Applications for Hydrous Ferric Oxide Mine Water Treatment Sludge – A Review

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Abstract Treatment of ferruginous mine waters using aerobic methods results in generation of Hydrous Ferric Oxide (HFO) precipitates, which are normally retained within treatment systems. Increases in environmental awareness upon mine abandonment over recent decades has led to programmes of treatment schemes to deal with polluting discharges. Given the large number of such schemes internationally (more than 60 in the UK at the time of writing), the management of accumulated HFO sludges is becoming an increasing problem. A perspective from a UK Government Authority is presented, considering a range of potential HFO applications and future prospects for sustainable waste management.

Keywords Hydrous Ferric Oxide, HFO, ochre

Introduction

Aerobic mine water treatment schemes, such as those operated by the UK Coal Authority, produce large volumes of ocherous sludge that predominantly comprises Hydrous Ferric Oxide (HFO). The UK Coal Authority is a statutory organisation, responsible for the legacy of abandoned coal mines and coal mining: www.coal.decc.gov.uk. It is estimated that up to 380,000 wet tonnes (at a nominal 5 % solids) of mine water treatment HFO has accumulated within the ≈ 60 UK mine water treatment systems and requires disposal (The Coal Authority 2010). A concerted effort has been made to investigate the potential 'resource' applications for HFO, which would otherwise be disposed of to landfill at substantial cost (both environmental and to the public purse). This paper provides a review of potential applications of HFO generated by mine water treatment.

Applications for HFO sludge

Dudeney *et al.* (2003) reports that the former British Coal Corporation (pre 1997) had established a market for mine water treatment HFO as a pigment within the brick and concrete industry. While this application is the only known (to the Authors) successful full scale commercial venture for the HFO in the UK, a number of alternatives have been investigated. This includes the use of HFO as a feedstock in the steel industry, conversion to a coagulant or as a sorption media in environmental applications; cited examples of which are provided in the following sections.

Pigment applications

Hedin Environmental, based in Pittsburgh PA, has developed a private enterprise marketing mine water treatment ochre generated at coal mine sites in the United States. Hedin's research, sponsored in part by a US Government Grant, identified the iron oxides (HFO) generated by coal mine water treatment were comparable to iron oxides mined for commercial pigments (Hedin 1998). In 1999, the US Patent Office granted Robert Hedin a Patent for the production of pigment grade iron oxides from polluted mine drainage (Hedin 1999). A subsequent report by Hedin (2002) identified economic issues with the production of high-grade iron oxide pigments from mine drainage HFO: primarily the requirement to process the material (screening, drying, calcination, milling and blending) to remove organic debris (vegetation and coal fragments) and reduce water content. While the end product was of a high quality, the costs associated with processing made the material more costly to produce than mined iron oxides, although this may be offset when considering conventional HFO disposal costs. A Brazilian case study presented by Marcello (2008) investigated the use of HFO from active coal mine drainage treatment as a pigment within ceramic tile glaze. The results of the study were interpreted as broadly positive However, most favourable results occurred when the HFO was blended with an industrial standard pigment. Alternatively, the incorporation of HFO in clay bricks as a pigment and filler has been suggested, and the Coal Authority has embarked on a large scale trial in partnership with a local brick works in Co Durham, UK. At present, the process demands the entire output of HFO from the Dawdon Mine Water Treatment Plant, equating to approximately 1,500 wet tonnes/year (approx. 50 %w/w solids).

While consistency of HFO has been suggested as a major issue in pigment applications (Marcello 2008); the presence of toxic substances may be less of a problem: Domínguez and Ullman (1996) successfully demonstrates the successful incorporation of 'steel dust' (a by-product of the steel making industry) within bricks. Characterised by circa 50 % Fe_2O_3 w/w, the dust also contains high concentrations of Pb, Cr, Cd, Ni, and in particular Zn with concentrations of up to 13.8 % ZnO w/w. Incorporation of 20 % material resulted in an inert categorisation of the resultant bricks within Argentinian national regulations.

