. These clays are normally dumped at sea in the UK. This disposal method causes environmental problems at the dump site, for example smothering of marine life on the sea bed. Dredging companies in the UK are required by the licensing authorities to consider potential beneficial uses of the dredged material.
- There are logistical and engineering problems to overcome before dredged clays could be used in large quantities. These problems are not technically difficult to solve, but would require investment by the dredging industry. Such investment is unlikely unless Government Agencies require dredging companies to stop dumping clays and silts at sea, as this is likely to remain the cheapest option.
- Toxicity tests using one of the most sensitive species of freshwater invertebrate (a snail called *Physa acuta*) showed that a suspension containing 1% Eling clay (dry weight) had a dramatic effect on the toxicity of an actual mine water discharge. The Eling clay produced a reduction in toxicity that was equivalent to a 100 fold dilution with clean water. This indicates that some marine clays that would otherwise be dumped at sea may have a genuine role in cleaning up polluted streams and rivers, both in the UK and overseas.
- Trials with industrial effluents from Printed Circuit Board Manufacturing and Metal Finishing showed that clays in suspension can remove 60-93% of copper from the final effluent, depending on the concentration of clay used. Other metals are also removed but not as efficiently as copper.
- Laboratory trials using a recirculating system showed that a 4 metre flume lined with Eling clay could remove copper highly effectively, even at high concentrations (110 ppm Cu) without causing any problems with increased concentrations of suspended solids.
- Eling clay beds and suspensions of Eling clay have a remarkable ability to neutralise acidic effluents. If such clays are used to treat acid mine drainage they are unlikely to require the addition of other neutralising agents such as limestone.
- China clay and ball clay quarries often have low value clays stock-piled within their quarries, and many of these clays could be used to remove metals from solution. Lignitic clays from WBB Minerals are relatively acidic and have the ability to neutralise alkaline effluents. The combination of carbonaceous material

and clay in these lignitic clays would be expected to increase the range of pollutants that could be removed.

- There are hundreds of kilometres of streams in the UK that are affected by metal and coal mines (mostly ones that have closed). Most of these could be treated using clays, either in suspension of as clay beds within the stream (in-stream treatment). Unfortunately there is only slow progress in the UK, as the responsible agencies do not have sufficient funding. In addition the Environment Agency sees itself as an enforcer of water quality standards in England and Wales, rather than a body with responsibility for cleaning up streams. Responsibilities will hopefully be clarified and money from central government should be made available as the deadlines of the EU Water Framework Directive approach.
- "In-stream treatment" of contaminated streams and rivers is a concept developed by Aquatonics Ltd. It appears to be a practical and economic alternative to the current methods, which involve either chemical treatment or constructed wetlands. In-stream treatment is predicted to be much cheaper in capital and operating costs than chemical treatment, but more expensive than constructed wetlands or clay lined lagoons.
- Permeable Reactive Barriers (PRBs) using a combination of synthetic aggregate made from clay and raw clays have considerable potential for cleaning up groundwater contaminated with metals and other contaminants. The synthetic aggregate can be designed to provide the desired level of permeability.
- Industries that could benefit from clay technology include:
  mining and quarrying, including active and abandoned mines
  radioactive facilities (eg nuclear power stations and Sellafield)
  oil refineries
  whisky distilleries (copper in effluent comes from the distillation vats)
  metal smelting
  metal finishing and other metal engineering works
  printed circuit board manufacturing
  leachates from landfill
  sewage treatment
  drinking water treatment
- In the light of current world events it is worth pointing out that clays could also be used to remove some nuclear and chemical contaminants from water following terrorist attacks on water supplies.

1. INTRODUCTION

Aquatonics Ltd has successfully completed a feasibility study into the use of dredged clays for removing metals from mine waters and industrial effluents. The feasibility study was funded under a DTI SMART award, administered by the Government Office of the South West. Methods used in the studies by Aquatonics Ltd are detailed in several reports (Smith, 2000a & 2000b; Smith, 2001; Smith & Hook 2002; Smith 2002a, Smith 2002b; Hook & Smith, 2003). This report summarises the main findings of the study, which lasted from April 2000 to March 2003.

The initial aim of the study was to use marine clays (similar to those obtained during capital dredging) to remove metals from effluents and contaminated streams. This aim was broadened towards the end of the study, when clays trapped behind dams and quarried clays of little or no economic value were also examined. Disposing of clays trapped behind dams can be very problematic and any beneficial uses that can be found would be of interest to the companies that manage the dams. Low value clays in quarries (eg lignitic clays) can be difficult for quarries to dispose of and are often stock-piled within the quarry.

Peat has been suggested as a potential adsorbent of metals (Brown et al, 2000), but there are significant environmental issues relating to removal of peat for such purposes. Lignitic clays offer an environmentally friendly alternative to peat for metal removal.

1.1 Metal Removal by Clays

Clays remove metals in a variety of ways:

- Cation exchange capacity, where metal ions present on the clay (eg Ca, Mg and Na) are exchanged for other metals in the surrounding medium (eg Cu, Zn etc).
- Clays have a very high surface area due to their small particle size. This allows them to bind to a large number of metal ions.
- Clays often contain organic matter which can form complexes with metals.

Although it is well known that clays can remove metals, including radiochemicals, from solution (Dumat et al, 2000), there do not appear to have been any studies of the use of clays from dredging operations to treat metal-rich effluents and streams contaminated by mining operations. Laboratory trials have been used to study the effectiveness of glauconitic sand to remove metals (Spoljaric and Crawford, 1978) and landfill leachates (Spoljaric and Crawford, 1979). Glauconite has many other uses, for example it was used from about 1900 to the late 1940s for water softening (Spoljaric, 1994). Large-scale use of glauconitic clays to treat streams affected by mine drainage and industrial effluents does not appear to have been investigated.

1.2 Clays from Dredging

Dredged materials arise from deepening and construction activities in waterways, estuaries and the coastal zone. In the UK alone about 50-60 million tons are disposed of each year to marine disposal sites. The minerals present, particle size and level of contamination varies greatly between dredging operations, and in many cases a single dredging activity will generate a wide range of dredged materials.

Maintenance dredging is used to remove sediment that has been transported into an area, often a dock or harbour or navigable channel. Capital dredging is used to remove deposits that are in their original position and need to be removed to allow construction of new facilities or for deepening a channel to allow the passage of larger vessels. Sediments from capital dredging have had only a minor or zero exposure to contaminants from human activities and may therefore be suitable for a wide range of beneficial uses. Even maintenance dredgings have beneficial uses (eg brick manufacture) provided that the contaminants present do not create any environmental problems.

Beneficial uses of the dredged material are being explored in a number of countries, including the UK. These beneficial uses include capping contaminated mudflats with clean sediment, recharging sandy beaches and mudflats with suitable sediment to replace material lost through erosion, and making bricks with clean and contaminated clay.

In Southampton Water the sediments that would be removed to construct the proposed Dibden terminal and deepen the approach channel include a large quantity of clean material from capital dredging. Some of this material (perhaps a million tons) would be from the Bracklesham beds, which are known to contain the mineral glauconite.

1.3 Impacts of Mining on Streams and Rivers in the UK

More than 600 km of streams and rivers in the UK are affected by discharges from mines and spoil heaps, of which at least 200 km are in SW England (NRA, 1994). These figures are known to under-estimate the true extent of the problem, as many smaller streams are not assessed. In northern Appalachia (USA) it has been estimated that about 4800 km of streams are affected by mine discharges. Impacts of mine water discharges include visual/aesthetic (mainly due to discolouration of the water and stream bed - see Figure 1), high metal concentrations and low dissolved oxygen concentrations, pollution of groundwaters including aquifers used for water supply and changes in the ecology of the stream that range from minor to an absence of fish and typical invertebrates (Jarvis and Younger, 2000).

These abandoned mines cause a variety of pollution problems, including aesthetic ones due to the orange colour of many of the watercourses, caused by the deposit of ochre (ferric hydroxide and ferric oxyhydroxide). There is no single organisation that is responsible for cleaning up these discharges (House of Commons, 1999). Any solutions to the problem of historical mine waters must be practical, robust and affordable. It would also be preferable to develop treatment systems that can cope with the diffuse nature of metal pollution on some catchments, with pollution at different locations due to adit drainage and mineral spoil heaps.

The EU Water Framework Directive requires all rivers to have "good ecological status" by 2015. Although this deadline may seem readily achievable, the scale of the problem means that government agencies in member states of the EU must start planning now.

Figure 1. Contaminated water from Dolcoath adit (on the right) enters the Red River (left) in Cornwall.

1.4 Treating Pollution from Mines and Spoil Heaps.

A range of treatment techniques are available for treating discharges from active and abandoned mines and spoil heaps. There are two main categories:

- Passive treatment systems, generally gravity fed and often employing constructed wetlands to treat the effluent. These constructed wetlands require a large land area but are generally cheaper in capital and running costs. Examples include Stanley Burn in County Durham (Jarvis and Younger, 1999) and the pilot treatment plant at Wheal Jane in Cornwall (Hamilton et al, 1999). Anoxic Limestone Drains (ALDs) can also be incorporated into passive treatment systems. Permeable Reactive Barriers (PRBs) are a passive treatment system, but are designed to treat contaminated groundwater rather than surface water (Younger et al, 2002).
- Chemical treatment systems, where limestone or other alkaline materials are used inside a treatment plant to neutralise the acidic effluent and precipitate iron and other metals as their hydroxides. Examples include the recently commissioned chemical treatment plant at Wheal Jane, with a capital cost of £3.5 million and an annual running cost estimated to be £1 million.

1.5 Metals in Industrial Effluents

Many industrial effluents contain metals in concentrations that would be toxic without treatment prior to discharge to sewer or watercourse. Clay technology appears to have the ability to treat a wide variety of industrial effluents, either alone, or more usually in combination with other techniques. Industries that could benefit include:

- Printed Circuit Board (PCB) manufacturing
- Whiskey distilleries (copper in effluent)
- Oil Refineries
- Mining and quarrying
- Metal finishing
- Metal smelting
- Nuclear facilities

1.6 Other Contaminants

Many pollutants bind strongly to sediments, and there is good reason to believe that clays could be used to treat a range of contaminants such as agrochemicals and hydrocarbons in industrial effluents. We noted that much of the colour was removed from a Printed Circuit Board manufacturer's final effluent. A small trial with a polycyclic aromatic hydrocarbon (benzo-a-pyrene) showed that it partitioned well onto the Eling clay.

2. SUMMARY OF EXPERIMENTAL RESULTS

2.1 Data on Eling Clay

The sediment used in the studies was a glauconitic intertidal clay from the upper reaches of Southampton Water (Eling Marshes). Although Eling Marshes will not be dredged as part of the proposed terminal developments at Dibden in Southampton water, the sediment from Eling is likely to be very similar to the glauconitic sediment that will be dredged at Dibden. The source of the clay is shown in the foreground of Figure 2.

