Quantifying Ochre Arisings: Output from the UK Coal Authority’s Mine Water Treatment Sites

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Keywords: Acid Mine Drainage; Constructed Wetland; Iron; Mine Waste; Ochre; Re-use; UK

ABSTRACT
A decade into the UK remediation programme, 36 Minewater Treatment Systems are fully operational and assessment of untreated discharge sites continues. Current national ochre production is calculated to be $3.7 \times 10^4$ tonnes annually across the 49 sites assessed, and was found to be increasing rapidly; of this total $2.8 \times 10^3$ tonnes per annum are iron solids. 85% of the annual ochre arisings are contained within operational MTS'. Storage and disposal of generated ochre is a growing problem; the volume produced and the unit disposal costs both continue to rise. This situation is exacerbated by implementation of the EC Landfill Directive, and regional, long-term sustainable solutions are needed. Ochre samples from 28 sites were analysed by ICP-AES, with iron and toxic metal concentrations found to be extremely variable. Waste Acceptance Criteria were applied to the ICP-AES data giving an indicative assessment that 23 sites may be classified as producing non-hazardous waste, and 5 sites classified as potentially producing hazardous waste. The ochre recovery potential of each site was evaluated using five criteria (ochre quality, where collected, iron content, access to potential markets and site access). 9 high potential MTS sites with large arisings were identified, with 15 further sites having reasonable potential.

INTRODUCTION
Since the early 1990s there have been several developments in environmental legislation contributing to current mine water practice within the UK. The UK Coal Authority is a Non-Departmental Public Body established under the Coal Industry Act 1994 and is funded through the Department of Trade and Industry. The 1994 Act was the formal starting point for management of historical mining liability sites, including mine water discharges. Another key piece of UK legislation is the Environment Act 1995. This Act united several bodies as the UK Environment Agency for England and Wales and the Scottish Environmental Protection Agency (SEPA) for Scotland. Both organisations have specific responsibilities to protect the aquatic environment and apportion liability for producers of waste and pollution. At this time a national review of mine waters was conducted, identifying over 100 significant discharges across the UK and prioritising their treatment based on severity of impact.

Treatment of such ferruginous coal associated mine waters typically combines pH adjustment and oxygenation. A wide variety of environmental conditions are encountered and site specific solutions are often required. The UK Coal Authority manages the construction of remedial systems known as Minewater Treatment Systems (MTS). Ferric oxy-hydroxide or ochre is the bi-product of treating the contaminated mine water, generated in significant volumes.

A driver for the timetable of the MTS programme, and this paper review is the European Water Framework Directive (WFD), which sets out a framework for sustainable protection and improvement of natural waters. The WFD (2000/60/EC) came into force in December 2000 and aims to establish integrated catchment scale management and to safeguard environmental quality for the long term. A key objective of the WFD is to improve controlled waters to “good or improving ecological status” by 2015. The UK Environment Agency became the “competent authority” responsible for implementation of the WFD in December 2003.

Part of surface water assessment under the WFD, uses chemical parameters to classify their quality. Strategic improvements are made by prioritising pollutants e.g. dissolved iron with the target of elimination by 2020, to allow these water bodies to pass the Environmental Quality Standards set for each priority substance. The expected achievements of the study are to summarise the MTS programme progress over last decade, and provide a UK wide update on previous information, including that held at The Coal Authority. Particular focus is placed on the volume and quality of ochre arising at the 36 constructed MTS’ and 13 discharges, to provide data which may enable other workers to present practical sustainable uses for this potential resource.

METHOD
Timetable of fieldwork and Scope of the study
Field visits to a total of 32 sites were planned and executed. This included 25 constructed MTS and 7 untreated discharges. 2 sites (Glyncastle, SW Wales and Mouse Water, Ayrshire, Scotland) have been addressed in the last year, and are included within the MTS list in this study.

To further update the study, information has kindly been made available by the UK Coal Authority for a further 11 constructed MTS and 6 untreated discharges which are scheduled for construction during 2005-6. This combined data set of 49 sites is approximately 40% of the prioritised list of discharges across the UK as listed regionally below in Table 1.

