

Characterisation of iron-rich sludge: correlations between reactivity, density and structure.

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ABSTRACT

This paper discusses the behaviour of iron-rich sludge, a problematic waste product of potable water treatment, minewater/groundwater management and hydrometallurgical processing. The work confirmed the highly hydrous and largely amorphous nature of the sludge and the significant differences that occur in reactivity (rate of acid leaching) and density (densification) depending variously upon the mode of sludge formation, pre-conditioning and storage. A structural study using a combination of FT-IR / ATR, XRD and TG/DTA correlated decreases in reactivity with ageing (i.e., with increases in particle size and/or degree of crystallinity) and increases in density with expulsion of weakly bonded water. The work underpinned studies on recycling of water treatment sludge with ion exchange resins and accelerated densification during sludge management.

Keywords

Dewatering; Flocculation; Thickening; Recycling; Wasteprocessing

INTRODUCTION

Abandoned coal mines, hydrometallurgical operations and potable water treatment processes are the main sources of iron-rich sludge. The sludge is a highly hydrous bulk waste product that in addition to iron may contain various proportions of organics and other metals. It is conventionally managed by discharge to rivers or sewers or by retention in lakes, wetlands, tailings ponds or landfills. Another source of iron-rich sludge in lakes and wetlands arises from naturally occurring iron-bearing groundwater (e.g., Carlile and Dudeney, 2000). Because of increasing sludge production and tightening environmental legislation – particularly restrictions on landfill and water pollution (EU Council Directives, 1999 and 2000) – numerous attempts have been made by industry to reduce the environmental impact of sludge and, where possible, to market or re-use the waste or its components. Despite low contained values, limited success has been achieved, e.g., with aesthetically pleasing wetlands and use as an additive in cement production. However, major processing difficulties persist, especially in dewatering (densification) and leaching processes.

Because of its widespread occurrence, there is much empirical knowledge of the characteristics and handling of sludge. However, unaccountably wide variability in properties depending upon sludge history and processing, and lack of clearly identifiable composition and structure, point to incomplete scientific understanding. Notwithstanding many studies that have been published (e.g., Cornell and Schneider, 1998; Jambor and Dutrizac, 1998; Houben, 2003), improvements in understanding remain important because uncontrolled changes in properties continue to affect the practicality and economics of sludge handling and disposal, and also the development of new sludge treatment processes. Recent environmental legislation mentioned above provides a strong incentive for renewed fundamental research and process development towards this end.

As part of an investigation into the re-use of iron-rich sludge (Tarasova, *et al.*, 2002), ion exchange resins have been employed to recover and recycle iron from water treatment waste and minewater ochre. The present contribution provides insight into support on fundamental aspects of this work through comparative acid leaching and densification experiments using recently available ion exchange and dewatering reagents. It employs a combination of instrumental techniques, including FT-IR /ATR, to correlate sludge density and reactivity with structural characteristics (composition, particle size and crystallinity) for sludges of different origin, treatment and age.

THEORY

Iron(III) hydroxyoxides have been extensively described in hydrometallurgical literature (e.g., Jambor and Dutrizak, 1998). They have often been regarded as amorphous ferric hydroxide, $(\text{Fe}(\text{OH})_3)$, by chemists or 'limonite' by geologists (Cornell *et al.*, 1996), but are probably better considered as ferrihydrite. Ferrihydrite, having an approximate composition $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ and XRD pattern of '2-line' or '6-line' typically at elevated temperature and low pH, is normally the first-formed product of ferric hydrolysis in acid media. Because of its unstructured nature, ferrihydrite, when first formed, has enormous surface area (typically $200 \text{ m}^2 \text{ g}^{-1}$), which is chemically active and which can absorb significant quantities of many anions, cations and organic species. It is precisely these properties of fresh ferric hydroxide that account for the widespread use of ferric salts as coagulants in water and effluent treatment processes. Ferrihydrite is metastable with respect to more crystalline products (goethite and hematite) on a variable time-scale. A number of reports consider factors affecting leaching (e.g., Liang *et al.*, 2000; Larsen and Postma, 2001; Houben, 2003), densification (e.g., Fan *et al.*, 2000; Lee and Hsu, 1995) and structure (e.g., Cornell and Schwertmann 1996; Cornell and Schneider, 1998). However, notwithstanding the variety of work that has been carried out on iron oxides and their properties, the different behavioural aspects have yet to be efficiently compiled and correlated, particularly with respect to industrial materials.

In the present context, three main correlations between sludge characteristics are of interest (Fig. 1): reactivity (particularly interaction with ion exchange resins), density (sedimentation, dewatering and drying procedures) and structure (changes in composition, particle size, bonding and crystallinity).

The reactivity of iron-rich sludge with an ion exchange resin encompasses three main rate-dependent processes: leaching, transport, and exchange (Table 1). Leaching is the chemical dissolution of the iron hydroxide, which is dependent on the concentration of hydrogen ions available from the resin. Transport is the dispersion by mixing and diffusion of dissolved ferric ions within the solution and onto the exchange agent. Exchange is the replacement of hydrogen ion on the exchange agent by ferric ion. The rate-limiting step may be any one or a combination of these processes depending upon the conditions.

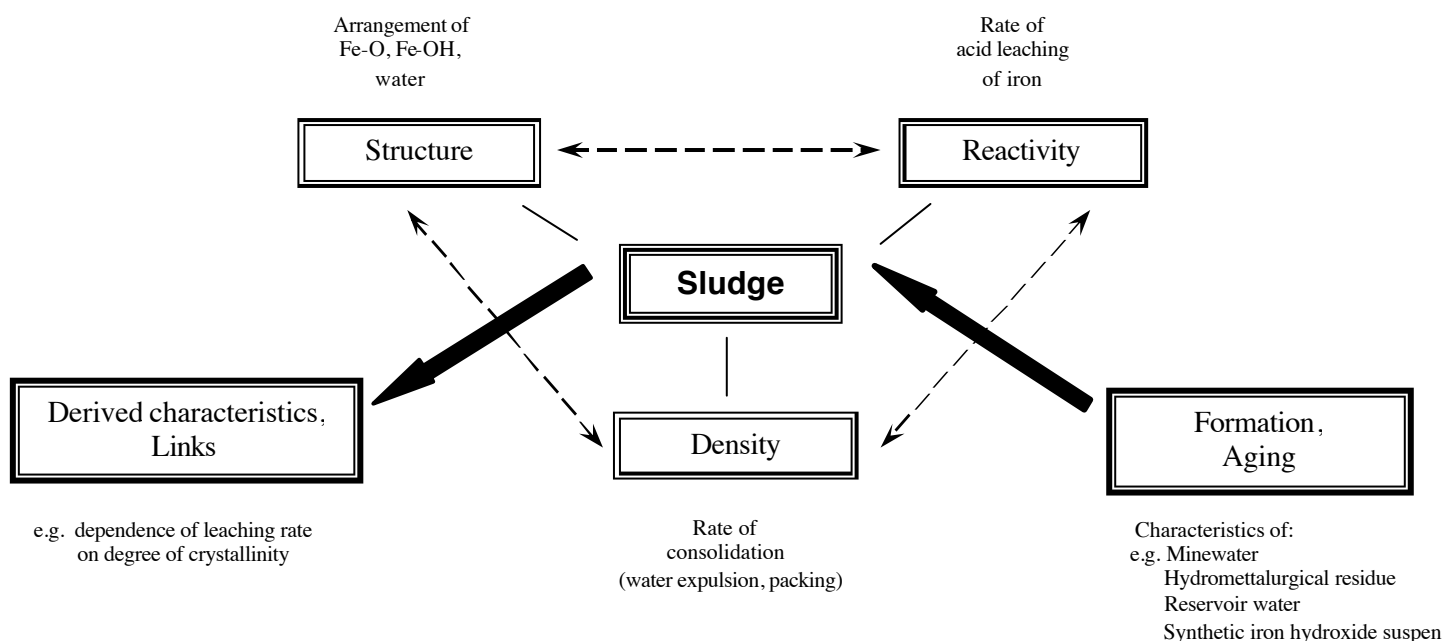
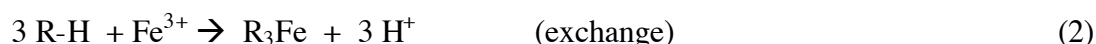
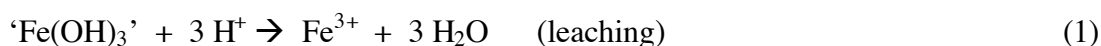


Figure 1. Correlations between the properties of iron-rich sludge.