Figure 2. Source of the Eling Clay (foreground) in Southampton Water.

Before the sediment was analysed it was considered to have a large component of glauconite, a name derived from the Greek glaucous for the colour bluish or pale green. Glauconite has a known ability to remove metals (Spoljaric and Crawford; 1978 & 1979). Unfortunately the term glauconite refers to two separate entities (McRae, 1972). The first is a morphological term for rounded, sand-sized, greenish, earthy-looking grains found in sedimentary rocks. The second is a specific mineral species, a hydrated iron-rich micaceous clay mineral related to the illites (McRae, 1972). Most of the results reported here relate to the second meaning of the term glauconite, the only exception is a glauconitic sand from a marine deposit in Namibia that was included in some of the experiments. Previous work on glauconitic greensand to remove metals used a Delaware coastal plain sediment that was up to 80% pellets about 0.5 – 1.0 mm in size, mixed with clay size glauconite and other quartz sand (Spoljaric and Crawford; 1978 & 1979).

The glauconitic clay from Eling Marsh in Southampton Water was a grey/brown soft, plastic mud with a greenish tinge. The organic matter ranged from none visible to a large number of short strands of plant material. Two separate analyses of the wet weight of organic matter gave figures of 3% (Hards, 2000) and 5% organic matter (own data). The dry weight was 47% - 51%. The wet density was approximately 1.33 kg/m^3. The macroinvertebrate fauna at this site was dominated by a polychaete worm known as *Nereis diversicolor* (ragworm) and a bivalve mollusc called *Scrobicularia plana* (peppery furrow shell). Occasional live and dead shells of *S. plana* were present in the mud that was brought back to the laboratory. It is likely that the calcium carbonate in the shells contributed to the ability of the Eling clay to neutralise acidic effluents.

The expected salinity range at Eling Marsh is about 20 to 30 psu (ie approximately 60-90% seawater (data from surveys by Associated British Ports in the upper reaches of Southampton Water in 1997). Much lower salinities would be experienced towards the low water channel, especially near low water.

The sediment at Eling Marsh is a mixture of clay (47%) and silt (50%). The remaining 3% was pieces of decomposing vegetation, mostly larger than 0.5 mm. Figure 3 shows the X-Ray Diffraction (XRD) analysis carried out by the British Geological Survey on the sample (Hards, 2000). This shows the presence of kaolinite, illite,

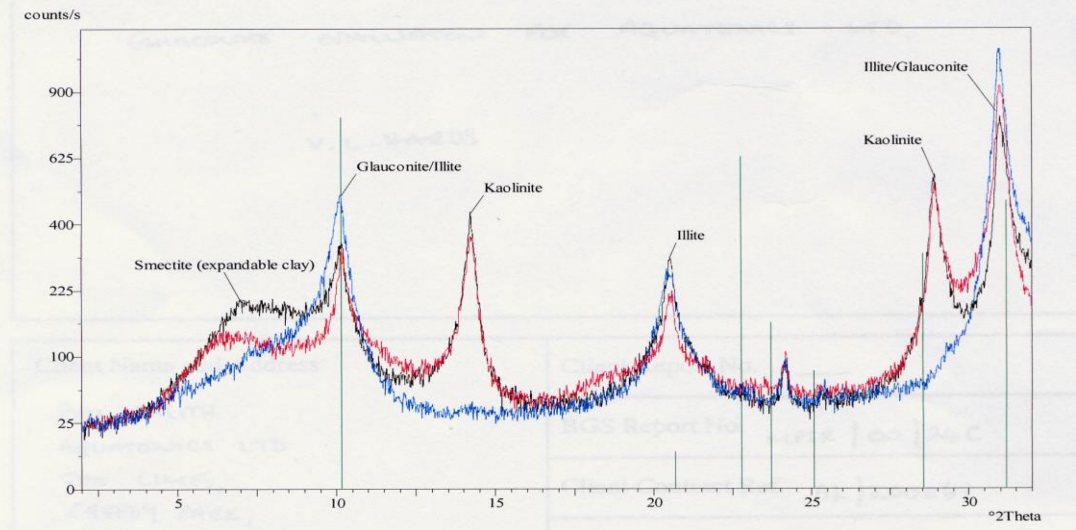


Figure 1. X-ray diffraction profile obtained from an oriented mount of <2mm fraction of the ?glauconite, with ICDD reference stick pattern (in green) for 10Å glauconite. Black = air dried state, red = glycol solvated, blue = after heating at 550°C for 2 hours.

Figure 3. XRD Analysis of Clay

glauconite and smectite. The metal content of the Eling clay was analysed early on in the study (Smith, 2000a). The iron content was 2.9%; other metals were measured at concentrations in the parts per million (ppm) range (equivalent to mg/kg): magnesium 3860 ppm, calcium 1530 ppm, zinc 63 ppm, chromium 22 ppm, lead 18 ppm, copper 17 ppm and cadmium 4 ppm. These results indicate an uncontaminated clay.

Some of the ability of the Eling clay to remove metal ions is due to its cation exchange capacity (CEC) of 29.5 meq/100 g (Smith, 2000a). Cation exchange is the process by which some of the metal ions on the clay are exchanged with more reactive metal ions in solution. In the case of clays the cations that are replaced include calcium, magnesium, sodium and potassium. Of these sodium and potassium were measured by the Environment Agency in the Dolcoath Adit study (Smith, 2002b). Sodium increased by 28% and potassium by 33%. Although the release of these ions may seem problematic, they are ions that aquatic life can cope with relatively easy, and some (eg calcium) are desirable as they protect against the toxic effects of other metals such as copper, nickel and zinc.

2.2 Eling Clay in Suspension

The first experiments with Eling clay in suspension used a natural mine water from the abandoned Phoenix United mine in Cornwall (Smith, 2000a). This had a copper concentration of about 0.8 ppm. Removal of copper by the Eling clay was very high, producing final concentrations that were below the detection limit that could be routinely achieved using this technique. It was therefore decided to increase the initial starting concentration of copper in the main series of experiments.

For the remaining experiments with Eling clay in suspension a synthetic mine water was used (Smith, 2000a). This was composed of 50 ppm each of copper, zinc and cadmium. The pH of this solution was adjusted using a 1 molar solution of sodium hydroxide. Most of the tests were carried out in 250 ml glass beakers, containing 100 ml of test solution. Eling clay was kept in its natural state in airtight containers at 4 ^{o}C, then added to the beaker at the chosen dose rate. Weights of sediments were recorded to 0.001 g. After addition of the sediment the mixture was stirred for 5 minutes on a magnetic stirrer at room temperature. Samples were filtered using a 60 ml Plastipak ® disposable syringe fitted with a Minisart® 0.2 μm filter, and the filtered solution was transferred to wide-mouth glass jars. Analyses were usually completed within 24 hours, and were not acidified.

2.2.1 Effect of Metal Concentration

The effect of metal concentration on the percentage removal of metals is shown in Table 1 (Smith, 2000a). As expected there was an increase in the percentage removal of metals by the clay slurry (0.5% dry weight) as the metal concentration was reduced. At the lowest metal concentration tested (5 ppm) very high percentage removals were obtained, even at a pH of 6.1. At pH 7.0 and an initial metal concentration of 5 ppm the percentage removal was 100% for copper, 95% for zinc and 93% for cadmium.

Table 1. Effect of Metal Concentration on Percentage Removal of Metals

pH 6.1	**50 ppm**	**20 ppm**	**5 ppm**
Zn	16.8 %	49.3 %	78.8 %
Cu	51.1 %	90.6 %	100.0 %
Cd	21.7 %	55.7 %	82.9 %
pH 7.0	**50 ppm**	**20 ppm**	**5 ppm**
Zn	48.9 %	58.8 %	95.0 %
Cu	99.6 %	99.5 %	100.0 %
Cd	48.4 %	64.5 %	93.0 %

2.2.2 Effect of pH

The effectiveness of the Eling clay increased as pH approached neutral, and increased with the quantity of clay present in relation to a standard solution of metals (Smith, 2000a).

The effect of pH was tested at a slurry concentration of 0.5% (dry weight). The removal of each metal was almost unchanged over the pH range 5.1 to 6.5 (copper 58 – 65%; zinc 20 – 21%; cadmium 25 – 26%) but increased strongly at a pH of 7.0 (copper 95%, zinc 31% and cadmium 38%).

2.2.3 Effect of Clay Concentration

At a pH of 7.0 a 2.5% slurry of Eling clay (dry weight) removed 99% of copper and 90% of zinc and cadmium from a 50 ppm solution (Smith, 2000a). These results compare very favourably with previous laboratory tests using glauconitic sand to remove metals from acidic solutions, where far higher concentrations of sediment were used and copper removal was 96%, zinc 90% and cadmium 95% (Spoljaric and Crawford, 1978).

Under the same experimental conditions but with the concentration of Eling clay reduced to 0.5% slurry (dry weight) the copper removal was still high (95%) but removal of zinc fell to 26% and removal of cadmium fell to 29%.

2.2.4 Concentration of Metals in Eling Clay After Treatment

As the weight of Eling clay fell the concentration of cadmium, copper and zinc on the sediment increased (Smith, 2000a). Figure 4 shows that after exposure to 100 ml of a 50 ppm copper solution the concentration of copper in the Eling clay reached 83,100 mg/kg (8.31%) at the lowest clay dose (0.09 g wet weight clay). The same quantity of clay contained the highest concentrations of cadmium (1.24%) and zinc (2.43%). These concentrations may be high enough to allow smelting of the metals from the clay.

These data for copper show that Eling clay could remove 262 meq of copper/100g of clay (under conditions of low clay doses, which maximise copper uptake per unit mass of clay). As this figure is approximately 9 times higher than the measured cation exchange capacity of 29.5 meq/100g it suggests that either the CEC measurement was in error or, more likely, that cation exchange is only partly responsible for the removal of copper. Recent studies using seawater neutralised red mud (a waste from aluminium refining) gave a metal binding capacity of approximately 100 meq/100g (McConchie, D et al, 1998). The Eling clay value of 262 meq Cu/100g is well in excess of this value.