Adsorption applications

Research over recent years has suggested some novel applications for mine water treatment HFO. Specific applications within the environmental field exploit the sorption capacity of the material:

Phosphate adsorption

It has been widely suggested that HFO can be used in applications for phosphate adsorption from point sources, such as sewage effluent, septic tanks and agricultural discharges (*e.g.* Sibrell and Tucker 2012; Heal *et al.* 2005; 2003). Laboratory scale investigations using HFO generated in Coal Authority mine water treatment systems as a phosphate remover show results of up to 30.5mgP/gHFO (Heal *et al.* 2003). These results are corroborated by a later study in the USA by Wei *et al.* (2008) who achieved adsorption capacity of up to 31.97 mgP/gHFO.

Dobbie *et al.* (2009) goes on to propose that phosphate saturated HFO, produced during nutrient abatement operations as outlined above, could be applied to agricultural land as a soil enhancer. Results of pot and field scale trials showed that the phosphate saturated ochre functioned as a slow release fertiliser, raising pH and posing no threat from the leaching of potentially harmful metals into the soil. Further field scale trials undertaken by Dobbie *et al.* (2009) demonstrated the applicability of mine water treatment ochre as a phosphate removing agent during optimal flow conditions at two sites in the UK. Currently, large-scale trials of phosphate sequestration using pellitised and granular HFO are underway at two Scottish Water Ltd. waste water treatment sites (The Coal Authority 2010; Dobbie *et al.* 2009). Removal rates of up to 65 (±48) mgP/kgHFO/d and 195mgP/kgHFO/d were achieved at the sites, which adopted different test bed configurations, the latter suffering greater rates of clogging.

Proposing what is perhaps a less technically elaborate approach to utilising the phosphate sorption capacity, Neville (2007) undertook a series of laboratory and field investigations into the application of ochre in artificial soils. A mixture of mine water treatment HFO, digested sewage sludge and colliery spoil was investigated as a growth medium, for application in spoil tip restoration projects. Results of this investigation are similar to those obtained by Dobbie *et al.* (2009), showing the retention of bio-available phosphates, whilst mitigating the leaching of potentially harmful metals. A significant benefit of this application is that the consistency of the HFO will not impede the performance of the artificial soil; indeed the heterogeneous nature and entrainment of organic matter was found to improve the overall performance of the material. The use of HFO from passive wetland treatment systems may be particularly beneficial for use in this media where organic matter in the form of reeds, root mass and leaf litter can make up a significant proportion of the sludge.

Metal adsorption

The ion sorption capacity of HFO has been considered for use to stabilise/remove contaminant metal(loid)s from water or stabilise them within soils. In particular, the adsorption of arsenic species (As) to HFO has been well documented (*e.g.* Jang *et al.* 2008; Katsoyiannis and Zouboulis 2002; Manning *et al.* 1998; Wilkie and Hering 1995; Bowell 1994; Pierce and Moore 1982). In a 2005 paper, Doi *et al.* demonstrated at laboratory scale that HFO generated at a coal mine discharge, removed As from solution and also reduced its uptake by crop plants (radishes in this case), indicating that the HFO could be used as a remedial amendment in As contaminated soils. Indeed, research proposals have been submitted to the Coal Authority, suggesting the application of HFO from coal mine water treatment systems for the remediation of As contaminated soils (Hodson 2008). To-date, however, full scale trials for such an application have yet to be completed, although a small amount of HFO has been provided to a commercial remediation company for Pb remediation: Approximately 200 t of dried HFO was screened and blended with other iron minerals, including iron(II)sulphate (Fig. 1) before being provided for use in a pilot trial. One concern with such applications, in particular for the metalloid As, is the risk of de-sorption following a shift in environmental redox conditions that may occur as land use changes at a site (Ascar *et al.* 2008). Such behaviour is perhaps analogous to the problem in Bangladesh where there has been release of As into groundwater that was previously bound to hydrous ferric oxide containing sediments (Polizzotto *et al.* 2006).

Pelletised HFO, produced from coal mine water treatment sludge, was trialled in the field by Mayes *et al.* (2009) as a sorption media to remove Zn from hard circum-neutral mine waters. Removal efficiencies in the pilot unit were relatively high (32 %) for an influent concentration of 1.5mg/L Zn, considering the low resi-

***Fig. 1**. Mine water treatment HFO being blended with iron(II) sulphate at a UK location*

dence time of the system of 49 minutes. Unfortunately, however, an effluent pH of up to 11.8 was observed, due to the dissolution of the portlandite cement binder that released hydroxide ions. The precipitation of calcite armour on the pellets and the inside of the tank (as a product of portlandite dissolution) combined with algae growth provided additional removal mechanisms for Zn. However, upon die-back of the algae in autumn, the system became a net-exporter of Zn: these issues need to be addressed in the design of subsequent systems.