<table>
<thead>
<tr>
<th>Region</th>
<th>Constructed MTS</th>
<th>Untreated Discharges</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE England</td>
<td>Whittle, Bates, Acomb, Edmondsley, Horden, Blenkinsopp</td>
<td>Lambley, Great Clifton</td>
</tr>
<tr>
<td>NW England</td>
<td>Ewan Rigg, Deerplay, Old Meadows, Aspull Sough, Bridgewater Canal, Hockery Brook</td>
<td>Clough Foot</td>
</tr>
<tr>
<td>Yorkshire/ Derbyshire</td>
<td>Bullhouse, Caphouse, Silkstone, Fender, Woolley</td>
<td>Sheep House Wood, Shepley Dyke, Jackson’s Bridge</td>
</tr>
<tr>
<td>Fife</td>
<td>Lathallan Mill, Mains of Blairingone, Minto, Frances</td>
<td>Fordell Castle</td>
</tr>
<tr>
<td>Mid/East/West Lothian</td>
<td>Monktonhall, Polkemmet, Cuthill, Blindwells</td>
<td>Elginhaugh</td>
</tr>
<tr>
<td>Ayrshire/Lanarkshire</td>
<td>Kames, Mouse Water, Dalquharran, Pool Farm</td>
<td>None</td>
</tr>
<tr>
<td>SW Wales</td>
<td>Corrwg Rhondda (Nant Gwynfi), Morlais, Ynysanwed, Lindsay</td>
<td>Glyncastle (Resolven), Tan-y-Garn</td>
</tr>
<tr>
<td>SE Wales</td>
<td>Taff Merthyr, Six Belis, Blaenavon</td>
<td>Rhymney, Glyncorrwg, Abersychan</td>
</tr>
</tbody>
</table>

The aims of this study are to:
(i) calculate annual ochre accumulation rates
(ii) analyse the elemental variability of ochre using ICP-AES
(iii) compare the ochre ICP-AES results with the Waste Acceptance Criteria (WAC) as listed in the Landfill (England and Wales) (Amendment) Regulations 2005
(iv) assess the potential for ochre recovery of all study sites i.e. constructed MTS and untreated discharges

Fieldwork and sampling
0.5 l bottles were kept in a clean bag, and rinsed prior to sampling with deionized water to avoid contamination. At MTS sites and untreated discharges, raw inlet water samples were prepared in the field for later analysis.

Flow estimation
Various methods of estimating flow were employed depending on the size of flow and accessibility to it. These included taking readings at V notch weirs and H flumes, bucket and stop watch method and float gauging as outlined by Brassington (1998). Where sites are pumped, instrumental readings were taken. Measurements were repeated 3 times, and the mean calculated. Discharges are generally small, so for the units of litres per second (l/s) have been used preferentially over the SI unit m³/s.

Analysis of Ferrous and Total Iron
The Hach DR/2010 Spectrophotometer was used to determine the amount of Ferrous and Total Iron present in water samples collected. One pillow of the appropriate reagent was added to a sterolin of the water sample immediately in the field. For ferrous iron, the 1,10 phenanthroline method with Ferrous Iron Reagent Powder Pillows was used. After addition of the reagents, the Steralins well shaken to give a coloured Fe²⁺-phenanthroline complex.

The samples were diluted with deionized water by 25 times as standard, but further dilutions of 50 and 100 times were also prepared as necessary. This analytical procedure is accurate for concentrations of up to 3 ppm (3 mg/l Fe) multiplied by the dilution factor; it is a reliable means of quantifying both the ferrous and total iron in collected water samples. The ferrous iron concentration was determined colorimetrically on the day of sampling.

Iron and Metal Content of Ochre Samples
Ochre was collected at MTS’ from settlement ponds and occasionally from the wetlands. Ochre at untreated discharges was also sampled. Ochre samples were stored in a cool dark box prior to analysis. Under laboratory conditions the samples were kiln-dried overnight and powdered by hand. A mass of 0.2 g of dried ochre was weighed on a digital balance. Concentrated hydrochloric acid dissolved the easily leachable iron and other metals into solution for ICP-AES analysis (Inductively Coupled Plasma – Atomic Emission Spectrometry). Iron concentrations for each sample were determined in g/kg.