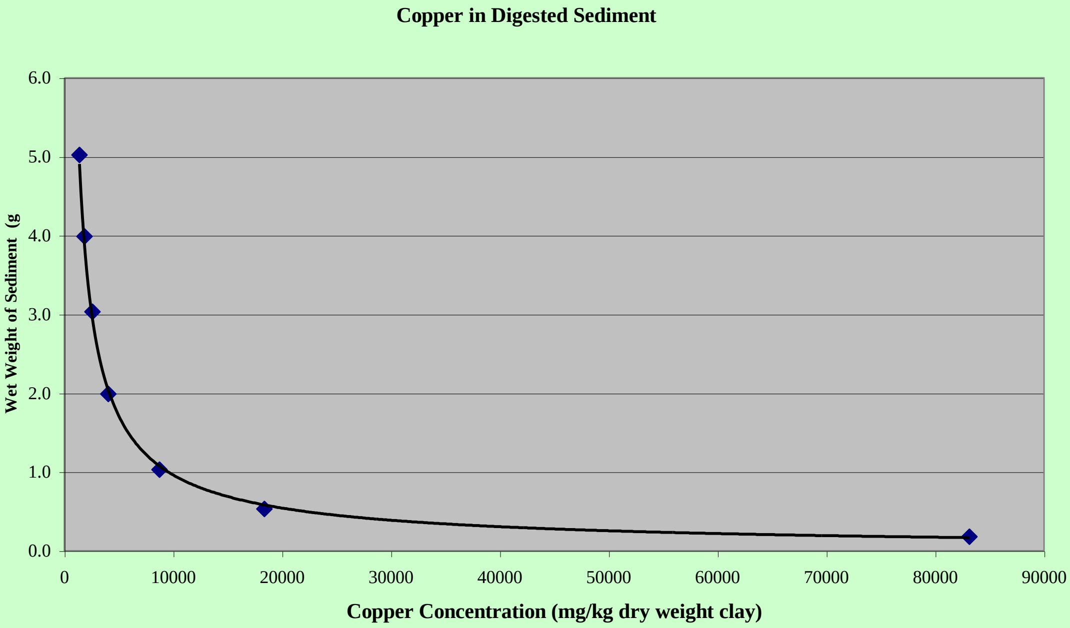


Figure 4. Copper in Eling Clay after it was used to treat copper solution

2.2.5 Toxicity Tests

Toxicity tests showed that a 0.5% suspension of Eling clay had a dramatic effect on the toxicity of a mine water discharge, using one of the most sensitive species of invertebrate (a snail called *Physa acuta*). The Eling sediment produced a reduction in toxicity that was equivalent to a 100 fold dilution with clean water. This indicates that Eling clays may have a genuine role in cleaning up polluted streams and rivers, both in the UK and overseas.

2.2.6 Effluent from a Printed Circuit Board Manufacturer

Laboratory tests using the final effluent from a Printed Circuit Board Manufacturing Plant produced a 75% removal of copper at clay dose of 1.5% (dry weight) (Smith, 2000b). This was achieved in a 5 minute contact time and a pH of 8.9. At a clay dose rate of 0.5% (dry weight) a 60% removal of copper from the final effluent was achieved, at a pH of 9.4. The removal of copper from other effluent streams within the plant ranged from 5% - 48%, at a clay dose of 0.5% and contact time of 5 minutes.

2.2.7 Effluent from a Metal Finishing Works

At the end of the study we compared the effectiveness of suspensions of Eling clay and a lignitic clay (from WBB Minerals) for treating a final effluent from a metal finishing works (Hook and Smith, 2003). For the metals tested (cadmium, chromium, copper, nickel and zinc) the Eling clay outperformed the ligntic clay, but for chromium, copper and nickel the differences were small. For these metals (and probably several others not tested) the lignitic clay has commercial potential, removing. As the lignitic clay is currently of little or no commercial value this provides a possible beneficial use of this material.

2.3 Comparison of Various Clays & Other Sediments

The laboratory experiments in 2002 examined 8 clays and a glauconitic sand (Table 2). Two main investigations were carried out. One examined the removal of copper by various weights of clay/sediment whilst the other examined the ability to remove copper at a standardised pH of 6.5. Suspensions of clay and slurry were prepared using a multi-flask magnetic stirrer (Figure 5). Full details of the methods are described in Smith and Hook (2002).

The clays and other sediments removed 90-98% of copper from a 20 ppm solution, even at slurry concentrations below 1% dry weight of clay. Another useful property of most of the clays was their ability to neutralise the acidic copper solution, even at low clay concentrations.

Table 2. Clays and Other Sediments Used in Laboratory Trials in 2001 (Smith & Hook, 2002)

ORIGIN	No.	DESCRIPTION
Twitchell Reservoir, California	1	Fine yellow clay, resulting from deposition in the reservoir, which is designed for groundwater recharge. Provided by Santa Maria Valley Water Conservation District
Sound of Sleat, Scotland	2	Firm marine clay. Provided by Scottish Office Agriculture Environment and Fisheries Division.
Glauconitic sand, Offshore Namibia	3	Black glauconitic sand with some shell fragments. Provided by Ocean Minerals.
Glauconitic clay, Offshore Belize	4	Glauconitic clay. Provided by Ambios Environmental Consultants.
Clay, Bathside Bay, Harwich, England	5a	Marine clay from a proposed dredging site. Provided by Harwich Haven Authority.
Clay, Eling, Southampton Water, England	7	Marine sediment (50% clay, 50% silt), very similar to clay that would be dredged if Dibden Container Terminal is built. Obtained by Aquatonics Ltd.
Semi-calcined clay Newton Abbot, England	8	Synthetic aggregate, fine gravel size. Speckled black and white. Provided by WBB Minerals, Newton Abbot.
Calcined clay, Newton Abbot, England	9	Synthetic aggregate, fine gravel size. Off white in colour. Provided by WBB Minerals, Newton Abbot.
Puraflo, commercial clay, Newton Abbot, England	10	Fine pale clay used in ceramics. Blended from natural clay deposits at Newton Abbot, Devon, England. Provided by WBB Minerals.

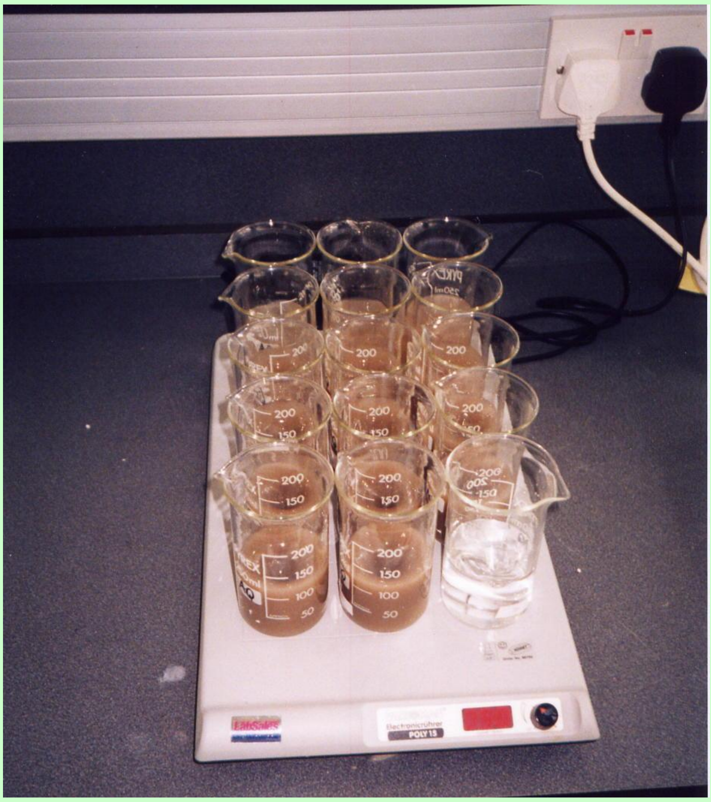


Figure 5. Multi-flask stirrer used to form clay suspensions.

2.3.1 Varying the Weight of Clay Used

Almost 100% removal of copper was possible when 20 ppm copper solutions were treated with a clay slurry (Figure 6). For most clays this was achievable with the addition of approximately 0.2g (dry weight) of clay in 100ml of solution (i.e.< 0.2% slurry). The majority of the removal of copper can be attributed to the pH neutralising ability of the clay. The only raw clay that did not perform very well was Puraflo, a commercially available clay for the ceramics industry obtained from clay deposits at Newton Abbot. It is likely that the inability of this clay to neutralise the acidic solution was the main reason for its poor performance.

Although the semi-calcined and calcined clays provided by WBB Minerals did not perform as well as the raw clays they may have applications where particle sizes above those of clays are required, eg synthetic aggregates.

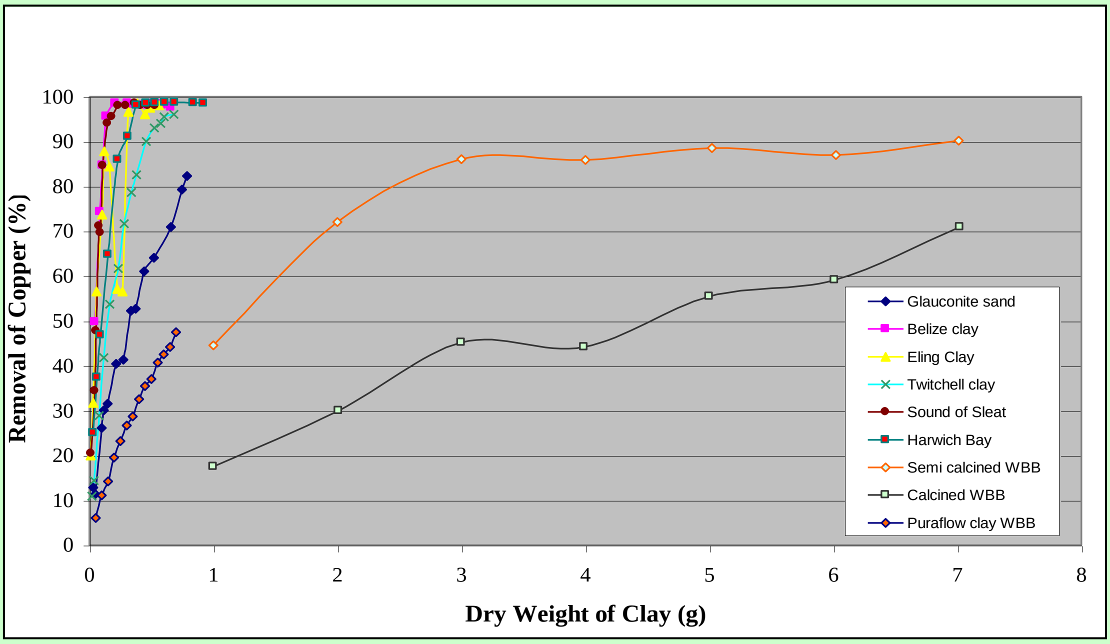


Figure 6. Copper Removal by Various Clays and Other Sediments

2.3.2 Standardised pH

At a standardised pH of 6.5 the glauconitic clay from Belize performed best removing ~88% of the copper (Table 3). The clays from Twitchell Reservoir USA, Sound of Sleat Scotland and the glauconitic sand from offshore Namibia all removed between 60 and 70% copper. The clays from Harwich (Bathside Bay) and Southampton Water (Eling) removed between 40 and 50%.

Table 3. Experimental Results (pH Standardised to 6.5).

