THE USE OF A GLAUCONITIC CLAY TO REMOVE METALS FROM SOLUTION.

Dr P R J Smith, Aquatonics Ltd, Glenthorne, Searle Street, Crediton, Devon, EX17 2DB.
Email phil@aquatonics.com

SUMMARY

A Department of Trade and Industry (DTI) SMART award is being used to fund an 18 month study of the use of a dredged spoil from Southampton Water (UK) to remove metals from effluents and polluted streams.

The results presented here are for the first 6 months of the project, and relate to the characteristics of the glauconitic sediment and its ability to remove metals from test solutions using batch processing.

The effectiveness of the glauconitic clay increased as pH approached neutral, and increased with the quantity of clay present in relation to a standard solution of metals.

At a pH of 7.0 a 2.5% slurry of glauconitic clay (dry weight) removed 99 % of copper and 90% of zinc and cadmium from a 50 ppm solution. These results compare very favourably with previous laboratory tests using glauconite 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).

When the pH and starting concentrations of metals was kept at 50 ppm, but the concentration of glauconitic sediment was 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%.

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%).

At the lowest dosing rate (0.09% dry weight) of the glauconitic clay the concentration of metals in the clay after exposure to 50 ppm of cadmium, copper and zinc was very high (cadmium 1.24%, copper 8.31% and zinc 2.43%). These concentrations may be high enough to allow smelting of the metals from the clay.

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

INTRODUCTION

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 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 approach channels would 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 glauconite.

Clays remove metals in a variety of ways:

- Cation exchange capacity, where metal ions present on the clay (eg Mg and Ca) 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 glauconite 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 1940's for water softening (Spoljaric, 1994). Large-scale use of glauconitic clays to treat industrial effluents and streams affected by mine drainage does not appear to have been investigated. The final 12 months of the SMART funding will be used to produce a prototype treatment plant using clay to treat large volume, metal-rich effluents.

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 3000 km of streams are affected by mine discharges (Jarvis and Younger, 2000). Impacts of mine water discharges include visual/aesthetic (mainly due to discolouration of the water), 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).

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 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 Wheal Jane in Cornwall (Hamilton et al, 1999).

- Chemical treatment systems, for example using limestone or other alkaline materials 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.

Although many discharges from abandoned mines and spoil heaps are acidic, others are circum-neutral (pH 6-7) and may be amenable to treatment with natural clays.

MATERIALS AND METHODS

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.

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). All of the results reported here relate to the second meaning of the term glauconite. 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% (BGS data) 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. The expected salinity range at this site 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 glauconitic clay has been examined by the British Geological Survey using X-ray diffraction (XRD) (Hards, 2000). It was found to be a mixture of 47% clay (ie particles < 2 μm) and 50% silt (2 – 63 μm). The remaining 3% was larger than 63 μm and virtually all organic matter. Most of the clay fraction appeared to be kaolinite, with the remainder being mica, smectite, illite and glauconite. The cation exchange capacity (CEC) of the sediment was 29.5 meq/100g, which is towards the upper end of the normal range of 5 – 39 meq/100 ml (McRae, 1972). The CEC of glauconite varies inversely with the amount of potassium and hence directly with the percentage of expandable layers (McRae, 1972 citing earlier studies).

The metal content of the glauconitic sediment was analysed by ICP-AES. The iron content was 2.9%, other metals were measured at concentrations in the parts per million 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.

Apart from drying and grinding of some sediment, no other pre-treatment (for example separation of different size fractions) was used, as one of the main aims of the research is to investigate the bulk use of this sediment, without the additional costs of pre-treatment. It is likely, however, that the various components of the glauconitic sediment that was used will differ in their ability to remove metals.

The first experiments used a natural mine water from the abandoned Phoenix United mine in Cornwall. This had a copper concentration of about 0.8 ppm. Removal of copper by the glauconitic sediment 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 all the remaining experiments a synthetic mine water was used. This was composed of 50 ppm each of copper, zinc and cadmium. The pH of this synthetic mine water 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. Glauconitic sediment 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.

Analysis of samples was done using the ICP-AES (inductively coupled plasma – atomic emission spectroscopy) technique on a Varian Liberty Series II radial pneumatic ICP. The selected wavelengths were:

Cadmium	228.802 nm
Calcium	393.366 nm
Chromium	267.716 nm
Copper	324.754 nm
Iron	259.940 nm
Lead	220.353 nm
Magnesium	279.553 nm
Zinc	213.856 nm

Standards were made up from 10,000 ppm stock solutions (in 5% nitric acid) obtained from Varian.

Effect of pH

The effect of pH on the ability of a 0.5% slurry (by weight) to remove metals (cadmium, copper and zinc) from 100 ml containing 50 ppm of each metal was assessed. Tests were carried out in 250 ml beakers, constantly stirred for 5 minutes.

Effect of Amount of Sediment

The effect of varying the amount of sediment was assessed using wet weights of sediment ranging from a 5% slurry (2.5 % dry weight) to 0.18% slurry (0.09% dry weight). Tests were carried out in 250 ml beakers, using 100 ml of a stock solution containing 50 ppm of each metal, constantly stirred for 5 minutes.