Data Quality
The ochre samples were analysed at Imperial College London by ICP-AES, using a multi-element calibration based on a design from Thompson and Walsh (1989). During the sample batch, a blank was periodically tested to ensure detection limits conformed to expected values. Three standard calibration solutions were also run periodically between the samples, to correct for instrumental drift.
Duplicates were not prepared or analyzed but the expected operating precision of ICP-AES is commonly approximately 5%. The RSD (relative standard deviation) for the analysed metals in the standard solutions were in the range 0.01-4.22%. This shows a small amount of random error in the precision of our sample analysis.

**Calculations and Error Assessment**

The core aim of this paper is to provide a scoping level overview of the likely volume and quality of ochres produced across the UK, and is not seeking to characterise the mine water and ochre at each of the study sites in depth. Sampling and analysis of water and ochre both significantly contribute to the substantial data uncertainty. Commonly single samples have been analysed (although in most cases compared to two or more years’ worth of monitoring data held at The Coal Authority). Complex temporal variability of the mine water (flow and quality) and ochre (age and distribution) collectively contribute to a combined set of results with high data uncertainty (Dudeney, 2004).

**RESULTS**

**Iron Loading**

The iron content and flow volume of the raw water at each MTS and untreated discharge was measured according to the outlined method. To validate the measurements recorded during our field visits, supplementary data representing typical parameter ranges recorded between 2003 and mid 2005 were obtained, as available, from information held at the Coal Authority (Morritt, 2005a).

Iron loading variation i.e. the flow rate multiplied by the total iron concentrations are plotted for 48 sites (except Blenkinsopp which is excluded to allow presentation of the majority of lower iron loaded waters). The principal sites with large ochre arisings of over 100 tonnes Fe/annum each are labelled on Figure 1 below.

Where it was possible ochre samples were collected for ICP-AES analysis. To develop an understanding of the variability of iron removal efficiency, and how it may vary with iron loading across the MTS network, iron concentrations of the raw water and ochre samples analysed are compared in Figure 2. Surprisingly, there was almost no correlation between dissolved aqueous iron concentrations and the iron concentrations measured in the samples of precipitated ochre (-0.07). There was also almost no clustering of sites within any given region for aqueous/precipitated iron concentrations as shown in Figure 2.
No sites were shown to have high iron concentrations in both raw water, and precipitated ochre as illustrated above in Figure 2. In terms of the raw mine water chemistry variation, several time-independent and time-dependent factors have previously been discussed (Wood et al, 1999).

**Ochre Composition**

Ochre concentrations of iron were at least one order of magnitude higher than the other present elements. The mean iron contents of dried solids by country are:

- **England 55%** (range of 42 to 67% for Sheephouse Wood and Fender respectively) and excluding Caphouse data as the dosing regime has radically changed since the original survey.
- **Wales 53%** (with all data in the range 50 to 60% except one of the Glyncastle discharges).
- **Scotland 47%** (with a large range of 20 to 58% iron, for the dosed Monktonhall and Fordell Castle respectively).

There is no clear correlation of the location of the ochre sample (wetland/lagoon/accretions/drying bay) within remedial systems and typical iron contents recorded. In samples with the highest recorded iron contents, it is likely that analytical errors were significant. There is significant variation of iron contents which will have real implications for the future aim of ochre utilisation on a site by site, and regional basis.

**Current Annual Ochre Accumulation**

The current annual tonnages of ochre produced have been collated regionally for constructed MTS and untreated discharges. A 15% Total Dissolved Solids (TDS) content and a dried iron content of 50% of the ochre are both assumed (the actual calculated UK mean iron contents was 51%). Such an approach can be a useful predictive tool, since the effective management of ochre is reliant on understanding the filling lifespan of ochreous sludge containers, and for design and construction of suitable future facilities. Table 2 summarises the annual regional ochre arisings, iron contents and relative contribution of total arisings for all study sites.