Sample	Type	Dry mass (g)	Copper concentration (ppm)	% removal Cu
1	Twitchell Reservoir California	0.302	7.1	63.96
2	Sound of Sleat, Scotland	0.109	6.5	67.01
3	Glauconitic Sand, offshore Namibia	0.790	6.0	69.54
4	Glauconitic Clay, offshore Belize	0.240	2.5	87.30
5A	Bathside Bay, Harwich, England	0.140	10.5	46.70
7	Eling, Southampton Water, England	0.070	11.8	40.10
Control, pH 5.5		NA	19.7	00.00

Although Harwich and Southampton Water clays were relatively poor performers at standardised pH they achieved higher copper removals when pH was not limited. This was also true for the Sound of Sleat clay; all three achieved approximately 98% removal in mass variation experiments.

The glauconitic sand from Namibia performed well in the isolated pH investigation, though its larger grain size (fine sand as opposed to silty clay for most others) was not able to provide the surface areas needed as receptor sites in cationic exchange. The mass therefore needed to attain >80% removal of copper was 4 times as great.

Early investigations by Aquatonics Ltd focussed on whether a clay with a high glauconite content had an unusually high ability to remove trace metals from solution (Smith, 2000a, 2000b, 2001). The results presented here for copper suggest this is not the case, as clays such as those from Harwich, Twitchell Reservoir and the Sound of Sleat did not contain this mineral in appreciable quantities. It appears that for removal of copper from acidic mine waters one of the most important attributes of a clay is its ability to neutralise an acidic solution. The cation exchange capacity (CEC) is also likely to be important.

2.4 Trials of a Prototype at Wheal Jane Mine, Cornwall

A prototype treatment system was tried at Wheal Jane in late February/early March 2001 (Smith, 2001). The prototype plant is shown in Figure 7. Treatment alternated between 2 pairs of 1 m^3 containers, with a contact time set at 21 minutes. Experimental details are contained in Smith (2001).

The trial was successful in showing that good mixing of the clay and effluent could be achieved using simple equipment, and that relatively large volumes of effluent could be treated (1.6 l/second). Unfortunately the puddling clay that was used in most of the trials was not very good at removing metals. In addition the effluent that was treated was not the mine water but various contaminated streams from with the Wheal Jane site. The concentrations of most metals in the effluent were below the analytical detection limits. The main exceptions were zinc and manganese. Zinc was removed reasonably well by Eling clay (41% removal) but the puddling clay only achieved a maximum zinc removal of 18% (Table 4).

As each trial required about 40 kg of clay it was not possible to continue the trials with the prototype using Eling clay, which at present is not available in quantity.

Table 4. Results from Trials of the Prototype at Wheal Jane

RUN	CLAY TYPE	pH	Conductivity (µS/cm)	DO (% saturation)	DO (mg/l)	Temperature (ºC)	Suspended solids (mg/l)	Mn (ppm)	Zn (ppm)	Zn (% removal)
1A In	Puddling	6.6	1530	114	NA	6.0	2.3	1.2	3.2	3
1A Out		6.7	1660	101	NA	6.0	115.3	1.2	3.1	
2A In	Puddling	6.9	1220	113	12.8	5.5	10.2	0.9	2.3	9
2A Out		NA	NA	NA	NA	NA	311.1	0.9	2.1	
3A In	Puddling	7.3	1270	97	10.6	7.2	7.1	0.6	1.7	12
3A Out		7.2	1200	96	10.7	6.3	3643.0	0.6	1.5	
4A In	Puddling	6.7	1800	110	13.8	4.0	5.2	0.7	1.7	18
4A Out		6.5	1380	101	12.0	3.6	5132.7	0.7	1.4	
5A In	Puddling	6.8	1380	103	11.7	4.5	5.5	0.7	1.7	18
5A Out		6.8	1300	102	11.7	4.4	4490.7	0.7	1.4	
6A In	Glauconitic	6.9	1290	81	9.7	6.0	6.5	0.7	1.7	41
6A Out		6.6	1950	102	11.7	5.2	2445.2	0.7	1.0	

Figure 7. The Prototype Treatment Plant at Wheal Jane

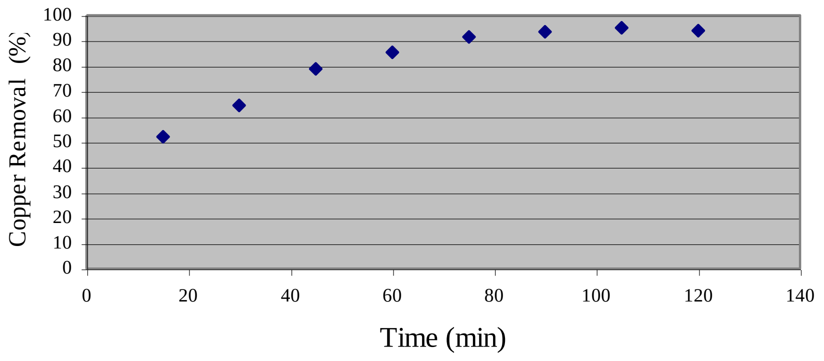
2.5 Clay Beds

2.5.1 Experiments at the University of Exeter

The ability of a 4m clay flume to remove copper was tested at different concentrations of copper, using indoor (Figure 9) and outdoor (Figure 10) recirculating systems at Exeter University.

At a starting concentration of 20 ppm copper repeated passage down the clay flume produced a rapid decrease in copper concentrations (Figure 8).

Figure 8. 20 ppm Cu solution. Eling Clay



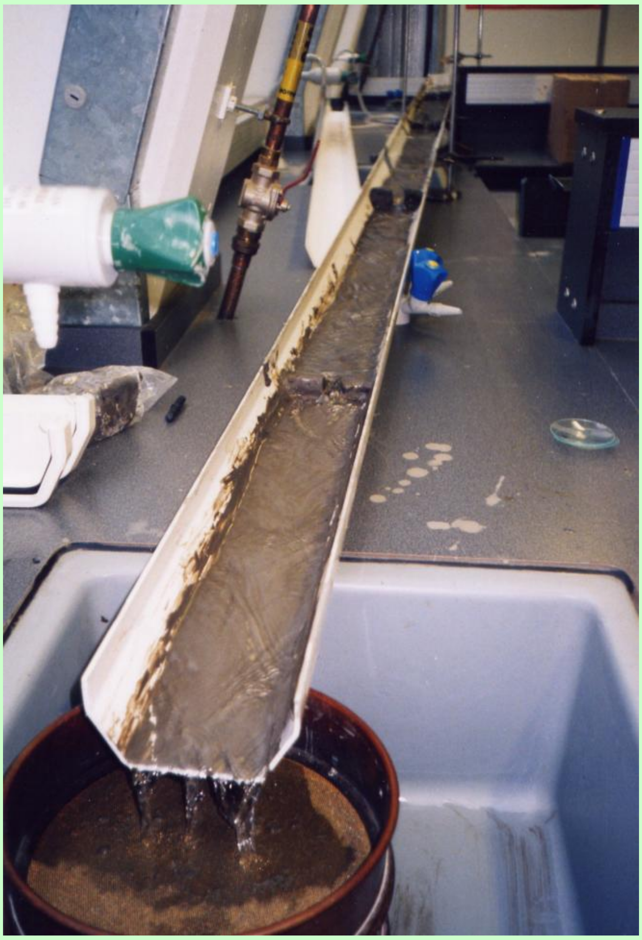


Figure 9. Indoor re-circulating flume showing clay bed.

Figure 10. Outdoor re-circulating flume at Exeter University.

To simulate conditions in a stream affected by mine water discharges a starting concentration of 0.84 ppm copper was used, with acidification to pH 5.3 at the end of every passage down the flume (Figure 11). This mimics conditions that may be expected as further acidic discharges join the main stream. The results show that the clay has considerable potential to neutralise acidic effluents. Although some copper is released the clay retains the ability to take up more copper from solution.

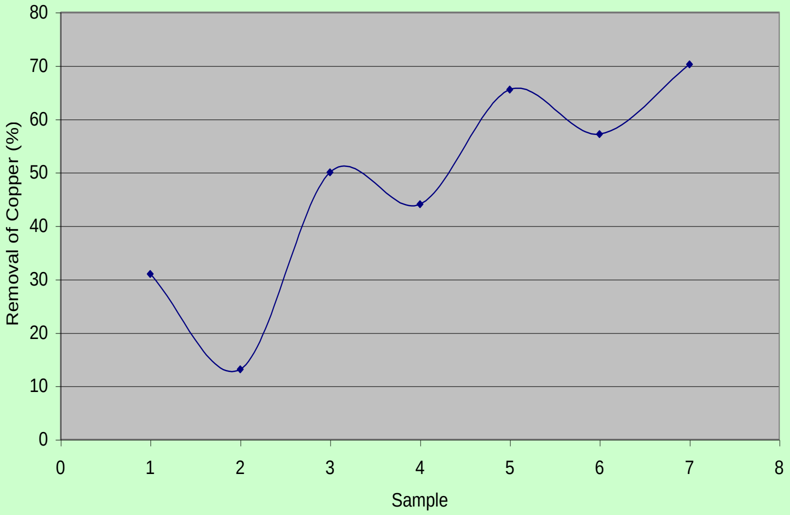


Figure 11. Repeated Acidification to pH 5.3.
Even sample numbers show the copper removed after passage down the flume. Odd numbers show copper in solution after acidification to pH 5.3 (before further passage down the flume).

At the highest copper concentration tested (110 ppm or 110 mg/L) the first pass down the 4m flume removed 22 mg/L from 20 litres of synthetic effluent. This means that 440 mg of copper was removed in 10 minutes by 0.32 sq m of clay. This is equivalent to 137 mg Cu/sq m/minute. As expected the rate of removal of copper by the clay fell with declining copper concentrations. Over the 4 hour test the mean removal rate of copper was 1.40 mg Cu/sq m/minute, due to the recirculating system continually feeding back lower copper concentrations. Over the last hour of the study the rate of removal of copper was 0.124 mg/sq m/minute (equivalent to 124 µg/sq m/minute). Data for this experiment are shown in Figures 12-14.

The clay flume rapidly neutralised the acidic test solution (Figure 14). The next experiment was intended to mimic recovery from a moderate acidification incident in a stream with a clay bed. Twenty litres of 1 ppm copper were repeatedly passed over the clay flume. After 30 minutes acid was added to cause the pH to drop. However, instead of dropping the pH to about 5 we inadvertently acidified to pH 1.9 (Figure 15). This released a lot of copper from the clay. We expected that the recovery from this severe acidification event would be very prolonged, and were surprised when pH climbed back to 6.8 within 90 minutes (equivalent to 36 m, ie 9 passes down the 4m of clay flume). Copper was rapidly removed from solution as the pH rose (Figure 15).