Metals in the Sediment after Contact with Synthetic Mine Water

Th metal content of the glauconitic sediment after contact with the synthetic mine water was analysed. The sediments were digested with 25ml of concentrated nitric acid (Analar grade) in a 250 ml beaker then heated on a hotplate to boiling point and left on hot plate for a further 15 minutes, then 2% nitric acid (Analar grade) added to bring the total volume to 100 ml. Heating was continued until the volume was reduced to about 50 ml. The contents of the beaker were transferred (with washings) to a 100 ml volumetric flask and made up to the mark with de-ionised water.

Effect of Metal Concentration

The effect of metal concentration on the ability of a 0.5% slurry (by weight) to remove metals (cadmium, copper and zinc) from 100 ml of stock solutions was assessed using starting concentrations of 50 ppm, 20 ppm and 5 ppm. Tests were carried out in 250 ml beakers, constantly stirred for 5 minutes.

RESULTS

Effect of pH

Over the pH range 5.1 – 6.5 the amount of cadmium copper and zinc removed was unaffected by changes in pH (Figure 1). Over this pH range copper removal was 58 – 65%; zinc 20 – 21% and cadmium 25 – 26%. At pH 7.0 copper removal rose to 95%, zinc to 31% and cadmium to 38%.

Effect of the Amount of Sediment

The percentage removal of cadmium, copper and zinc showed a clear relationship with the amount of sediment present (Figure 2). At the highest dose of 5% wet weight (2.5% dry weight) removal of cadmium and zinc was 90% (from a 50 ppm solution). Copper removal was higher, at 98.8%.

Release of Calcium and Magnesium

The amount (as millimoles, mM) of calcium and magnesium released by cation exchange processes during the 5 minute mixing is shown in Figure 3. The calcium and magnesium released is not sufficient to account for all of the cadmium, copper and zinc removed, suggesting that either other metal ions are also exchanged (for example aluminium) or that cation exchange processes are only responsible for some of the metal removal. In the latter case the additional removal of metals would be due to adsorption onto the surfaces of the clay particles and organic matter.

Metals in the Sediment after Contact with Synthetic Mine Water

At the lowest slurry concentration that was tested (0.18% wet weight, 0.09% dry weight) exceptionally high metal concentrations were present in the sediment after it had been in contact with the 50 ppm solution of metals. Cadmium concentrations reached 1.24% (Figure 4), copper 8.31% (Figure 5) and zinc 2.43% (Figure 6).

Effect of Metal Concentration

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 (Table 1). 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

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 %

DISCUSSION

Overview

The results show that the glauconitic clay can remove 100% of copper, 93% of cadmium and 95% of zinc from a starting solution at pH 7.0 containing 50 ppm of each metal and at a sediment concentration of 0.5% (dry weight) and with a contact time of 5 minutes. These results are better than anticipated, and it is clear that clays have the potential to become of great importance in cleaning up a wide variety of industrial effluents, for example from active mines, smelting works, printed circuit board manufacture, and metal plating works.

Many industries produce high strength effluents at relatively low volumes, and these would be readily amenable to a treatment technique that incorporates clay technology either for final polishing of the effluent to meet discharge consents for metals, or to treat the entire effluent.

Economic Assessment

The results indicate that a treatment technology using glauconitic clay could be used to clean up industrial effluents and streams affected by mining. For low volume effluents the amounts of clay required are small, but to treat whole streams large quantities of clay would have to be transported to the site. For example the flow at the Phoenix United mine in Cornwall is estimated to be 66 litres per second. At the lowest dose rate tested in the laboratory (0.18% wet weight) this would require approximately 10.3 t of clay per day, or 3750 t per year. Commercial clays sell in bulk for about £30 per tonne, so the minimum cost for the clay alone would be £112,500 per annum to treat one polluted tributary of the River Lynher. The annual cost for all of the contaminated tributaries of the River Lynher may approach £1 million for the clay alone. This is similar to the annual running costs of the new chemical treatment works at Wheal Jane.

FUTURE DEVELOPMENTS

The main challenge is to develop a treatment method that gets the clay into intimate contact with the contaminated water, but recovers the clay particles so that the effluent meets discharge consents for suspended solids. This aspect of the research will be addressed during the remainder of the SMART award to Aquatonics Ltd.

The concentrations of metals in the clay after it has been used to treat an effluent may be high enough to allow the sediment to be smelted, and the metals recovered. This issue will also be examined during the remainder of the SMART award.

Dr Phil Smith, Aquatonics Ltd, 9 October 2000

REFERENCES

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, Vol 34, 2985-2989.

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, Vol 13, 93-103.

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

Jarvis, AP and Younger, PL (2000). Design, construction and performance of a full-scale compost wetland for mine-spoil drainage treatment at Quaking Houses. Water and Environmental Management Journal, Vol 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, Vol 20, 85-96.

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

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

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

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

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