**Table 2: Annual Regional Ochre Arisings**

<table>
<thead>
<tr>
<th>Region</th>
<th>Collected in constructed MTS</th>
<th>Uncontained at untreated discharges</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^7$ Tonnes/yr Fe</td>
<td>$10^7$ Tonnes/yr ochre</td>
</tr>
<tr>
<td>NE England</td>
<td>0.93</td>
<td>1.2</td>
</tr>
<tr>
<td>NW England</td>
<td>0.22</td>
<td>0.29</td>
</tr>
<tr>
<td>Yorkshire/Derbyshire</td>
<td>0.26</td>
<td>0.34</td>
</tr>
<tr>
<td>Fife</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>Mid/East/West Lothian</td>
<td>0.16</td>
<td>0.21</td>
</tr>
<tr>
<td>Ayrshire/Lanarkshire</td>
<td>0.21</td>
<td>0.28</td>
</tr>
<tr>
<td>SW Wales</td>
<td>0.32</td>
<td>0.43</td>
</tr>
<tr>
<td>SE Wales</td>
<td>0.17</td>
<td>0.22</td>
</tr>
<tr>
<td>Totals:</td>
<td>2.4</td>
<td>3.2</td>
</tr>
</tbody>
</table>
The current total UK output of MTS ochre is approximately $3.2 \times 10^4$ tonnes/annum ochre (15% solids, $2.4 \times 10^3$ tonnes/annum Fe content). At untreated discharge sites total ochre arisings are estimated to be $0.5 \times 10^4$ tonnes/annum ochre (15% solids, $0.38 \times 10^3$ tonnes/annum Fe content).

**Likely Future Ochre Accumulation Rates**

The majority of untreated discharges included in this study are at an advanced stage of design or construction. At present the calculated tonnages of iron and ochre are being precipitated into watercourses without containment, however it is still pertinent to consider their relative importance and distribution; the regional balance of ochre production within the network of constructed MTS sites is likely to be altered as a result over the coming years.

To summarise Table 2, the MTS cumulative total ochre arisings are:
- England: $1.9 \times 10^4$ tonnes/annum
- Scotland: $0.66 \times 10^4$ tonnes/annum and
- Wales: $0.65 \times 10^4$ tonnes/annum

The cumulative uncontained total ochre arisings are:
- England: $0.20 \times 10^4$ tonnes/annum
- Scotland: $0.11 \times 10^4$ tonnes/annum and
- Wales: $0.19 \times 10^4$ tonnes/annum

The combined ochre arisings of all 49 sites is calculated to be $3.7 \times 10^4$ tonnes ochre/annum. Relative regional contributions of current ochre arisings are defined in Figure 3 for the whole data set.

![Figure 3: Current Regional Ochre Arising](image)

Ochre arisings vary regionally and contribute the following proportions: NE England (35%), SW and SE Wales combined (22%), all sites in Scotland (21%), Yorkshire/Derbyshire (12%) and NW England (9%).

**Classification of Ochre Recovery Potential**

Each of the 49 sites was assessed in terms of its ochre recovery potential including:
- **Ochre Quality** (toxic metal content, whether chemically dosed)
- **Where ochre collects in MTS system** (lagoon vs. wetland)
- **Quantity of Iron per annum** (<20 tonnes, >20 and <100 tonnes, and >100 tonnes)
- **Location in terms of potential markets**
- **Site and local access conditions** (suitability for lorry removal off site)

By considering these factors collectively, each site was broadly characterised as being of no, poor, reasonable or high ochre recovery potential. 9 key ochre producing sites were identified satisfying all of the above criteria, each producing over 100 tonnes of iron per annum.