Table 1. The main variables in sludge reactivity.

Process	Main variables
Leaching	Temperature; pH; ionic strength; surfactants (e.g., colloidal silica); complexation (e.g., with humic and fulvic acids)
Transport	Agitation; resin structure
Exchange	Ion concentration; resin cation exchange capacity

The main measure of reactivity of iron-rich sludge is regarded as the rate of transfer of iron from sludge to resin by means of an essentially steady state leach-transport-exchange process. Thus, after initial reaction (see below), iron is leached from sludge at a constant rate and pH by the steady release of hydrogen ions from the resin, while the ferric leachate is loaded onto the resin (Eqs. 1 and 2).



In general, three types of reaction affect the dissolution of iron oxides (Banwart, *et al.*, 1989): proton-assisted dissolution, ligand controlled dissolution (complexation) and reduction. These reactions are surface controlled and can be inhibited in the presence of ligands which are able to block reactive sites. In ion exchange dissolution, proton-assisted reaction is assumed to predominate. Because of

initial rapid exchange of dissolved cations, e.g., calcium, with hydrogen ion on the resin, initial leaching is also rapid before the steady state develops.

Densification of iron-rich sludge implies increased mass of iron per unit volume, which may occur by loss of water and/or increase in structural order. Water may be classified as free, interstitial, surface or bound (Fig. 2), although different authors employ different interpretations (e.g., Vesilind and Martel, 1990; Lee and Hsu, 1995; Klein and Sarsby, 2000; Herwijn, 1992). Iron-rich sludge usually contains well over 70% water in its structure, and therefore water expulsion leads to a consolidated sludge with a considerable volume reduction. Free water removal typically occurs via unassisted gravity sedimentation (although flotation is possible) and yields products containing up to 15% solids. Some free, interstitial and surface water can be removed mechanically, e.g., by centrifuge, freeze-thaw cycles and/or application of polyelectrolyte surfactants, to achieve 15-30% solids content (e.g., Lee and Jean, 1999; Parker and Collins, 1999; Chen *et al.*, 2001). Solid content in the same range results from accretion or encrustation (Dudeney, *et al.*). Bound water removal requires drying (evaporation) and/or thermal degradation of the particles. Thus, large changes in density can be attributed to different types of processes, the details of which remain controversial (Sato, 1982; Katsiris and Kouzeli-Katsirit, 1987; Robinson and Knocke, 1992).

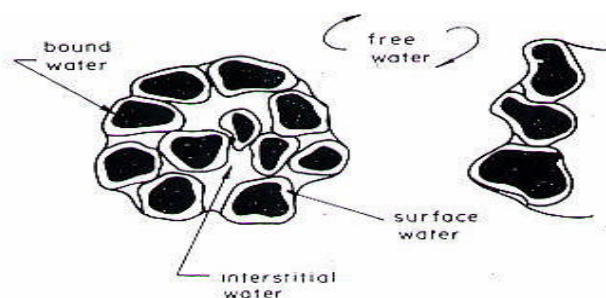


Figure 2. Water liquid distribution in sludge flocs (after Klein and Sarsby, 2000).

Structural analysis by FT-IR /ATR, XRD and TG/DTA provides information on phase composition, bonding and crystallinity. It is a key methodology for sludge characterisation and assessment of reactivity, dewatering, development of crystallinity and aging. For instance, FT-IR is able to rapidly determine bound water content and structural order. The particular FT-IR /ATR equipment employed (see experimental) operates into the far infrared region (where iron oxides exhibit characteristic adsorption peaks) on both solid and slurry samples without any pre-conditioning. Classical XRD and TG/DTA provide complementary structural information on crystal order and water content respectively.

EXPERIMENTAL

1. Materials

Ochreous minewater sludge was collected from two abandoned coalmine sites, namely Bullhouse (BH) and Woolley (W), South Yorkshire, UK (Laine and Dudeney, 2000; Demin and Dudeney, 2003). Water treatment sludge was obtained from the sedimentation treatment plant of the Yorkshire Water Services Langsett WTW, South Yorkshire, operated with iron sulphate coagulant. Commercial iron coagulant (EA West), containing ferric sulphate [$\text{Fe}_2(\text{SO}_4)_3$] (19.1 % w/v Fe), was diluted with deionised water (DW) and/or iron depleted minewater (IDMW), to form hydrolysed ferric hydroxide flocs, as a 'model' iron-rich sludge. Natural minerals (goethite, limonite, hematite) were supplied by the Natural History Museum (London, UK). Synthesised goethite and ferrihydrite were also employed as basis for comparison. They were precipitated following the procedures described by Schwertmann and Cornell (2000). Lewatit MonoPlus S100 strong acid ion exchange resin in hydrogen form was obtained from Bayer (Germany). The resin beads were composed of a chemically and osmotically highly stable styrene-divinylbenzene copolymer. The resin was monodisperse with a mean bead diameter of 0.6 ± 0.05 mm, and had an ion exchange capacity of 2.12 mEq/ml. Dispex 2695 dispersant (acrylic polymer in aqueous solution) was provided by CIBA Specialty Chemicals (Water Treatments) Ltd. Four high molecular weight polyelectrolytes (polyacrylamides), Zetag 7878, Zetag 7867, Magnafloc 110L and PC-320 were used in sludge conditioning. Zetag 7878 is a high charge density, cationic polymer; Zetag 7867 is a medium charge density, cationic polymer and Magnafloc 110L is a medium charge, anionic polymer - all obtained from CIBA. PC-320, a product from the Taiwan Polymer Company, is a cationic copolymer of acrylamide and diallyldimethyl-ammonium chloride, with a molecular weight of 1.2×10^7 on average and charge density (20%), which is the mole percent charged monomers quoted by the manufacturer.