Adsorption of anionic substances has also yielded promising results at laboratory scale: Wei and Viadero (2007) present data from adsorption trials of 'Congo Red' synthetic dye using mine water treatment HFO, yielding 389.1 mg/gHFO removal capacity.

Future prospects for HFO utilisation

Active treatment systems produce HFO on a continuous or batch basis, which often requires prompt disposal due to the lack of sludge retention capacity that is commonly seen in passive wetland systems. Whilst HFO sludge may vary chemically and mineralogically, depending upon the influent water quality, treatment process and reagents applied, it is relatively consistent at any one active treatment site. For this reason, HFO from active treatment plants is well suited as a feedstock to industrial processes, such as use as filler or as a pigment in brick manufacture, where current trials are providing encouraging results; although at present, the Environment Agency has yet to grant approval for the activity to be undertaken outside of waste management regulations (The Coal Authority 2010). The Environment Agency for England regulates waste activities, amongst other duties: www.evironment-agency.gov.uk. An additional benefit of these applications is that potentially harmful metals (such as those contained within drainage from metal mines) could be immobilised within the end products (*i.e.* bricks), thus offsetting a substantial disposal cost of a material that may otherwise be classified as hazardous waste.

Adsorptive applications of HFO within the environmental sector are yet to be realised at any substantial scale, possibly due to the practical and financial obstacles of effectively managing and processing the material in the raw voluminous sludge. Trials are underway at an abandoned metal mine site in the Lake District, UK, where HFO is being applied to remove zinc from a mine water discharge. At this site, large surface area media (extruded plastic sections), coated with HFO at a nearby coal mine water treatment site, are being trialled within a pilot system by Newcastle University. Results of these trials are yet to be published.

Scottish Water Ltd. trials are yielding encouraging results for phosphate removal from waste water, although full scale trials of the design are needed with an effective backwash system or similar to increase lifecycle. If achieved, phosphate saturated ochre from this system could be used as a slow release fertiliser. A large scale field trial of utilising HFO as a component in artificial soils, analogous to the methods suggested by (Neville 2007) is planned for 2014. It is proposed that poor quality (*i.e.* heterogeneous) HFO from reed beds is applied to an unrestored tip, to facilitate the growth of crops that could be used as a biofuel. If successful, the principle could be applied to a multitude of otherwise low value brownfield sites. Production of a preserved horticultural mulch that incorporates the material through a patented process has also been a great commercial success (Deswarte *et al.* 2007).

Other less well documented avenues for HFO utilisation have been investigated by the potable water treatment industry, where a similar material is generated as part of the treatment process. It has been suggested that HFO could be incorporated within a steelworks feedstock (pers comm., L. Dennis, Northumbrian Water Ltd 2012), where the benefit of this application, despite its relatively low volume in comparison to demand, is that the high water content can assist in stockpile dust control (pers comm., R. Lord, Strathclyde University 2012). Observations by Younger *et al.* (2002) of impounded HFO note gradual changes from amorphous (low density) iron hydroxides (*e.g.* ferrihydrite) to more crystalline oxides such as haematite (Fe_2O_3) over a period of 1 – 2 decades. Haematite, the principle ore of iron, is eminently marketable if available in sufficient quantities. Such timescales may appear unrealistic for resource recovery, if not considered in the long-term context of mine water treatment site operation.

While significant potential exists for the application of mine water treatment HFO, ultimately in the UK setting, regulatory obstacles and less expensive alternatives provide the greatest obstacle in realising its resource potential.

References

Ascar L., Ahumada I. and Richter P. (2008) 'Influence of redox potential (Eh) on the availability of arsenic species in soils and soils amended with biosolid', Chemosphere 72(10):1548-52.

Bowell R. J. (1994) 'Sorption of arsenic by iron oxides and oxyhydroxides in soils', Applied Geochemistry 9(3):279-286.

Deswarte F. E. I., Clark J. H., Wilson A. J., Hardy J. J. E., Marriott R., Chahal S. P., Jackson C., Heslop G., Birkett M., Bruce T. J. and Whiteley G. (2007) 'Toward an integrated straw-based biorefinery', Biofuels, Bioproducts and Biorefining, 1(4):245-254.