The 9 key ochre production sites in order of descending importance are:
- **NE England** (Blenkinsopp 420, Bates 300 and Horden 133 tonnes Fe/annum)
- **SW Wales** (Morlais 150 and Ynyraswed 140 tonnes Fe/annum)
- **SE Wales** (Six Bells 140 tonnes Fe/annum)
- **Mid/East/West Lothian** (Polkemmet 140 tonnes Fe/annum)
- **Yorks/Derby** (Bullhouse 120 tonnes Fe/annum)
- **Fife** (Frances 100 tonnes Fe/annum)
A further 15 sites are deemed to be of reasonable ochre recovery potential, with iron arisings at each site being between 20 and 100 tonnes per annum, 11 are constructed and 4 not. The constructed sites are Deerplay (78), Woolley (65), Pool Farm (53), Caphouse (47), Old Meadows (42), Monktonhall (30), Lindsay (24), Bridgewater Canal (23) and Minto (21). Both Dalquharran (73) and Blindwells (30) represent high future ochre recovery potential, if an ochre collection facility were to be installed. The 4 unconstructed MTS sites of significant ochre recovery potential are Rhymney (87), Jackson’s Bridge (59), Elginhaugh (44) and Fordell Castle (41).

Ochre Quality
Within the 2005 amendments of the Landfill Regulations, WAC are used to delineate hazardous and non-hazardous waste. To broadly evaluate the quality of ochre samples analysed by ICP-AES, the data was processed using the CAT-WasteSOIL tool provided by Atkins Ltd and J McArdo Contracts and is summarised in Table 3.

<table>
<thead>
<tr>
<th>Ochre Recovery Potential</th>
<th>Classification according to CAT-WasteSOIL</th>
<th>No ICP AES data available to assess</th>
</tr>
</thead>
<tbody>
<tr>
<td>High (key producing sites)</td>
<td>Bates, Polkemmet, Bullhouse</td>
<td>Ynysanwed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blenkinsopp, Horden, Mortla, Six Bells, Frances, Blindwells, Dalquharran</td>
</tr>
<tr>
<td>Reasonable</td>
<td>Deerplay, Woolley, Minto, Caphouse, Old Meadows, Monktonhall, Cuthill, Rhymney, Fordell Castle, Sheephose Wood</td>
<td>Elginhaugh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pool Farm, Lindsay, Bridgewater Canal, Jackson’s Bridge</td>
</tr>
<tr>
<td>Poor/None</td>
<td>Taff Merthyr, Kames, Fender, Acomb, Blaenavon, Lathamian Mill, Silkstone, Edmonsley, Clough Foot, Glynycastle</td>
<td>Whittle, Mouse Water, Mains of Blairingone</td>
</tr>
</tbody>
</table>

*Sites in italics are not constructed yet*

Ochre samples from 5 sites are indicatively classified as hazardous using this tool, on the basis of the cumulative concentrations of the following toxic metals: As, Cd, Cr, Cu, Pb, Hg, Ni and Zn. A further 23 sites were assessed using the same tool and preliminarily classified as non-hazardous. All of the sites in Table 3 classified as non-hazardous had appreciable levels of Cr and Ni; Clough Foot additionally had notable zinc contents.

Where ICP-AES data is not available for the sites with high ochre recovery potential this information should be sought to verify their suitability for recovery. Similarly ochre quality data is unavailable for several sites with reasonable ochre recovery potential, and should be acquired.

It is important to note that the ochre quality as assessed using ICP-AES methods and the CAT-WasteSOIL tool characterised a very small sample (0.2g) of a highly variable material, produced in hundreds of tonnes. Greater consideration of how to improve the representativeness of sampling and reliability for future ochre quality assessment is required.

The Future for Ochre Recovery
Data presented here is intended to scope the recovery potential of ochre across the UK. Uncertainty and errors within this data mean that information collated here cannot be used to verify/eliminate the suitability of ochre from a given site for a nominated use. Improvements must be made to ensure a greater level of certainty in the representativeness of ochre samples, which is only likely to be achieved by analysis of larger samples which have homogenized a significant volume of ochre (Dudeney, 2004). By achieving this, it will be possible to begin the
process of matching sites, ochre (quantity and purity) to specific extraction techniques and ultimately sustainable end uses.

Consideration of future ochre arisings will enable better planning on the individual site level, and strategic co-ordination of ochre control and potential re-use at regional and national levels. Ochre volume/tonnage is a central problem and the ideal outlet(s) would have a large volumetric capacity. These bulk processing streams are likely to generate lower revenues per unit mass of ochre than some of the higher end value products researched to date.