2. Equipment

A sedimentation jar tester (Standard Jar tester PB-700, Phipps & BirdTM) was used to monitor the rate of acid leaching. The apparatus contains six paddles, which stir the contents of six 2-litre containers. The method allows continuous mixing under uniform, comparative or replicated, conditions at RT (23-25°C). The change in pH and concentration of iron remaining in solution with time were tabulated. Adjustments in pH, variations in iron or resin dose, mixing speeds, and testing of different sludge types were possible. Infrared analysis was mainly carried out using an FT-IR/ATR (Vector 22 FT-IR, Bruker Company Ltd.) with caesium iodide beamsplitter (spectral range of $4000\text{-}220\text{ cm}^{-1}$), especially designed to record absorption bands into the far infrared region. For this purpose the standard system

was equipped with the Golden Gate diamond Attenuated Total Reflectance (ATR) accessory (single internal reflection system), fitted with a KRS-5 lens for the frequency range 300-200 cm^{-1} . In the case of single reflection diamond measurements, contact efficiencies were as high as 100% for both liquid and solid/powder samples, and high quality spectra could be therefore generated for both slurry and sludge cake samples. Infrared measurements were also made using a Diffuse Reflectance FT-IR (DRIFTS), on an Excalibur FTS-3000 with a KBr beamsplitter (samples needing dilution before analysis) (BioRad Company Ltd.), and an ATR-FTIR, with a Normal Horizontal ATR accessory with a zinc selenide crystal (spectral range of 4000-600 cm^{-1}) (samples needing no previous treatment).

3. Methods

3.1 Reactivity

Sludge floc precipitation was carried out under conditions related as closely as possible to those employed at Langsett WTW, i.e., initial nominal iron concentration 12 mg/l Fe and pH 5.3-5.8. Thus, 0.12 ml of 19.1 % Fe w/v commercial coagulant was diluted to 2 l in tap water stirred at 110 rpm and pH adjusted with acid and/or alkali. After ten minutes (when the iron hydroxide flocs had fully formed) 3 or 6 ml of wet resin (i.e., 5 or 10 times stoichiometric excess) was added to leach the flocs. Total iron concentration and pH were recorded at time zero and set time intervals (0, 5, 10, 15, 30, 60, 120 minutes, etc) thereafter for up to a day, under continuous stirring. The resin beads remained largely on the bottom of the jar tester beakers and did not interfere with the sampling procedure. Total iron was determined in duplicate with a portable UV Hach spectrophotometer using the o-phenanthroline method at 510 nm. Preliminary experiments with 6 replicates, each of 2 l, stirred at 80/min for 3 hours indicated a precision of ± 5 %. Experimental slurries of ochre and water treatment sludge were preconditioned by means of a high speed blending for 2 minutes to reduce the effects of particle accretion. In these cases precision was approximately ± 10 -20 %. Variations of the basic method involved: (i) calcium sulphate additions with calcium concentrations in the range 5-250 mg/l in DW in the place of tap water (ii) IDMW dilutions in DW to prepare solutions of different ionic strengths with conductivity of 0.16, 0.20, 0.29, 0.62, 0.82 and 1.00 mS/cm and (iii) dispersant additions; a few drops of Dispex 2695 in the sludge suspension (iv) temperatures of 40 and 80 °C under constant stirring at 210 and 410 /min in a separate Quickfit apparatus.

3.2 Densification

Changes in sludge density were determined by measurements of sludge volume and determination of residual water by oven drying at 103°C overnight. Conditioned sludge was prepared by sedimentation and water expulsion in three ways: chemical precipitation, surface chemical reaction and bulk

freeze/thaw processing. For chemical precipitation, historical aged sediments originating from BH mine water (nominally 60 mg/l Fe) were assessed. The sludge was formed in 1999 in 90 l tubs filled directly from the mine water cascade under the following conditions: (a) no additions, (b) alkali (NaOH) to pH 7 (about 1/3 of full neutralization) (c) alkali (NaOH) to pH 11.5 (full neutralization) and (d) hydrogen peroxide. After two weeks standing the supernatant was decanted and the sediments were transferred to measuring cylinders. The volumes of the sediments were thereafter recorded at suitable intervals over 2-4 years. For surface-chemical reaction, freshly sedimented mine water ochre and accretion ochre were employed and conditioned with single and dual polyelectrolyte additions. The first mentioned was obtained by allowing fresh BH minewater to sediment in a 225 l tank for 2 weeks; the second by scraping ochre from pipework accumulations. Polymer of 0.1% w/w was prepared according to manufacturer's recommendation: 0.2 g of the polyelectrolyte (50% active solution, 50% oil) was dissolved in 100 ml of water with stirring for 30 min. In single polyelectrolyte conditioning, about 0.4 ml of the prepared polyelectrolytes (Zetag 7878, Zetag 7867 or Magnafloc 110L) was mixed with 100 ml of freshly sedimentated ochre (12% solids) in a graduated cylinder. The sludge suspension in the graduated cylinders, after three inversions, was monitored for sedimentation rate. In the case of fresh accretion ochre (20% solids), the ochre was mixed as above, with Zetag 7867 and a combination of dual polyelectrolytes (a) Zetag 7878 with Zetag 7867, and (b) Zetag 7878 with Magnafloc 110L. The concentration ratio of the two polyelectrolytes in each pair was 1:1 in all experiments. Conditioned sludges were carefully transferred to centrifuge tubes and centrifuged at 1500 /min for 10 minutes. For bulk freeze/thaw processes, a volume of 15 ml of fresh slurry (2-10 % w/v solids) was placed in each of ten 20 ml Steralin tubes. The tubes were cooled in a refrigerator (3 °C for one day) and freezer (-18 °C for one day) before the solids were thawed at 80 °C for 1 hour (Chen *et al.*, 2001) and centrifuged. The difference in sludge height after centrifugation was observed. The supernatant was decanted and the dry solids content of sludge cake was determined after drying at 103°C for 24 hours.

3.3 Structure

FT-IR, XRD and TG/DTA were employed with fresh, aged and conditioned sludge samples according to standard procedures. In the case of FT-IR analysis, both dried and slurry samples were tested for in the wavelength range 4000-200 cm^{-1} , typically under the following conditions: resolution 4 cm^{-1} ; scan time and background scan time 5 min. Samples, either a drop of sludge or a small quantity of ground powder, were placed on the crystal surface of the ATR accessory and clamped in place. Each sample was analysed once with XRD, whereas replicates were employed with FT-IR and TG/DTA.

RESULTS AND DISCUSSION

Reactivity

Preliminary work indicated, as expected, that the rate of leaching of ochreous sludge with a strong acid cation exchanger was essentially bimodal in character, i.e., initially rapid reaction at variable low pH followed by slow steady state leaching at higher constant pH. At set initial pH (5.3-5.8) and sludge dispersion concentration (12 mg/l Fe), the kinetics were primarily dependent upon four parameters: ratio of resin to iron-in-sludge, ionic strength of the medium, temperature and stirring rate, i.e., the rate of reaction increased with all of these parameters (Figs. 3-5). Thus, more resin provided more hydrogen ion and exchange sites, higher ionic strength (greater concentration of dissolved cations, e.g., calcium or mixed ions found in minewater) released greater concentrations of hydrogen ion at the start of the reaction, elevated temperature increased the rate of chemical dissolution and faster stirring improved reactant transport and contact within the system. These observations were consistent with the reaction sequence outlined in Table 1 and with analogous work by Wong and Dudeney (1991) on alumina sludge. They were also complementary with results from the literature on direct acid leaching of iron-rich sludge and crystalline minerals without resin. Thus, the initial kinetics with resin were analogous (although at different pH) to those observed when making all the acid available at the beginning of the reaction (Henman, 1996) while the steady state phase was similar to leaching in an essentially constant concentration of acid (Houben, 2003).