Figure 12. 110 ppm Copper Solution Repeatedly Passed Over a Clay Bed

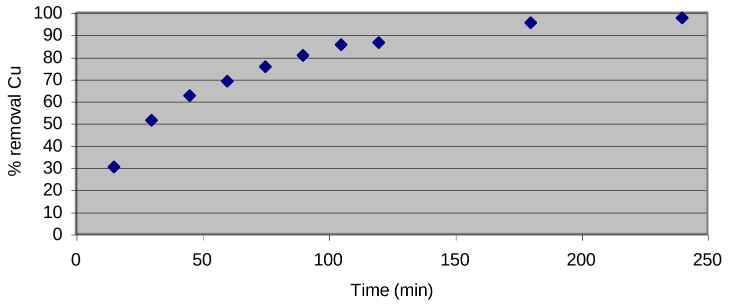


Figure 13. Change in pH in Relation to Cumulative % Removal of Copper from 110 ppm Solution

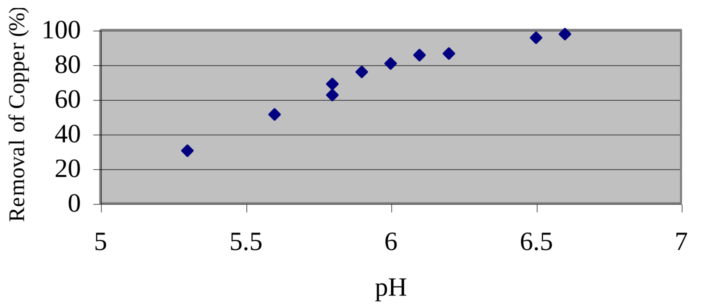


Figure 14. 110 ppm Copper Solution - Change in pH over Time

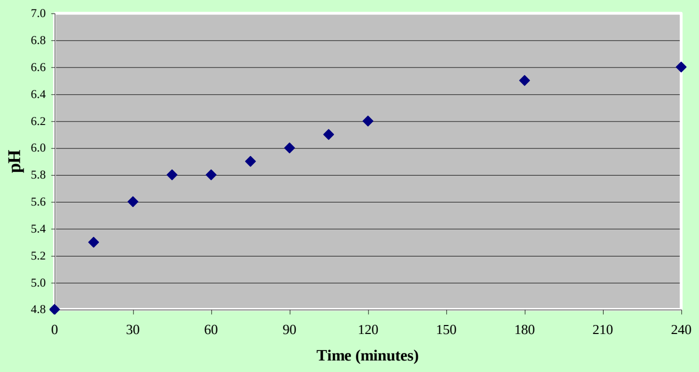
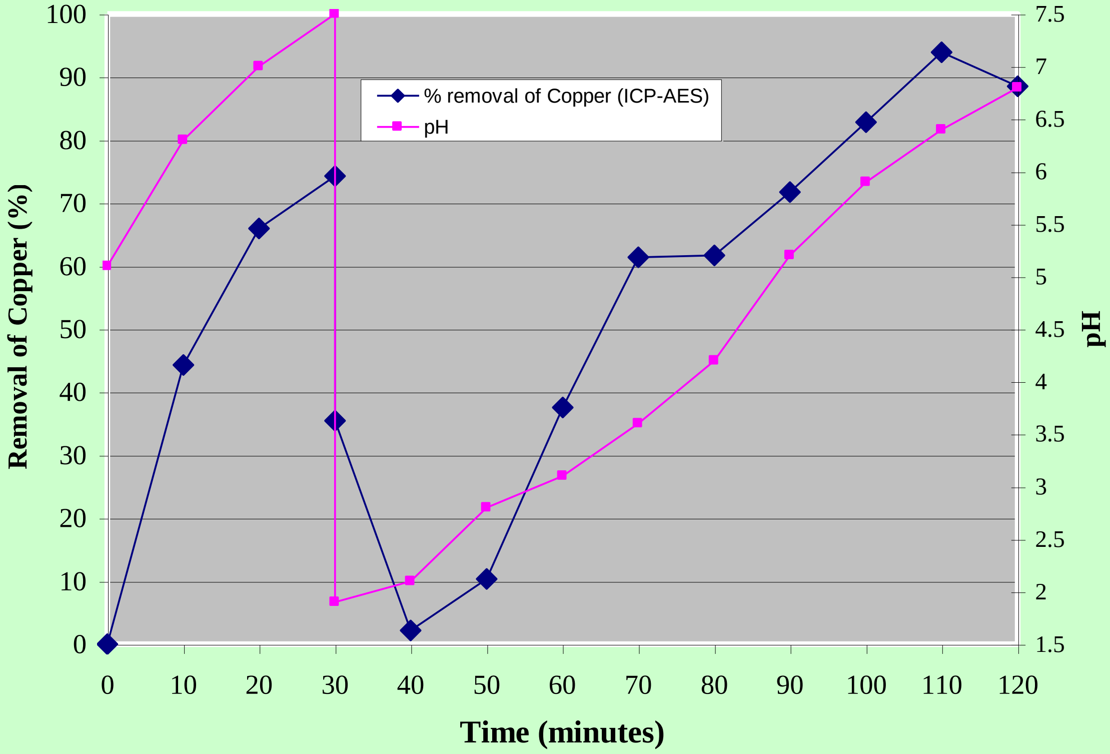


Figure 15. Removal of Copper During a Severe Acidification Event



2.5.2 Field Trials with Clay Flume at Dolcoath Adit

Field trials of the 4m clay flume were carried out at Dolcoath Adit, near Camborne, Cornwall (Figure 16). The results have been very useful in determining the rate of removal of copper per square metre of clay at much lower concentrations of copper (approximately 0.12 mg/L or 120 µg/L) than in the laboratory experiments. The Dolcoath Adit data showed a rate of removal of 102 µg/sq m/minute, quite similar to the rate of removal of 124 µg/sq m/minute at the end of the recirculating flume study described above. Data on removal of other metals were also obtained (Smith, 2002b).

Figure 16. Experimental Trials of Clay Flume at Dolcoath Adit

2.6 Packed Columns

2.6.1 Semi-calcined granules

Experiments were carried out at WBB Minerals using a clay named LWA which had previously been semi-calcined by WBB. Experimental methods and results are contained in Hook and Smith (2003).

A clear vertical Perspex column of 6” (152 mm) internal diameter and approximately 2.0m in height was used (Figure 17). Two outlets were fitted, one at the top (outflow) and one at the base (inflow), both had been prepared using standard 15mm plumbing fittings (Hep$_2$O). The calcined beds were formed by adding the material from the top of the column.

LWA semi calcined granular material was filled to a height of 0.5m from the base of the column (7.5kg). Ten litres of 20mg/l copper solution was passed through the column. The removal of copper removed up to 90% of the copper (Figure 18). After flushing with water the semi-calcined granules were treated with 10 litres of 1% H_2SO_4, this released about 55% of the copper taken. Further washing was water was used to neutralise the pH to about 7.0, then a further 10 litres of 20mg/l copper solution was passed through the column. This time the copper removal abilities of the semi-calcined granules were much lower (lower line in Figure 18), suggesting an interaction with the dilute acid and available receptor sites occupied by copper ions.

Figure 17. Perspex column used in packed bed experiments at WBB Minerals.

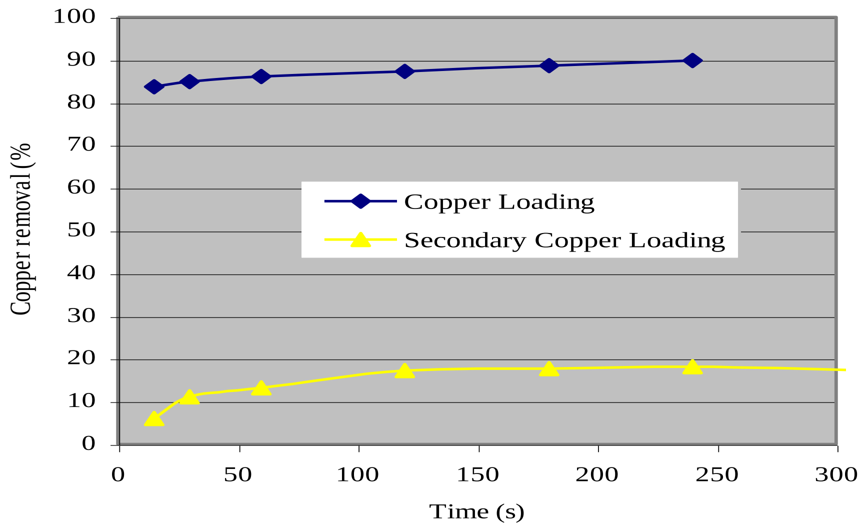


Figure 18. Copper removal by semi-calcined LWA granules in a packed column. Upper line shows initial removal. Lower line shows copper removal after acidification of the granules with 1% sulphuric acid.

In a separate experiment we examined the time taken to exhaust the copper removal ability of the LWA semi-calcined granules. The results are shown in Figure 19. The LWA semi-calcined granules were initially effective at removing copper but within a period of 30 minutes had become almost exhausted. The LWA semi-calcined granules removed a total of 224 mg of copper per kg; this equates to 0.71 meq copper per 100g.

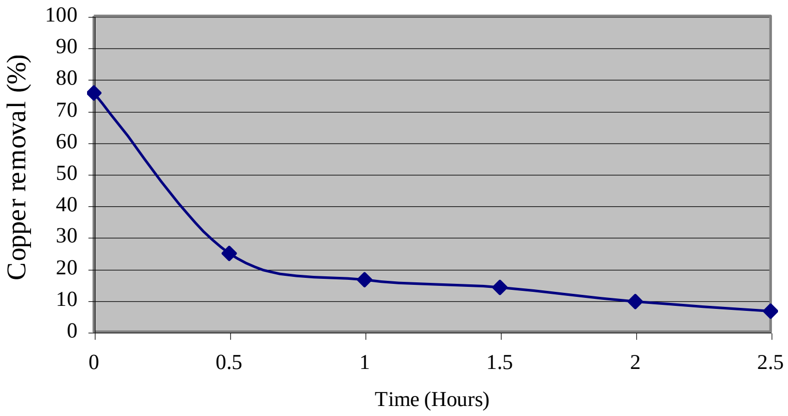


Figure 19**.** The exhaustion curve of the LWA semi calcined granules as a result of passing 640 l of 20 mg/l copper solution.

2.6.2 Coated Calcined Granules

Studies at WBB Minerals also examined the possibility of coating semi-calcined and calcined clays with clay slurries. The clays used to coat the granules were FRS, Lignitic clay, RUGC and Eling Clay, all of which had shown good copper removal abilities in previous experiments. Experimental methods and results are presented in Hook and Smith (2003).

Slurries of 40% solids were prepared. The times that the slurry was left in contact with the granules were varied (15, 30, 60 and 300 seconds). The coated material was dried to constant weight before any further experimentation took place.