Dobbie K. E., Heal K. V., Aumonier J., Smith K. A., Johnston A. and Younger P. L. (2009) 'Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater', Chemosphere 75(6):795-800.

Doi M., Warren G. and Hodson M. E. (2005) 'A preliminary investigation into the use of ochre as a remedial amendment in arsenic-contaminated soils', Applied Geochemistry 20(12):2207-2216.

Domínguez E. A. and Ullman R. (1996) "Ecological bricks' made with clays and steel dust pollutants', Applied Clay Science 11,(2–4):237-249.

Dudeney B., Demin O. and Tarasova I. (2003) 'Control of ochreous deposits in mine water treatment', Land Contamination & Reclamation 11(2):259-266.

Heal K., Younger P. L., Smith K., Glendinning S., Quinn P. and Dobbie K. (2003) 'Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution', Land Contamination & Reclamation 11(2):145-152.

Heal K. V., Dobbie K. E., Bozika E., McHaffie H., Simpson A. E. and Smith K. A. (2005) 'Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment', Water Science and Technology 51(9):275 – 282.

Hedin R. S. (1998) 'Potential recovery of iron oxides from coal mine drainage.', Nineteenth Annual West Virginia Surface Mine Drainage Task Force Syposium.

Hedin R. S. (1999) Recovery of Iron Oxides from Polluted Coal Mine Drainage. US Patent and Trademark Office, reference: 5954969.

Hedin R. S. (2002) 'Recovery of Marketable Iron Oxide from Mine Drainage', Presented at the 2002 National Meeting of the American Society of Mining and Reclamation.

Hodson M. E. (2008) 'Research Proposal: Remediation of arsenic contaminated soils with mine ochres'.

Jang M., Chen W. and Cannon F. S. (2008) 'Preloading Hydrous Ferric Oxide into Granular Activated Carbon for Arsenic Removal', Environmental Science & Technology 42(9):3369-3374.

Katsoyiannis, I. A. and Zouboulis, A. I. (2002) 'Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials', Water Research 36:(5141–5155).

Manning B. A., Fendorf S. E. and Goldberg S. (1998) 'Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes', Environmental Science & Technology 32(16):2383-2388.

Marcello R. G. S., Peterson M., Riella H. G. and Bernardin A. M. (2008) 'Inorganic pigments made from the recycling of coal mine drainage treatment sludge', J Environ Manage 88(4):1280-4.

Mayes W. M., Potter H. A. B. and Jarvis A. P. (2009) 'Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide', Journal of Hazardous Materials 162(1):512-520.

Neville K. (2007) 'The use of mine water ochre in artificial soils.’ PhD thesis. Imperial College, University of London.

Pierce M. L. and Moore C. B. (1982) ‘Adsorption of arsenite and arsenate on amorphous iron hydroxide’, Water Research 16(7):1247-1253.

Polizzotto M. L., Harvey C. F., Li G., Badruzzman B., Ali A., Newville M., Sutton S. and Fendorf S. (2006) ‘Solid-phases and desorption processes of arsenic within Bangladesh sediments’, Chemical Geology 228(1–3):97-111.

Sibrell P. L. and Tucker T. W. (2012) Fixed Bed Sorption of Phosphorus from Wastewater Using Iron Oxide-Based Media Derived from Acid Mine Drainage. Water, Air, & Soil Pollution 223(8):5105-5117

The Coal Authority. (2010) UK Department of Energy and Climate Change, Outine Sludge Strategy. Unpublished report

Wei X., Viadero Jr, R. C. and Bhojappa S. (2008) ‘Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants’, Water Research 42 (13): 3275–3284.

Wei X. and Viadero R. C. J. (2007) ‘Adsorption and Precoat Filtration Studies of Synthetic Dye Removal by Acid Mine Drainage Sludge’, Journal of Environmental Engineering 133(6):633-640.

Wilkie J. A. and Hering J. G. (1995) ‘Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes’, Colloids and Surfaces 107:97–110.

Younger P. L., Banwart S. A. and Hedin R. S. (2002) ‘Mine Water: Hydrology, Pollution, Remediation’, Kulwer Academic Publisher, Environmental Pollution (5):464.