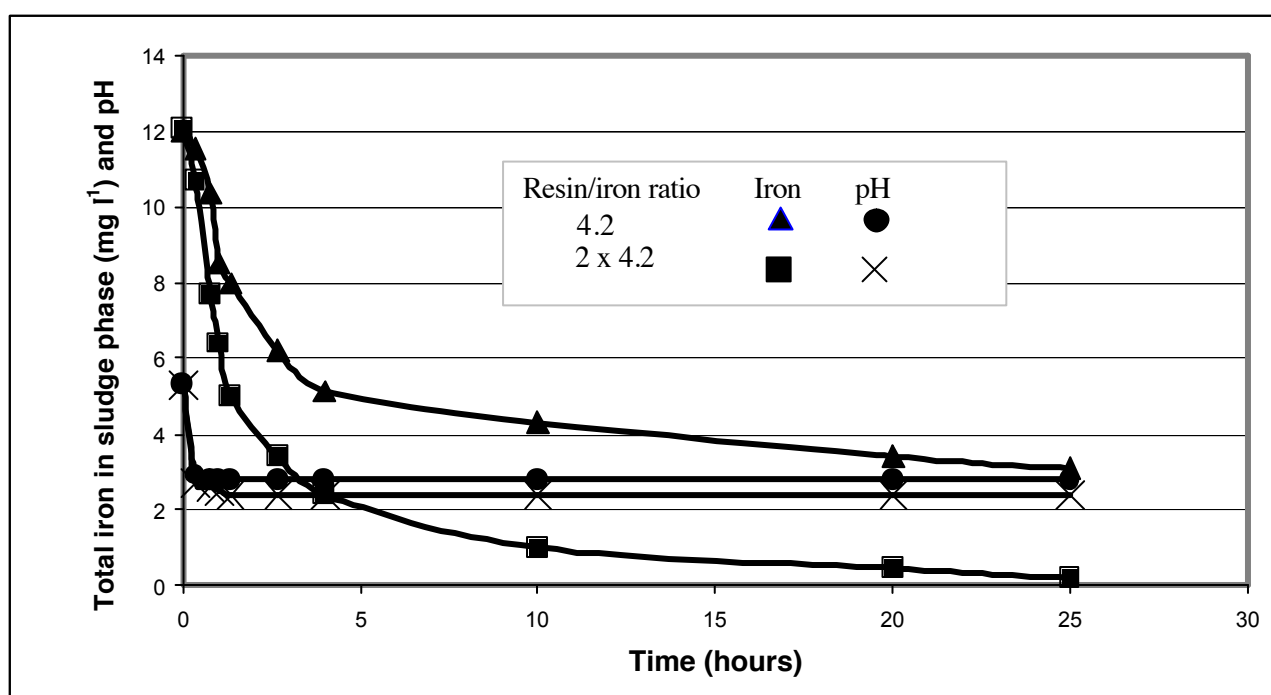


Figure 3. Time dependence of iron concentration and pH for leaching synthetic sludge with two stoichiometric ratios of resin at 24°C, initial conductivity 0.83 mS/cm.

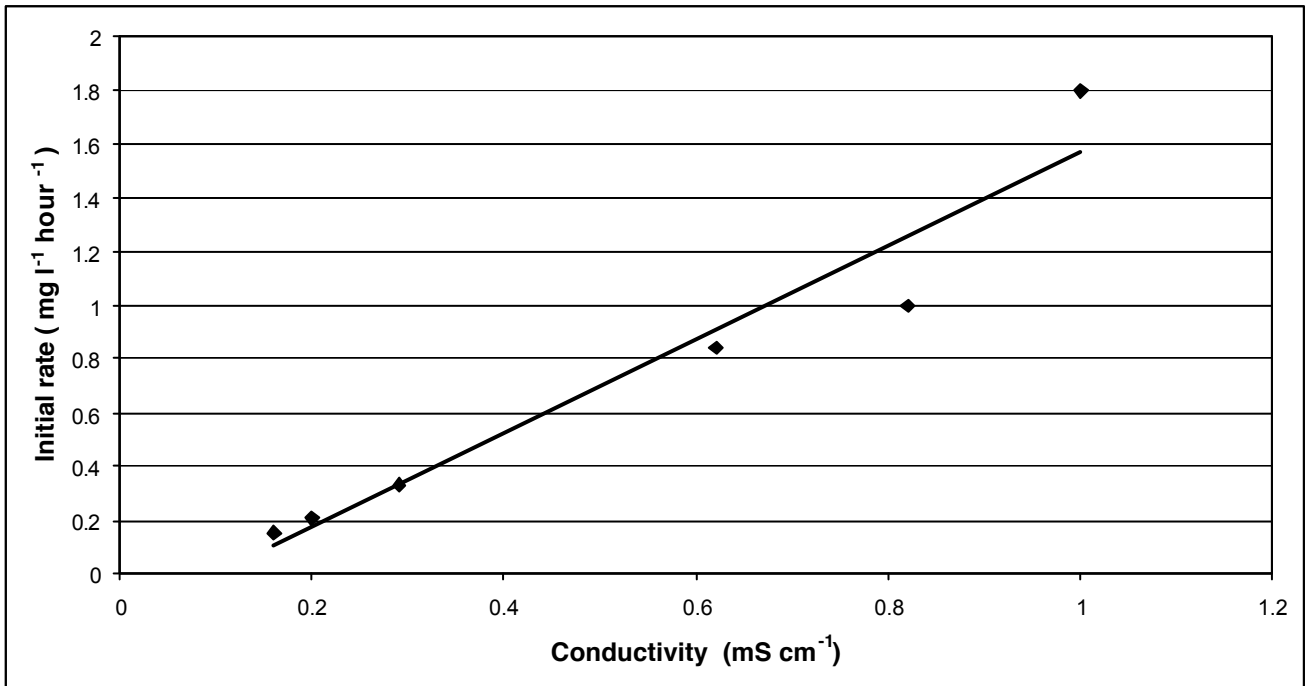


Figure 4. Effect of initial conductivity on initial rate of sludge leaching at 25°C.