A 1 litre glass burette was used to hold 100g of the CCG, this was supported over glass wool at the neck of the burette to avoid blockage. 250 ml of 20 mg/l copper solution was added and allowed to pass over the CCG material.

Figure 20 shows that contact time had only a minor effect on copper removal. Overall RUGC performed best, followed by lignitic clay then FRS.

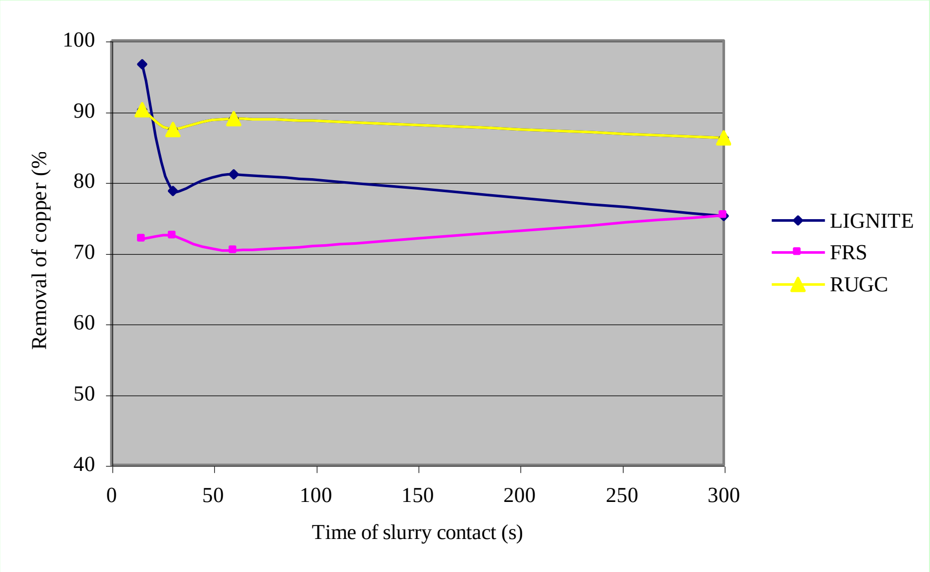


Figure 20. Effect of contact time on copper removal by coated calcined granules

A further experiment used RUGC clay due to its ability to remove copper and its relatively low economic value. An initial 10% slurry was formed by adding 30 litres of water to 3 kg of product. Mixing was conducted using an industrial mixer. 5.589 kg of either LWA calcined or semi calcined material was mixed in a large container with 12.5 kg of slurry. The granules were left in contact with the solution for 60 seconds after which time they were transferred to sieves for draining and drying in an oven.

A clear vertical acrylic column of 6" (152 mm) diameter and approximately 2.0 m in height was used throughout the experiment. Hydraulic flow through the column was controlled by an inflow at the base, consisting of a valve and 15 mm input pipe and an outlet pipe of 15 mm diameter. The LWA granules were poured from the top and allowed to consolidate by gentle agitation. Flow rate was 2.98 l/minute.

The results in Figure 21 show that initially copper removal was high (74-86%) but this declined rapidly with time, falling to 19-28% by the end of the experiment. The calcined granules performed better than the semi-calcined granules.

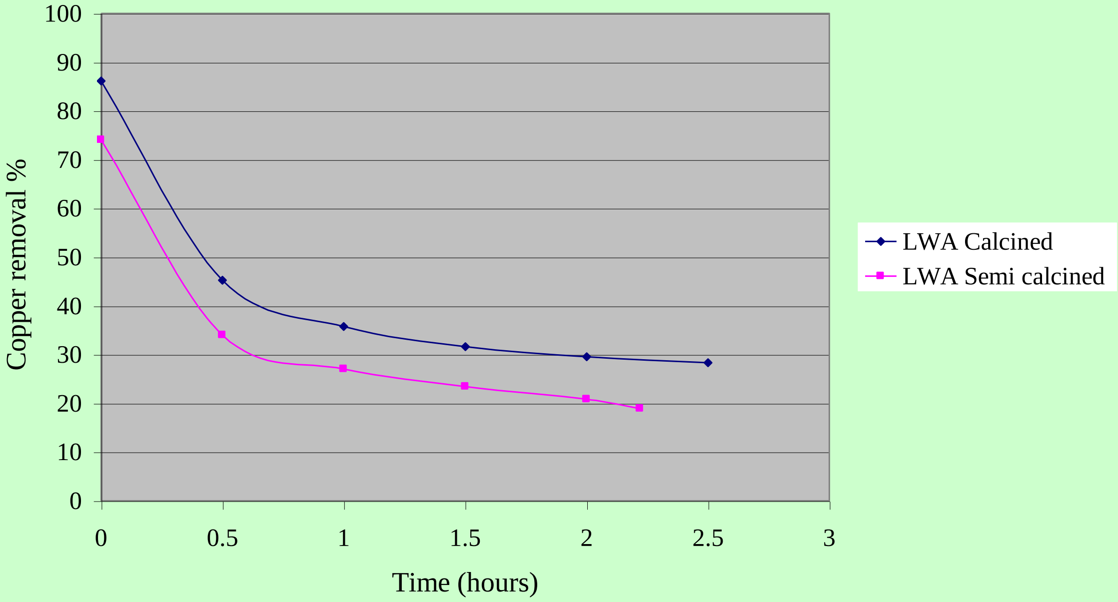


Figure 21. Copper removal by calcined and semi-calcined granules coated with RUGC.

2.6.3 Lignite Coated Calcined Spheres (LCCS)

WBB Minerals have stocks of a low value clay which has a high lignite content. This is referred to as Lignite or Lignitic Clay in this report. We examined the effect of coating FRS clay with a layer of lignitic clay. Experimental methods are given in Hook and Smith (2003).

Briefly, 25 kg of FRS Puraflo (powdered clay) was added to a 100 litre industrial clay mixer (Figure 22). The further addition of 8.5 litres of water and mixing for 15 minutes resulted in the formation of small spherical balls ranging from 2 mm to 20 mm in diameter (the majority were in the range of 5 - 9 mm). To form a less cohesive mixture a further 1.5 kg of powdered FRS was added and mixed for a further 10 min. The spheres were transferred to an oven (100^{o}C) for 12 hours to reduce the moisture content to less than 1%.

As a separate coating process, a lignitic clay powder was prepared. 20 kg of lignitic clay (size range of 0.2 – 2mm) was passed through a rotary mill to reduce the size fraction to between 300μm - 600μm. The spheres in the mixer were then sprayed with a small amount of water to increase the surface moisture content before the lignite powder was sprinkled over the tumbling spheres. The coating was built up in repeated applications of lignitic clay powder, forming an average outer skin thickness of 0.9 mm. It was found that 1 part lignitic clay to 2 parts FRS clay achieved the best results. The spheres were moved to a drying oven (50 °C) to reduce total moisture content to around 0.5 – 1%. It was noted that as the moisture content decreased, the adhesion of the lignite to the coating surface on the clay became less robust and the spheres became brittle.

Figure 22. Clay spheres being prepared in the industrial mixer

The coated spheres were then calcined in a commercial kiln with 3 temperature zones. The temperature in zones one and two needed to exceed 800 °C for calcining to occur. Low transport rates through the kiln caused an excessive amount of calcinification to occur and were therefore undesirable.

Four different products were tested for their ability to remove copper from a 20 mg/l solution. Results are shown in Figure 23. The best performance was with the uncalcined (raw) FRS spheres coated with lignitic clay. The two kiln speeds that were investigated (4.5 mm/s and 12 mm/s) showed that a physically more robust sphere was created by the longer firing time (4.5 mm/s) though copper removal was improved by the shorter firing time (12 mm/s). The shorter firing time caused less calcining of the clay core.

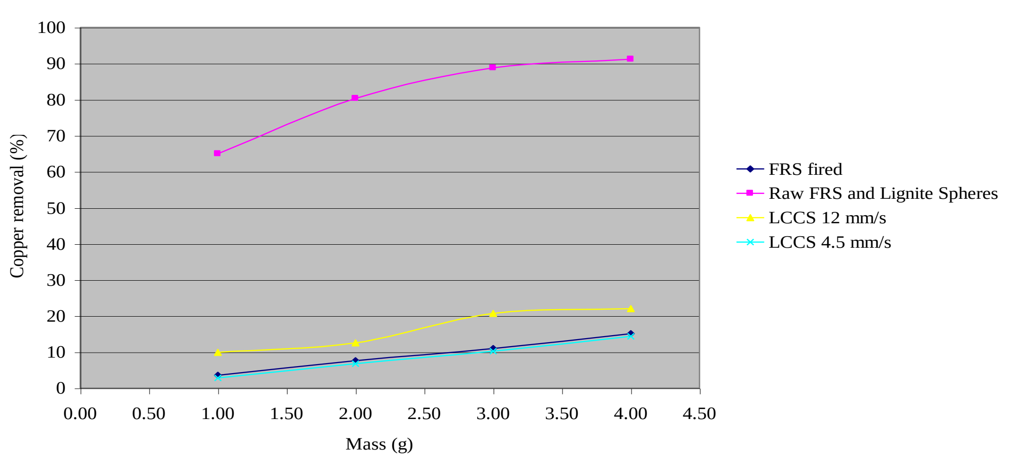


Figure 23. Comparison of LCCS with other Clay Spheres

2.7 Lignitic Clay used in a Permeable Reactive Barrier

Permeable Reactive Barriers (PRBs) need to combine permeability with removal of contaminants. We used the LWA calcined material to provide permeability, and crushed lignitic clay to remove the contaminant (copper). Experimental methods and results have been reported (Hook and Smith, 2003).

The abundance of poor quality lignitic clay within WBB's quarries and its relative low commercial value make it potentially suitable for treating metal rich effluents and streams. Lignite and peat are known to be able to remove metals from solution (Brown *et al*, 2000).

The calcined granules acted as the permeable inactive zones and sandwiched a 'core' of lignitic clay. The inactive zones also acted as filters, suppressing the erosion of the lignite. The quantities of each are given below, from top to bottom of the Perspex column:

1. 1.610 kg LWA calcined granules
2. 2.500 kg Crushed lignitic clay (0.2 – 2mm)
3. 5.000 kg LWA calcined granules

The inflow was administered from a 650 litre solution of ~100mg/l copper solution, at a rate of 1.24 l/min. Flow was controlled by use of a diaphragm pump that fed the solution through the base of the Perspex tube and up through the three zones. Effluent was discharged through the top of the column.

As expected, copper removal decreased with time, but considering the very high copper concentration used (100 mg/l) the results were encouraging. A total of 372 litres of contaminated water were treated over a 5 hour period by 9.1 kg of PRB. The mean removal rate was about 7.5 mg Cu per minute. The total quantity of copper removed was about 2230 mg. If all this was removed by the 2.5 kg of the lignitic clay it would be equivalent to 890 mg/kg.

