USE OF A GLAUCONITIC CLAY TO REMOVE COPPER FROM EFFLUENTS PRODUCED DURING MANUFACTURE OF PRINTED CIRCUIT BOARDS

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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 manufacture of printed circuit boards (PCBs) produces effluents containing copper. The aim of these laboratory tests was to determine if a natural glauconitic clay could be used to reduce the concentration of copper in various effluents from a PCB manufacturer.

The tests indicate that natural clays may have a role to play, particularly in final polishing of the effluent. The main problems are the quantities of clay that would be required, large area required for tanks, and disposal of the contaminated clay.

Using the final effluent from the plant a 75% removal was obtained at a clay dose of 3% (wet weight/volume). This was achieved in a 5 minute contact time and a pH of 8.9. At a clay dose rate of 1% (wet weight/volume) 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 1% and contact time of 5 minutes.

METHODS

The ability of the glauconitic clay to remove copper was tested in five separate effluents, all generated by Graphic PLC, a PCB manufacturer, in late October 2000. The removal of copper from the final effluent was assessed at clay dosing rates of 1% and 3%. For all the other effluents the clay dosing was 1% (wet weight/volume).

Wet glauconitic clay from Southampton Water was used in each test. Chemical and physical data on this clay is contained in a previous report (Smith, 2000). Previous laboratory results showed that the water content was approximately 50%. In most trials 1.0g of wet clay was weighed and transferred to a 250 ml glass beaker containing 100 ml of the effluent. A magnetic stirrer was added and the contents of the beaker were mixed at a standardised rate for 5 minutes. Whilst the contents were being mixed a disposable syringe was used to take a portion of effluent that had not had clay added. This was then discharged from the syringe through a disposable 0.2 μm filter into a labelled glass container. After the 5 minute mixing period the sample containing clay was also filtered through a 0.2 μm filter into a labelled glass container. Both samples were then analysed within 1 hour by staff from Graphic PLC, using a Shimadzu AA-6601F Atomic Absorption Spectrophotometer, and the percentage removal of copper was calculated.

Some samples were too acidic to be amenable to treatment using clays, these were neutralised with 1.0 M NaOH.

RESULTS

The results are shown in Table 1. The percentage removal of copper by a 1% clay slurry was highly variable, ranging from 5% to 60%. The highest percentage removal of 75% was obtained using a 3% clay slurry.

TABLE 1. COPPER REMOVAL FROM VARIOUS EFFLUENT STREAMS

COPPER REMOVAL	Final Effluent (A)	Final Effluent (B)	Tank 2, neutralised to pH 8.6	Press Collection Tank	Tank 15, neutralised to pH 7.2	Electroless Copper Rinse
Clay dose (g/100ml)	1.0	3.0	1.0	1.0	1.0	1.0
pH	9.4	8.9	8.6	9.5	7.2	4.4
Copper Before (ppm)	3.93	1.97	0.15	11.80	12.50	1.42
Copper After (ppm)	1.56	0.50	0.08	9.53	11.90	1.03
Copper Removal (%)	60.3	74.6	48.1	19.2	4.8	27.5

DISCUSSION

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 highly variable nature of copper removal from different waste streams of PCB manufacturing is difficult to explain from the data available. High removal rates have been previously recorded using a 1% clay slurry and copper concentrations of up to 50 ppm (Smith, 2000).

It is possible that the EDTA complexed copper present in some waste streams could be less easily removed by the glauconitic clay. The main effluent with EDTA in was the “Electroless Copper Rinse”, and the copper removal from this waste stream was only 27.5% (Table 1). The lowest percentage removal was from Tank 15, after it had been neutralised to pH 7.2. Tank 15 contained floor washings and drainage from the laboratory, and should have been amenable to treatment with the clay.

The clay worked well on the final effluent, removing 60- 75% depending on the clay dose. The total amount of clay that would be required to remove approximately 60% of the copper, with a dose of 1% clay (wet weight) can be estimated from the total volume of effluent discharged per day (180 cubic metres). Each cubic metre requires 10 kg wet weight of sediment, so 180 cubic metres will require 1800 kg of wet sediment. This is a relatively large quantity of material to handle, and the plant in question does not have space to add in the necessary mixing and settlement tanks. It would, however, be possible to incorporate a clay based treatment in new plant being designed, or at an existing plant with more space available. The best solution may be final polishing of effluent in treatment lagoons, as there is no need for the process to be under cover.

Another way of calculating the amount of clay required is to assume that the 8% copper content of the clay which was achieved in some laboratory tests (Smith, 2000) can be replicated in a PCB effluent treatment plant. The PCB plant where the trials were carried out discharges about 500g of copper per day. If all of this could be incorporated onto the clay to produce a sediment concentration of 8% it would only require 6.25 kg of clay per day. This could only be achieved at very low clay dosing rates, with an extended contact period, probably in the order of hours or a few days. This type of treatment would be most suited to extensive lagoons or large exterior tanks. This would be practicable at some locations, and could be economically attractive wherever effluent charges are related to the amount of copper discharged.

Clays also offer a potential emergency treatment in situations where the main plant malfunctions. It would be possible to add dry powdered clay to the final effluent tank to remove at least a proportion of the copper that would otherwise be discharged. This option would be particularly important for those PCB plants that discharge to rivers, due to the high toxicity of copper to fish, especially in soft waters.

ACKNOWLEDGEMENTS

I would like to thank Chris Gould and other Graphic PLC staff for their help with sampling their effluents and analysing the samples from the tests, which were carried out in their laboratory in Crediton, Devon.

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