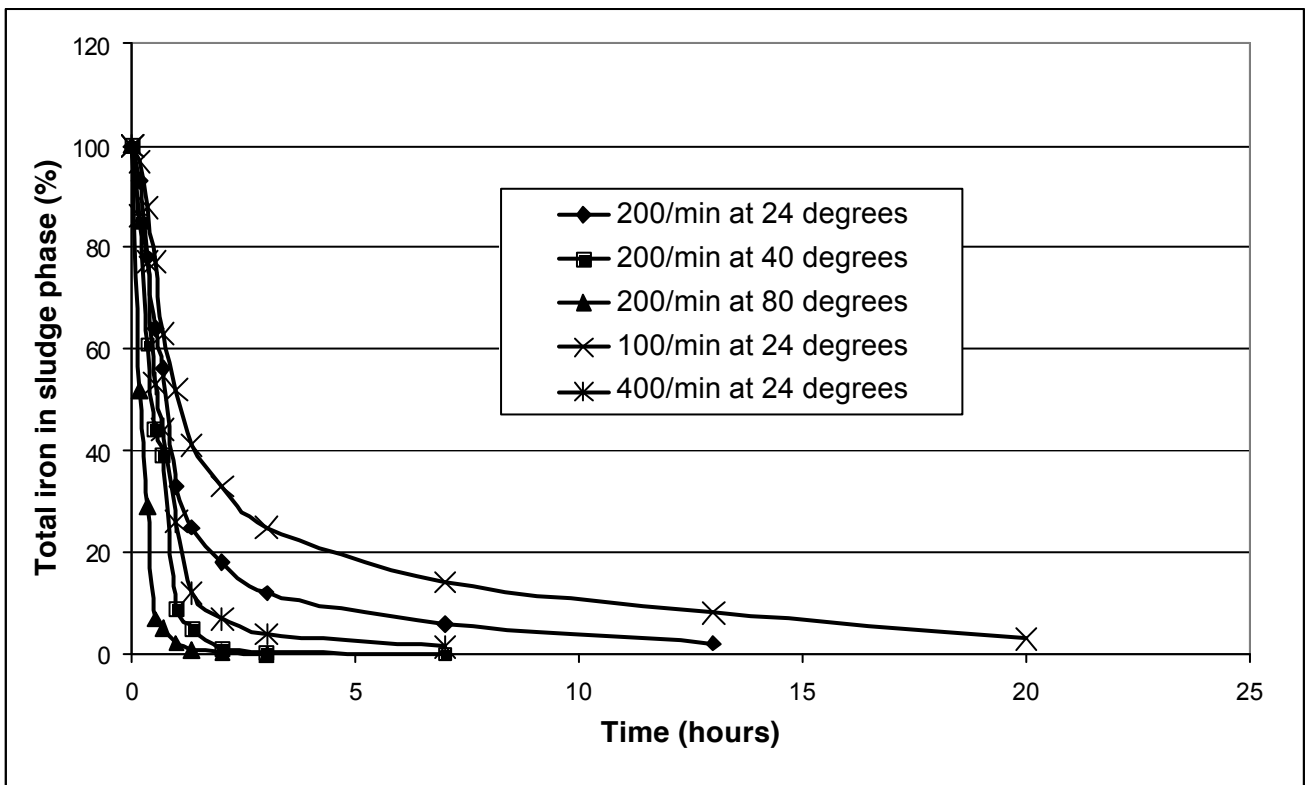


Figure 5. Time dependence of iron concentration for leaching synthetic sludge at varying stirring rate and temperature.

In order to determine the leaching rate dependencies of structural parameters (composition, particle size and bonding), the above mentioned parameters had to be kept constant as far as possible at values consistent with complete sludge dissolution and with conditions normally available in water treatment: ratio of resin to iron-in-sludge (initial 5-10 fold stoichiometric excess), ionic strength (830-1000 $\mu\text{S}/\text{cm}$), temperature (25 °C) and stirring (110 /min). Reactions had then to be maintained for lengthy periods (up to three days) while periodically sampling potentially unstable dispersions for analysis. Sampling was impeded by the tendency of sludge particles to aggregate and, particularly for larger particles, to form impact accretions or loose accumulations on internal surfaces of the equipment – processes that could be controlled only partially by initial high energy blending of suspensions (and not at all by use of surface chemical dispersants, see later). As indicated earlier, under these conditions overall precision was reduced to $\pm 10\text{-}20\%$ and only relatively large changes in rate dependencies could be measured with confidence.

Figs. 6-8 show composite plots of leaching behaviour for sludge of different origin, pre-treatment and age, respectively. In Fig. 6, the rate of leaching decreases in the order synthetic sludge, water treatment sludge and mine water ochre. As the synthetic sludge had been precipitated in the laboratory by rapid hydrolysis of iron(III) sulphate, the particles should have maximum structural disorder, i.e., have almost complete amorphous character, and minimum ultimate particle size distribution (as against loose floc size distribution). These conditions were thus expected to give an upper limit for reaction rate. The water treatment sludge was formed in a similar way in industry, but was, of course, contaminated with reservoir water impurities, particularly humic and fulvic acid residues. These residues clearly impeded reaction (presumably by blocking hydroxyl groups on the sludge), but not greatly. Mine water sludge normally forms by slow aerial oxidation of iron(II) followed by rapid hydrolysis and precipitation of iron(III) hydroxyoxide. As the sludge employed in the present work therefore precipitated from homogenous solution over a relatively long period of time (about one week), it was expected to have better developed structure (see later) and lower reactivity. Fig. 6 shows that the rate was in fact approximately half that of synthetic sludge. No doubt part of this difference resulted from different impurity levels, i.e., different minerals and less organics than water treatment sludge. Woolley ochre gave similar results.

In Fig. 7, the rate of leaching is seen to decrease significantly with addition of Dispex dispersant for both synthetic and mine water sludge. The effect was greatest for synthetic sludge, presumably because a greater proportion of active groups were available for blocking. Comparison of Figs. 6 and 7 suggests that the attachment of the dispersant to sludge surface groups is firmer than with humic acid

derivatives. Similar results (not shown here) were obtained with polyacrylamide flocculants. These effects fit well with well-established applications of organic surfactants, e.g., of polyelectrolytes in sludge flocculation, but mitigate against efficient leaching. Conversely, addition of sodium silicate (often employed as a dispersant and often present in mine water) had an insignificant effect on leaching rates. In principle, leaching rates can be increased by addition of catalysts, e.g., iron(II) or copper(II) cations. However, specific application would be impractical in water treatment, although a small proportion of iron(II) is always likely, on thermodynamic grounds, to be present and to contribute to observed leaching rates.

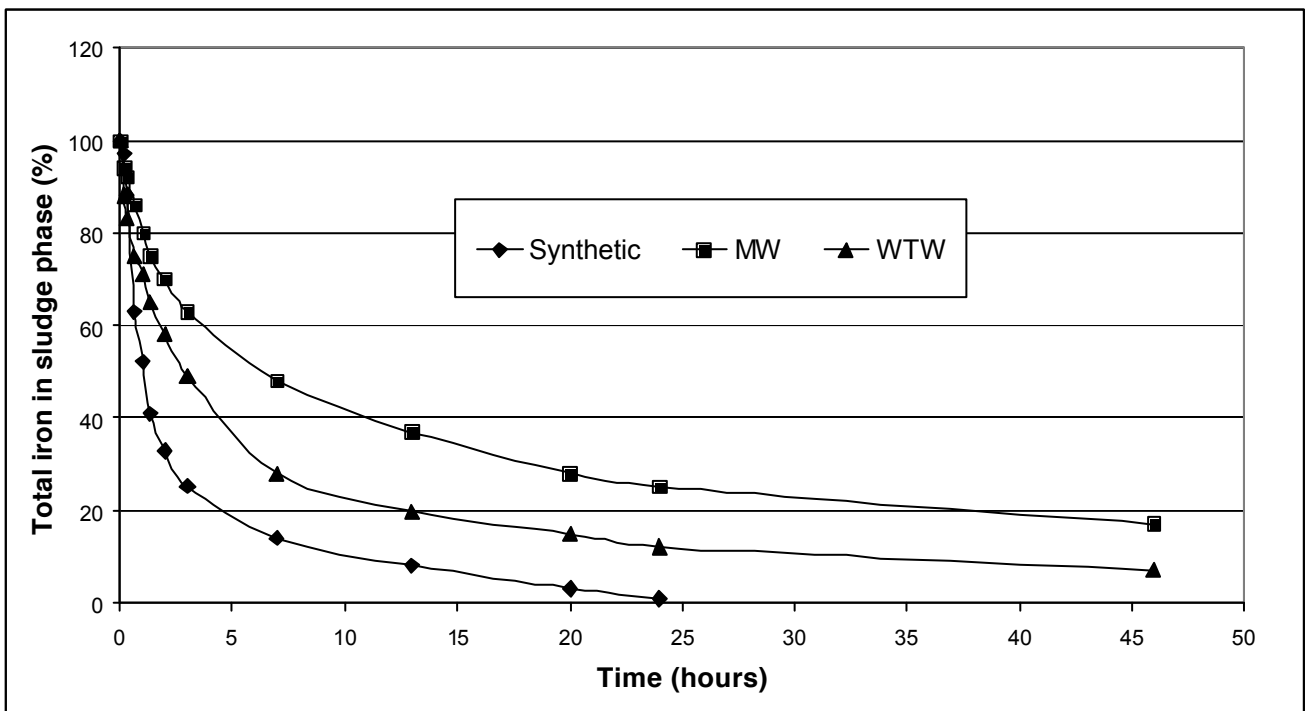


Figure 6. Time dependence of iron concentration for leaching sludge of different origin: synthetic; BH mine water; and water treatment works sludge at 24°C, initial conductivity of 0.83 mS/cm and age one week.