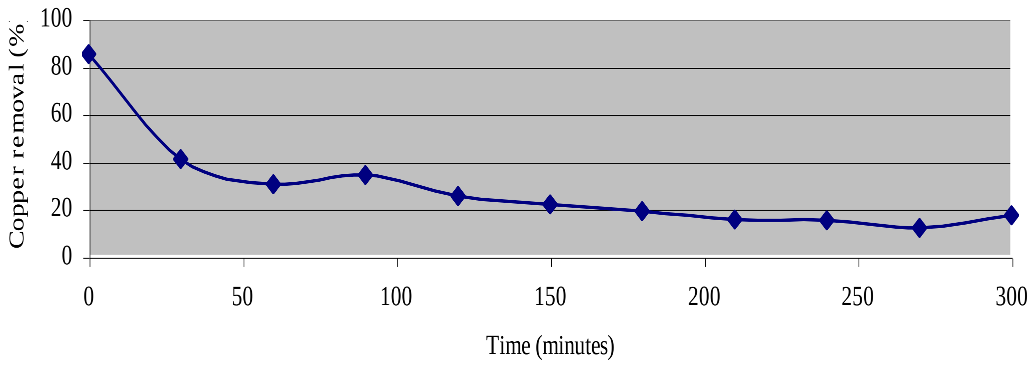


Figure 24 Lignitic clay PRB showing the decrease in copper removal efficiency over time. Flow rate is 1.24 l/min.

2.8 Noodled Clays in Permeable Bags for Emergency Response to Spills

Noodled versions of Lignite, TA and Eling clays were prepared using an industrial extruder, producing noodles 6 mm in diameter (Hook and Smith, 2003). These were then dried to <1% moisture before being used in any experimentation. It was considered that in this form they could be transported in porous sacks enabling them to act as permeable barriers if placed in contaminated streams and rivers.

In all cases the deterioration of the clay due to hydraulic forces caused unsatisfactory results. The erosion of TA was very rapid; there were no noticeable reductions in the flow rate during this time and a period. After 20 minutes all the clay had passed through the sieve. The Eling clay remained intact for 13 minutes after which the upper surface of the noodled clay formed an impermeable barrier effectively rendering the clay useless. The lignite performed very similarly to the Eling clay, remaining permeable for 14 minutes.

3. TECHNICAL AND LOGISTICAL ISSUES

The Eling clay (or equivalent) would be highly effective at removing many metals, including copper, zinc, cadmium and iron. Unpublished data shows that arsenic removal is relatively low, and clay technology may not be appropriate in streams where arsenic concentrations are toxic to aquatic life.

3.1 Disposal of Contaminated Clay

Any method of clay treatment results in relatively high concentrations of metals on the clay. The contaminated clay could be treated in a variety of ways:

- Leaching with acid to form a concentrated liquor suitable for electrolysis
- Smelting at a metal refinery - most likely for high value metals
- Production of bricks for the construction industry
- Production of bricks for long-term storage (eg radiochemically contaminated clays obtained by treating effluents from nuclear facilities)
- Landfill.

3.2 Applications of Clay Technology

We have identified several methods of using clay to treat metal-contaminated streams and effluents:

- Clay in Permeable Bags (for emergency response to river pollution incidents and treatment of factory spills)
- Synthetic Aggregates of Clay in Packed Columns
- Clay in Suspension
- Constructed Wetlands
- "In-stream Treatment"
- Clay lined adits
- Permeable Reactive Barriers (PRBs)

The advantages and disadvantages (or remaining technical issues to be overcome) are considered below.

3.2.1 Clay in permeable bags

Although the Environment Agency has emergency response measures for a range of events and spills that could affect watercourses, they do not have any method of responding to spills of metals, eg from tankers or in fire-fighting water draining from an industrial site. One potential method for emergency response to spills involving metals would be to stockpile permeable bags containing clay at all the EA response centres.

Initial experiments at WBB Minerals (Hook and Smith, 2003) examined the behaviour of dried clay (Eling, Lignite and TA clay) in hessian bags. The water flow caused the noodled clay to disintegrate within 14 minutes, which made the clay impermeable. There was insufficient time to examine whether increased noodle size or drying regime would improve performance. Calcined and semi-calcined Eling clay may offer a combination of good copper removal and resistance to erosion. Another possibility is a core of calcined clay with a coating of raw clay. This coating would erode quickly to produce clay in suspension. It should be possible to have a concentration of suspended solids that would remove metals without causing turbidity problems.

We would expect that any product for use in emergency response would only have to maintain its structural integrity and permeability for 24-48 hours, as the pollution incident would pass downstream in a few hours.

Assuming that further trials showed that calcined Eling clay was effective at removing metals, the technical problems to overcome would mainly be in relation to the bagging of the clay in a form that could be handled efficiently by Environment Agency staff. The EA may also want to be able to recover the bags of clay afterwards.

The main advantage of this method is that it would be cheap and relatively quick to use. In an emergency permeable bags of clays could be delivered into the river from bridges. It would be important to have stockpiles of the bagged clay throughout the country. Industrial premises where metal spills could occur would be able to have their own stockpile at a relatively low cost.

3.2.2 Synthetic aggregates of clay in packed columns

Packed columns of clay in the form of synthetic aggregates would be well-suited to industrial applications and filter beds at sewage works. The main technical difficulties would be removing the exhausted clay and determining whether to leach out metals from the clay to form a strong liquor for electrolysis or send the material to a smelter, brick works or landfill.

3.2.3 Clay in suspension

One of the main concerns over any proposal regarding introducing suspended clays into streams would be the potential deleterious effects on wildlife, both in the treated section of river and downstream areas that may currently support aquatic invertebrates and fish. Clays can be very damaging to aquatic life, either in suspension (when they affect gills and reduce respiratory ability) or when they settle onto the stream bed and can change the substrate and cause blocking of interstitial gravels used by salmonids (salmon and trout) for egg-laying. Mining is one of the causes of increased suspended solids in streams, and studies show that mining of placer deposits can have a deleterious effect on aquatic invertebrates (Quinn et al, 1992).

Aquatonics Ltd is very familiar with the problems caused by sediments in rivers, and therefore ensured that clay technology could be used without having an adverse effect on streams. Calculations for treating a typical minewater affected stream in Cornwall (Darley Brook, see Section 4) with clay in suspension show that any impacts would be minor within the stream, and would be negligible after the confluence with the River Lynher. In addition, experiments with the Eling clay at the University of Exeter showed how effective various flocculants are in removing the clay from suspension

(Rogers, 2001). A polyelectrolyte flocculant (Superfloc C-1596, provided by Cytec Ltd) performed best, and was effective at concentrations of only 0.003% (for a 1% wet weight clay slurry) to 0.005% (for a 3% wet weight slurry).

It would be necessary to install suspended solids monitors in streams treated with clay in suspension, preferably at least a year before starting treatment to give an idea of variability before treatment. This is a relatively inexpensive and simple task.

3.2.4 Constructed wetlands

Constructed wetlands are already used to treat mine water. The only change that we suggest is to deliberately engineer the wetland to have only a shallow layer of water in contact with a clay lining.

The main advantages over conventional constructed wetlands is that aquatic plants are not required. The disadvantage is that any aquatic plants that grow naturally may have to be controlled in order to maintain an intimate contact between the mine water and the clay bed.

3.2.5 In-stream treatment

In-stream treatment has several advantages:

- simplicity - very little to go wrong
- robustness - unlikely to have down-time
- flexibility 1 - could be installed at many different sites down a stream to treat diffuse discharges
- flexibility 2 - as mine water quality improves the length of stream treated can easily be reduced. Conversely extra units could be added if EQS values are tightened.
- low capital costs
- low maintenance costs
- potential for community involvement

The main disadvantage is that a considerable proportion of the total length of stream may need to have treatment, and this is likely to be visible. However, compared to the very poor aesthetic quality of most streams that are adversely affected by mine waters this should not be a problem.

3.2.6 Clay lined adits

In many cases mine water from abandoned mines emerges from adits. These are almost horizontal shafts that were constructed to allow access to productive seams and removal of the ore. These adits could be lined on the base with clay, so that the pH of the discharge is raised and the metal content lowered before the mine water reaches surface streams.

Although there would be technical problems to overcome they are likely to be well within the skills of the mining industry. Apart from the relatively low cost of using clay, the main advantages of treating the mine water underground would be a reduced aesthetic impact and less land required for constructed wetlands or other forms of treatment.

Although many mine water discharges start off close to neutral, there are many examples of the discharge becoming more acidic over time, due to exhaustion of the neutralising ability of calcium carbonate within the rock (Younger, 2002). The acid generating capacity of the pyrite in the rock may not have been exhausted, in which case the pH of the discharge can fall quickly, resulting in higher metal concentrations and greater damage to aquatic life downstream. If the minewater was being treated the treatment method may have to be amended due to the changed pH. Aquatonics believes that these problems could be overcome with clay lined adits, especially if marine clays with a high natural buffering capacity and calcium carbonate content (eg in bivalve shells) are used.

3.2.7 Permeable Reactive Barriers (PRBs)

Permeable Reactive Barriers could be created using clays by forming synthetic aggregates from dredged clays or low value clays such as lignitic clays from the WBB Minerals quarry. These PRBs could be used to treat a variety of metal-rich discharges, eg leachate from landfill or drainage from mine spoil heaps.

PRBs have already shown that they can be an effective method of treating contaminated groundwater (Younger et al, 2002). The largest PRB in the world is at Shilbottle in Northumberland, UK which treats contaminated acidic water draining from a colliery spoil heap. It has a volume of 1080 m^3, being 180m long, 3 m deep and 2 m wide (Younger et al, 2002). It was constructed using a cut and fill method. The trench was filled with 50% limestone, 25% composted horse manure and straw and 25% green waste compost.

Our ideas for a PRB would be simpler, requiring only clay as the fill material in the trench. The purpose of the synthetic aggregate component would be to increase the permeability of the PRB. The size of the synthetic aggregate would be detrmined by the permeability required. Depending on the amount of metal to be removed raw clay could be used to coat the synthetic aggregates.

There are no significant technical problems to overcome, but it will be necessary to commission a full demonstration project before there is widespread acceptance of this new idea. We expect that in situations where the leachate is acidic the Eling clay would be particularly effective at neutralising the leachate and no limestone would be required in the PRB. This has a significant environmental benefit, as it reduces the amount of limestone quarried.

The lignitic clay may be particularly useful in situations where there are other contaminants such as pesticides and hydrocarbons present. PRBs could be created around sites containing contaminated groundwater by digging trenches to intercept the groundwater before it reaches sensitive receptors such as streams or aquifers used for drinking water.