By satisfactorily dewatering ochre it is possible to reduce costs of transport, pumping equipment and disposal where required. For this reason, ochre drying facilities are included in all new MTS (Parker, 2003). Current operating practice is neither financially or environmentally desirable and ochre management is likely to become the most important operational consideration; commercially and practically astute solutions are required.

The Role of Legislation
Under the 2005 amendments of the Landfill Regulations, hazardous waste producers will be obligated to ensure correct disposal of their waste. Part of such assessment will include WAC, which will in turn impose a requirement for higher data certainty of waste quality (in this case ochre quality). This may be applicable to certain Coal Authority sites, although the WAC as applied within this paper is intended to be indicative only.

The WFD continues to be the central piece of legislation driving the MTS programme in the UK, but may also present an excellent opportunity for the future. As part of the WFD, River Basin Management Plans will be developed by the EA and SEPA as drafts for consultation, scheduled for 2008-9. This holistic catchment scale assessment will reinforce present forms of cost-benefit analysis implemented for UK mine water remediation. Hydrogeological decision making for long term sustainability, must take into account the natural attenuation rates of dissolved metals in the subsurface; however active treatment is likely to be required in the order of decades at certain sites (Younger and Harbourne, 1995).

Long term sustainability is the key aim of most of the relevant environmental legislation applicable to mine water remediation and ochre reuse. Wherever possible, passive treatment is utilised for a variety of reasons. In terms of ochre recovery potential, passive treatment has one crucial advantage in terms of ochre production and quality over active alternatives: its capability to selectively concentrate toxic elements into smaller volumes of ochre (Swash and Monhemius, 2005). This is highly desirable and allows more careful planning for and disposal or use of ochre. In terms of the Landfill regulations (2005) this may be instrumental in realising methods to reuse ochre from sites deemed to be potentially hazardous.

Coal Authority Challenges
During 2005-6 an ochre strategy will be developed to identify key production locations, their relative ochre accumulation rates, optimal dewatering methods and potential market uses for ochre (Coal Authority, 2005). Regional strategic solutions will be a key part of this national review.

For the future it is possible that potential end users may impose design requirements on ochre collection facilities (especially lagoons, drying bays and site access) in the development of treatment systems for the next selection of sites to be addressed.

CONCLUSIONS
Only a few of the surveyed sites are large ochre producers, and not all of the regions are represented. These key sites should be the focus for linkage to potential markets, with the majority of other sites surveyed appearing to be too remote, produce an insignificant volume and/or lower quality ochre.

Following construction of the first 36 MTS, further progress to assess remediation of the remaining discharges will continue, driven by the WFD timetable at an annual rate of 8 new MTS. It may be expected that over time the raw mine water quality will significantly improve, for the majority of MTS sites. The rate of change of influent water quality into these treatment systems is difficult to confidently predict. With such temporal changes, it is hoped that where active dosing occurs, these MTS sites will become passive schemes, and that the volumes of ochre produced at all MTS will decrease over time (in the order of decades).

To be economic, ochre must be available to reuse markets at a competitive cost including dewatering and transport. Recoverable iron content from MTS is suitable for consideration for a whole suite of end-market uses. Currently, much ochre is unsustainably landfilled; to reduce reliance on this disposal option, ochre utilisation must be addressed with renewed vigour. Legislative changes are likely to dominate which remedial systems are selected for any given situation, and thus govern the type and volume of ochre arising. If ochre is to be realised as a future resource, MTS’ may need to be designed on this basis.

ACKNOWLEDGEMENTS
The author wishes to warmly thank Dr Bill Dudeney, Kim Neville and Barry Coles at Imperial College London for guidance, joint field visits and laboratory assistance respectively. Special thanks go to the environment team of the Coal Authority, particularly Keith Parker MBE, Andy Morritt, Stuart Widdowson, Alex Norton, Ian Watson, Carl
Banton and Steve Hill. The support of the Atkins mine water team and Catriona Woods in Birmingham is gratefully acknowledged.

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