Fig. 8 shows that sludge reactivity decreases markedly with age over 4 years. Similar results (not shown) were obtained with water treatment sludge. Such ageing effects might result from increased average particle size and effective surface area (Houben, 2003) and/or change in mineral phase, e.g., through water expulsion, ion exchange and crystallization. The effects of particle size changes were difficult to assess because of reversible particle aggregation, but initial dispersions did not appear to differ appreciably under the optical microscope. Water expulsion was also difficult to assess because of the large bulk of water admixed with the sediment. However, ion exchange certainly occurred in sedimented ochre, as indicated by a reduction of pH to about 2.5-3.0 in the surrounding medium.

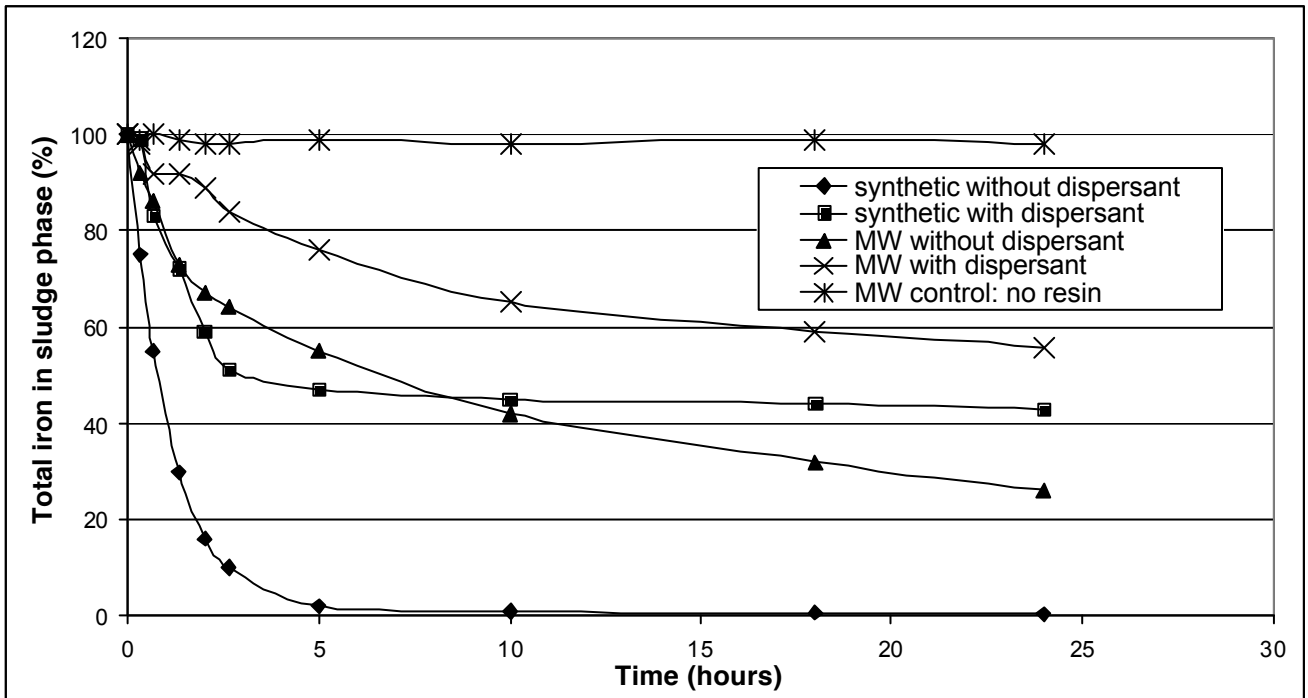


Figure 7. Time dependence of iron concentration for leaching synthetic sludge and BH mine water of age one week with and without addition of dispersant.

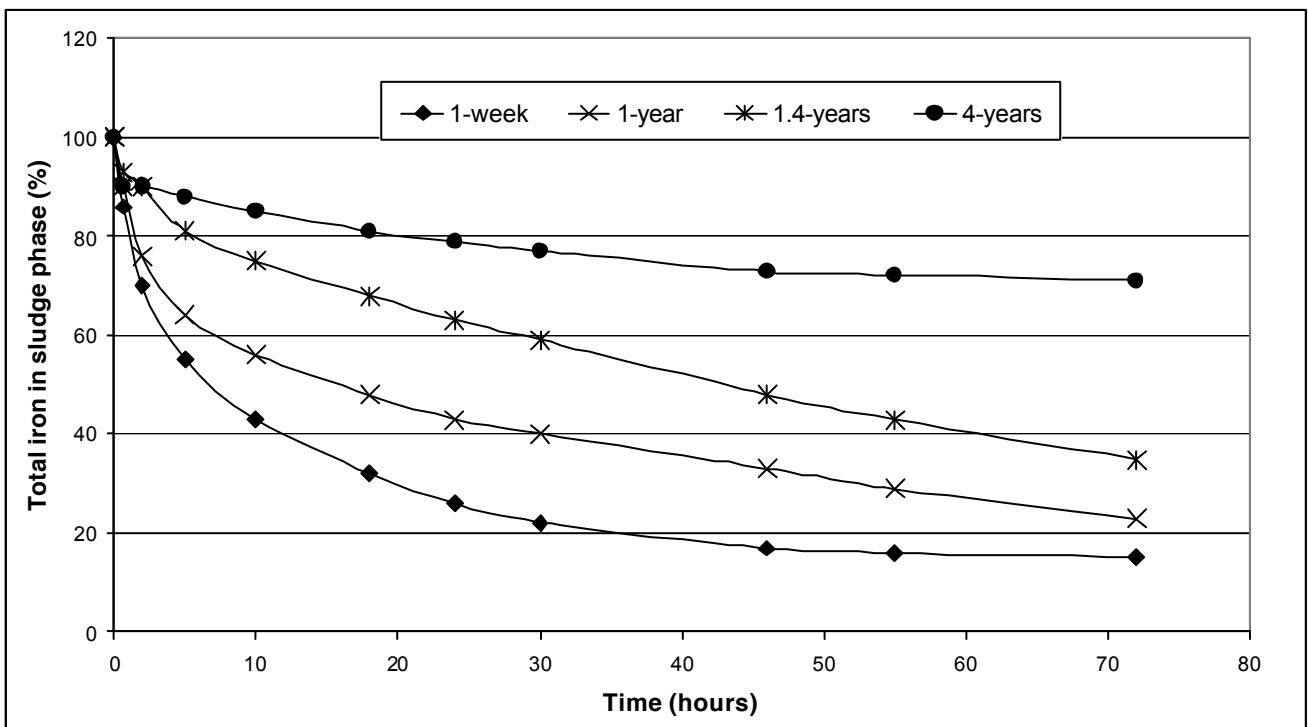


Figure 8. Time dependence of iron concentration for leaching BH mine water sludge of various ages.