4. CASE STUDY: APPLICATION OF CLAY TECHNOLOGY TO RESTORATION OF DARLEY BROOK, CORNWALL

A visit by Aquatonics Ltd to the River Lynher in June 2000 showed that there were contaminated tributaries that were potentially suitable for treatment using clays, due to the high copper concentrations (approaching 1000 µg/litre or 1 ppm in some stretches) and relatively low flows.

Data for metal concentrations and flows in tributaries of the Rivers Lynher are contained in a PhD thesis (Burton, 1998). The most copper polluted site in that study was in the upper reaches of the Darley Brook. Mean dissolved copper concentrations fell from the highest point on the Darley (D5, mean 766µg/L) to the lowest point sampled (D1, mean 128 µg/L). Maximum copper concentrations fell from 928 µg/L at D5 to 247 µg/L at the lowest site, D1.

Mean pH increased from 6.2 at site D5 to 6.6 at site D1. Maximum flow at D5 was 39 L/s, this increased to 261 L/s at D1. The total quantity of dissolved copper transported during high flows was 1.94 g/minute at D5 (autumn flows) and 3.87 g/minute at D1 (winter flows). If mean copper concentrations are multiplied by mean flows the rate of copper transported is 1.15 g/minute at D5 and 1.45 g/minute at D1. These figures suggests that there is either no natural treatment within Darley Brook or that it is offset by other inputs of copper.

The data for Darley Brook have been used by Aquatonics Ltd to calculate the amount of treatment required using either clay beds or clay in suspension.

We have estimated the amounts of clay required per year to clean up Darley Brook to the point that a range of invertebrates and fish could thrive. The treatment methods considered were:

- constructed wetlands (with the emphasis on contact with a clay bed rather than growing aquatic plants)
- "in-stream treatment" using partitioned flow within the stream over clay beds. This is an original concept that may be patentable and so full details cannot be provided.
- treatment with clay in suspension.

Each of these is discussed below.

4.1 Constructed Wetlands

Darley Brook has a mean copper concentration at D5 of 766 µg/L. We predict that a copper removal rate of 200 µg/sq m/minute can be achieved by a clay bed (which is at the lower end of the removal rates we have achieved). The total area required to remove dissolved copper at site D5 would be 8962 square metres. If this area could be provided as a shallow pond it would be 95m x 95m (approximately 0.9 ha).

In West Virginia the cost to build wetlands is estimated at \$10 per m^2 without plants and \$20 per m^2 with plants (www.wvu.edu/~agexten/landrec/treatment.htm). Due to the generally lower costs in the US we estimate that these figures would be similar in £ per m^2 . The estimated cost of 8962 square metres of wetland (no plants) at Darley Brook is therefore £89,620. The purchase price of the land (almost a hectare including access track) is estimated to be £10,000 including legal fees. The estimated 2500 tonnes of clay required would cost about £100,000 for purchase and transport. The overall cost would therefore be in the region of £200,000 (about £23 per square metre). As the expected life of the constructed clay wetland would be in excess of 15 years (Jarvis and Younger, 1999), the cost per annum would only be £14,000, plus perhaps £4,000 per annum for maintenance. As 3 km of stream would be treated the cost per km of stream per annum would be about £6000.

As a comparison, a small (440 m^2) wetland was constructed at Quaking Houses, County Durham (Jarvis and Younger, 1999). Materials used at Quaking Houses included pulverised fly ash, cattle manure, municipal waste compost, horse manure, and limestone. The construction costs were £18,000 (land purchase was not included), equivalent to about £41/m^2 (Jarvis and Younger, 1999). This was below the UK average for constructed wetlands of £51/m^2. The clay technology developed by Aquatonics Ltd approach therefore seems to be competitive with existing methods.

4.2 In-stream Treatment

If an area of 8962 square metres had to be provided within the existing dimensions of the stream (which is about 2m wide) the total length of clay bed required would be 4481m, which is longer than the total stream length (estimated at 3000m). If the flow can be compartmentalised so that there are 10 horizontal layers of treatment the total length required falls to 448m. We estimate that the amount of clay required per annum would be in the range 500 - 1500 tonnes (dry weight). Much of this clay would be eroded during the treatment process, and this would act in the same way as clay in suspension. Due to the increased copper removal by this eroded clay it is likely that the amount of clay required would be reduced by a factor of 2, ie approximately 250 - 750 tonnes per annum.

4.3 Treatment with Clay in Suspension

Smaller quantities of clay are required if clay suspensions could be used and the clay trapped in settling ponds. Assuming three settling ponds down the stream with an average area of 10m x 10m the total area required would be 300 square metres. In addition there would be a small area for dosing the clay into the stream above each settling pond. The details of the design could only be determined after further field trials, but it is possible to calculate the amount of clay required.

In the laboratory trials it was possible to obtain 83000 mg/kg (8.3%) copper on the clay, when very low clay concentrations were used. This was achieved with a copper concentration of 50 mg/L and a mixing time of 5 minutes. Lower concentrations of copper on the clay would be expected in Darley Brook, due to the lower copper concentration in the water (mean 0.766 mg/L). This would be offset to some extent by the much longer contact time, which could be a few hours. As an estimate it may be possible to get 1% copper on the clay. The amount of dissolved copper transported by Darley Brook at site D5 is estimated to be 600 kg/annum. To remove all of this onto the clay would require 60,000 kg of clay to be dosed in each year. This is equivalent to 0.0019 kg/sec, or 1.90 g/sec, or 1900 mg/s. The mean discharge at D5 was 25l/s (Burton, 1998). If none of the clay added to the stream settled out the additional suspended solids would be 1900/25 = 76 mg/L. At least 67% of this material would need to be removed by settling to meet suspended solid criteria for salmonid rivers if flow remained the same down the stream. However, flow increases down Darley Brook, with a mean discharge of 189 L/s at D1. At the point where the Darley joins the River Lynher the additional suspended solids concentration in Darley Brook is predicted to be 10.1 mg/L, which may be acceptable to the Environment Agency. This water would receive further dilution on reaching the River Lynher.

The above calculations assume that all of the copper is present at site D5, but an estimated additional 160 kg of copper a year is transported at site D1 (approximately 762 kg of dissolved copper per annum). This would require an additional 16,000 kg of clay to be dosed annually somewhere between D5 and D1. At D1 the total additional suspended solid concentration is estimated to be 12.8 mg/L (10.1 mg/L from main dosing plus 2.7 mg/L from additional dosing).

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6. REFERENCES

Brown, PA, Gill, SA and Allen, SJ (2000). Metal removal from wastewater using peat. Water Research Volume 34, 3907 - 3916.

Burton, SM (1998). Evaluation of stream meiofauna as a monitor of trace metal contamination. PhD Thesis, Department of Biological Sciences, University of Plymouth.

Dumat, C; Quiquampoix, H and Staunton, S (2000). Adsorption of cesium by synthetic clay – organic matter complexes: effect of the nature of organic polymers. Environmental Science and Technology, Volume 34, 2985-2989.

Gomer, JS; Yopps,SW; Sandoval, SP & Clark, AE (1992). Copper exchange capacity of clays and their potential effect on in situ copper leaching. US Department of the Interior Bureau of Mines. RI 9396.

Hamilton, QUI; Lamb, HM; Hallett, C and Proctor, JA (1999). Passive treatment systems for the remediation of acid mine drainage at Wheal Jane, Cornwall. Water and Environmental Management Journal, Volume 13, 93-103.

Hards, VL (2000). Glauconite evaluation for Aquatonics Ltd. Unpublished. British Geological Survey Short Report No. MPSR/00/24C.

Hook, ML and Smith, PRJ (2003). Report on Studies at WBB Minerals. March 2003.

House of Commons (1999). Treatment of Acid Mine Drainage. House of Commons Research Paper 99/10.

Jarvis, AP and Younger, PL (1999). Design, construction and performance of a full-scale compost wetland for mine-spoil drainage treatment at Quaking Houses. Water and Environmental Management Journal, Volume 13, 93-103.

Jarvis, AP and Younger, PL (2000). Broadening the scope of mine water environmental impact assessment: a UK perspective. Environmental Impact Assessment Review, Volume 20, 85-96.

McConchie, D; Clark, M and Hanahan, C (1998). The use of seawater neutralised red mud from bauxite refineries to control acid mine drainage and heavy metal leachates. Geological Society of Australia, Abstracts No 49. 14th Australian Geological Convention, Townsville, Australia.

McRae, SG (1972). Glauconite. Earth Science Reviews, Volume 8, 397-440.

NRA (1994). Abandoned Mines and the Water Environment. National Rivers Authority (now the Environment Agency) Water Quality Series No 14.

Quinn, JM, Davies-Colley, RJ, Hickey, CW, Vickers, ML and Ryan, PA (1992). Effects of clay discharges on streams. 2. Benthic invertebrates. Hydrobiologia Volume 248, 235-247.

Rogers, J (2001). Heavy Metal Removal from Wastewaters and Effluents using Glauconitic Clay. Volume 1. BSc Project, Department of Engineering, University of Exeter.

Smith, PRJ (2000a). The Use of a Glauconitic Clay to Remove Metals from Solution. Aquatonics Ltd.

Smith, PRJ (2000b). Use of a Glauconitic Clay to Remove Copper from Effluents Produced During Manufacture of Printed Circuit Boards. Aquatonics Ltd.

Smith, PRJ (2001).Trials of a Prototype Plant using Clay Slurry to Remove Metals from a Mine Effluent. Aquatonics Ltd.

Smith, PRJ & Hook, ML (2002). Comparison of Different Clay Slurries for Removing Copper from Solution. Aquatonics Ltd.

Smith, PRJ (2002a). Use of Waste Clays to Treat Mine Drainage & Industrial Effluents. Presentation to Wheal Jane Link Project members, Camborne School of Mines, September 2002.

Smith, PRJ (2002b). In-Stream Treatment of Mine Water Using Clay. November 2002. Aquatonics Ltd.

Spoljaric, N (1994). Glauconite. In: Industrial Minerals and Rocks (6th Edition) Ed Carr, DD.

Spoljaric, N and Crawford, WA (1978). Glauconitic greensand: a possible filter of heavy metal cations from polluted waters. Environmental Geology, Volume 2, 359-363.

Spoljaric, N and Crawford, WA (1979). Removal of contaminants from landfill leachates by filtration through glauconitic greensands. Environmental Geology, Volume 2, 359-363.

Tullett, D (2001). Heavy Metal Removal from Wastewaters and Effluents using Glauconitic Clay. Volume 2. BSc Project, Department of Engineering, University of Exeter.

Younger, PL (2002). Mines of Information. Chemistry in Britain, February 2002, pp 32-34.

Younger, PL; Jayaweera, A; Elliot, A; Wood, R; Amos, P; Daugherty, AJ; Martin, A; Bowden, L; Aplin, AC and Johnson, DB (2002). Passive treatment of acidic mine waters in subsurface-flow systems: exploring RAPs and permeable reactive barriers. In: Mine Water Treatment: a Decade of Progress, Nutall, CA (ed).