Synthetic and natural goethite and limonite all leached much more slowly than mine-water sludge, regardless of age. Increased particle size and crystallisation processes, which are likely to be involved, are discussed in the context of structure below.

Density

It has been shown that iron-rich sludge typically sediments in time to 10-15% w/v solids (density 1.030-1.045 kg/dm³) in water treatment applications, mine water ochre lagoons and naturally iron-rich waters. In many cases this facilitates recovery of some 96-99% of supernatant water. However, the rates of sedimentation (and of subsequent consolidation) and the final water content are obvious issues because of the costs of sludge management. In our work, some 60% of this sedimentation occurred within a few days and most of the consolidation (densification) within five months under normal gravity, provided the sludge remained submerged and undisturbed (Fig. 9). Slow bulk reactions, such as sulphate reduction (in the presence of organics under anaerobic conditions), had little apparent effect on density. The essentially amorphous, gel-like, structures initially formed retained over 85% of water, i.e, less than 15% of solids. Dewatering processes (sand filtration, centrifuging, etc.) increased the solids content to 20-35 % w/v (density 1.061-1.111 kg/dm³) and drying processes to essentially 100% solids (density 1.4 kg/dm³), although structural water was still retained.

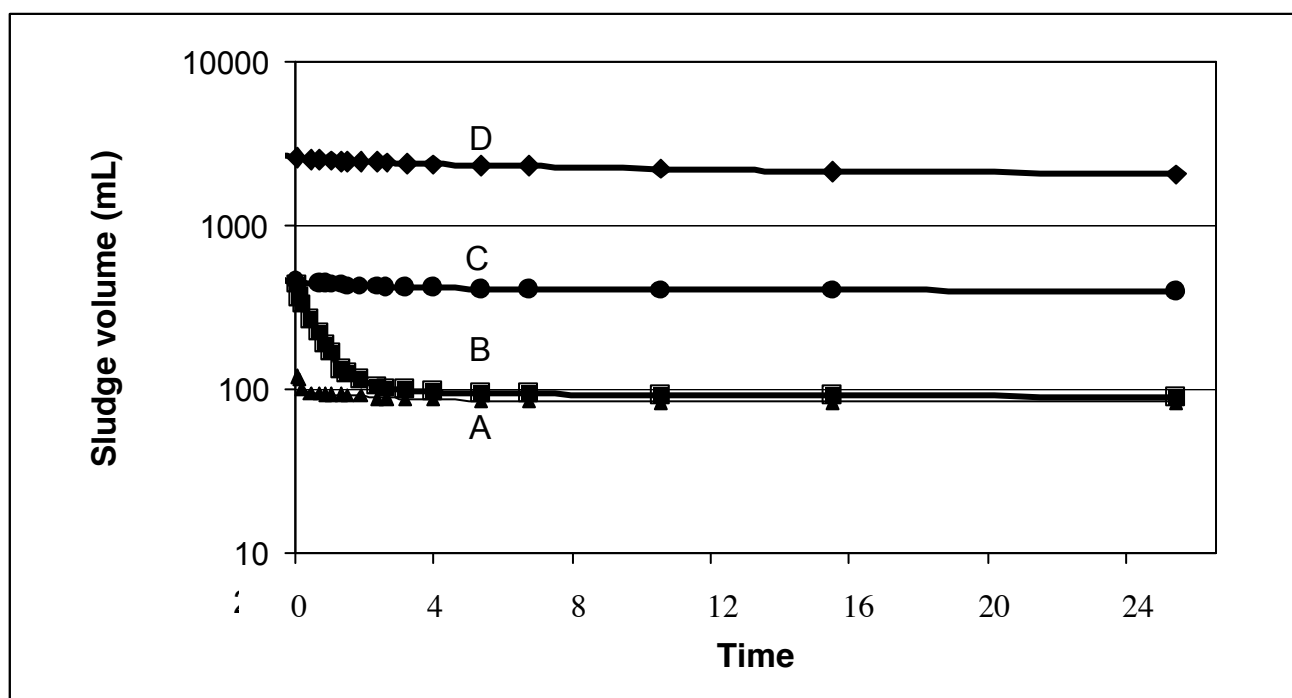


Figure 9. Sludge volume versus time (months) for sedimentation of BH mine water ochre: A, spontaneous (pH 4-5); B, hydrogen peroxide (pH 4-5); C, alkali (pH 6-7); D, alkali (pH 11-12).

Particular methods of sludge formation had different effects on the rate of sedimentation, initial sludge density and subsequent densification. For instance, although initial precipitation of ochre from 90 l mine water by slow spontaneous aerial oxidation at pH 4-5 required some seven days, whereas accelerated chemical oxidation with hydrogen peroxide at the same pH gave immediate precipitation, re-suspension and re-sedimentation of the resultant sludge phases from 500 ml mine water indicated that, for aerial oxidation, a consolidated sludge of less than 100 ml (nominal density 1.045 kg/dm³) was obtained after one week while, for chemical oxidation, the same volume was reached only after two months. As is often the case, rapid precipitation thus produced smaller (in this case, colloidal-sized), and therefore slower settling, particles. As expected, addition of Magnafloc polyelectrolyte greatly increased initial settling rates. However, because consolidation was significantly hindered by the larger aggregate particles (having poorer packing characteristics) thus formed, little difference was observed in the mud lines after two months. This type of analysis could form the basis of a careful balance in practice between conflicting requirements of fast precipitation, maximum water recovery and efficient sedimentation/consolidation.

Accelerated spontaneous oxidation by alkali addition gave even slower settling and much more voluminous sediments (Fig. 9). Thus, at initial pH 6-7 and 11-12 the sediment occupied some 4 and 100 times, respectively, the pH 4.5 settled volume after 2 years. The large increase in sediment volume was attributed mainly to the dispersive effects of alkali, although other mineral phases would undoubtedly contribute. In fact neutralization with alkali is well known in industry to give a relatively voluminous sludge.

As indicated previously, a number of techniques have been tested to release weakly bound water from sludge sediments and thus facilitate densification by consolidation and/or dewatering. In the present work, the effects of dewatering polymers, freeze/thaw and accretion, with and without centrifuging, were briefly compared with untreated gravity sediments (12 and 20% solids, un-centrifuged and centrifuged, respectively). After polymer addition, un-centrifuged and centrifuged solids contents were typically 12 and 24%, respectively. The different polymer types mentioned earlier, used singly and in pairs, gave similar responses. Freeze/thaw procedures correspondingly gave 20 and 24%, while accretion gave 20-25%. These results are consistent with industrial practice. Thus, without centrifuging, freeze/thaw or accretion would in principle be preferred. A form of lime-intensified accretion on recycled particles is in fact employed at the Wheal Jane mine water treatment plant (Coulton, *et al.*, 2003). Freeze/thaw can be employed where the climate allows. Where centrifuging is employed, a marginal benefit may be gained by simultaneous use of one of the special treatments.

Structure

Preliminary work confirmed the applicability of FT-IR/ATR for recording spectra of iron sludge in the range $4000\text{-}200\text{ cm}^{-1}$. Target regions of the spectrum for present purposes were $3000\text{-}3500$, $1600\text{-}1300$ and $800\text{-}900\text{ cm}^{-1}$, representative of water, organic (e.g., carboxyl) and Fe-O/Fe-OH vibrational modes, respectively (Schwertmann & Fischer, 1973). Fig. 10 compares typical spectra for mine water and water treatment sludge. In both cases an intense and broad water absorption was evident. Water treatment waste was characterised primarily by two large organic absorptions and mine water sludge by two smaller peaks at the wavelengths indicated.

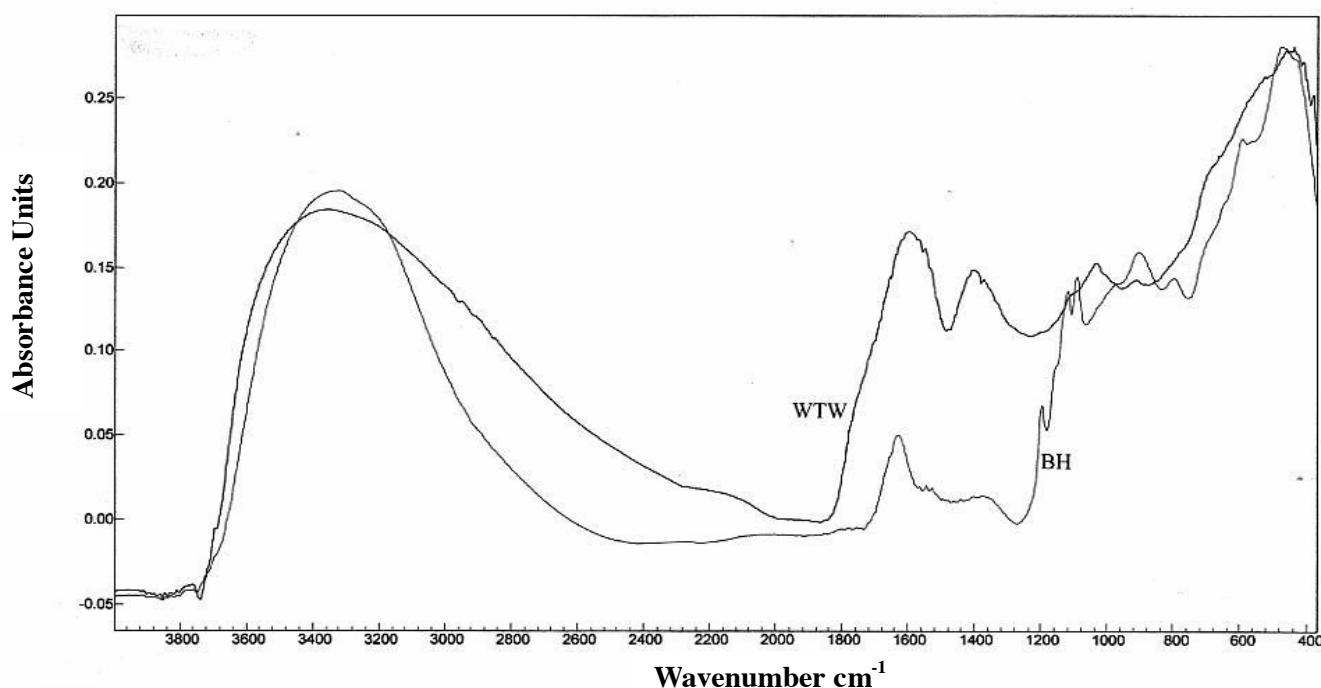


Figure. 10. FTIR comparison of BH minewater ochre and an organic rich (50%) WTW sludge cake.

Fig. 11 compares typical spectra of mine water sludge from BH and W (termed sites 1, 2 and 3) of varying age with that of goethite ($\text{FeO}(\text{OH})$). As can be seen the two peaks (at 792 and 890 cm^{-1}) were always present, but sharpened and increased in intensity with time. Sludge from various coalmines gave similar results. A semi-quantitative plot of peak height versus sludge age (Fig. 12) indicated a clear correlation, having an apparent limit equivalent to goethite. A similar correlation (not shown) was evident from corresponding XRD spectra. The results were thus consistent with slow conversion of largely amorphous ferrihydrite to substantially crystalline goethite. Limonite, an impure rock form of goethite, gave only one FT-IR peak (798 cm^{-1}) in the same spectral region. Comparison of Figs. 8 and 12 indicated a clear link between sludge reactivity and crystallinity (*cf* Fig. 1) and may add a further dimension to the particle size based rate deductions of Houben (2003).

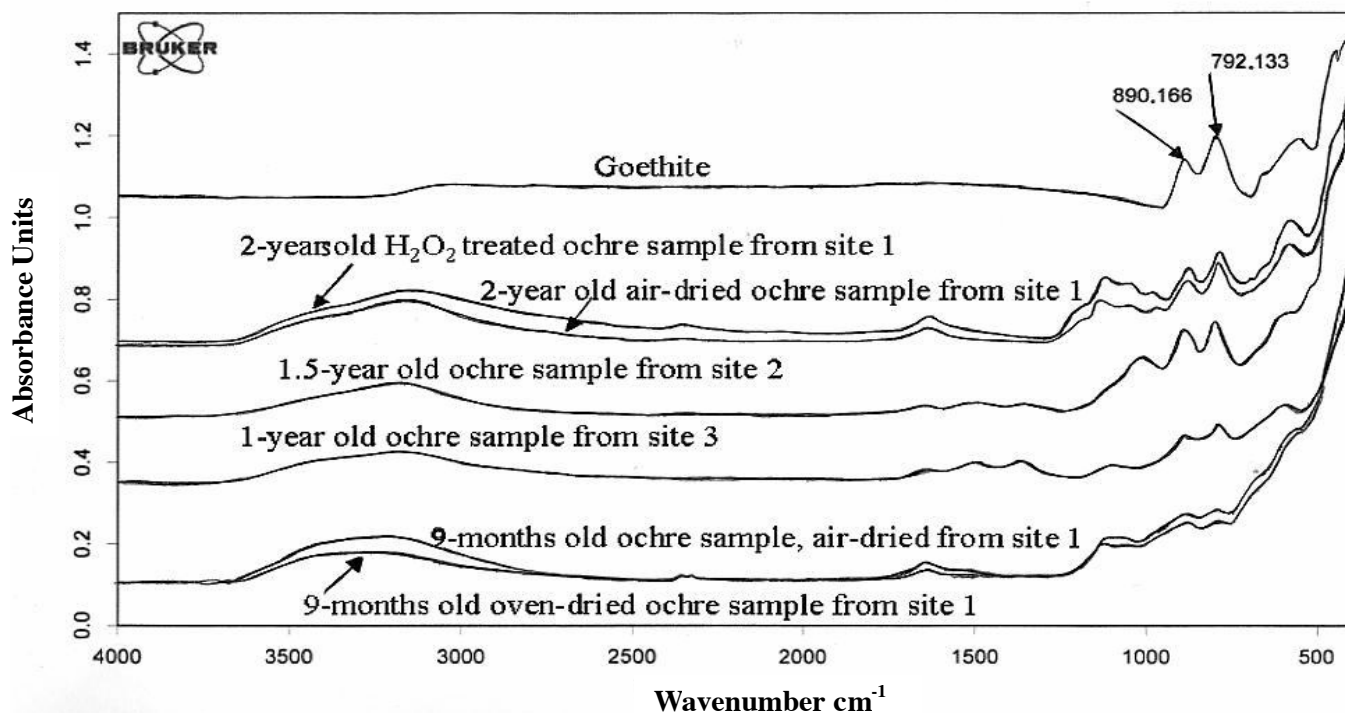


Figure 11. FT-IR/ATR of goethite and various aged sludge samples from mine water sites 1, 2 and 3.

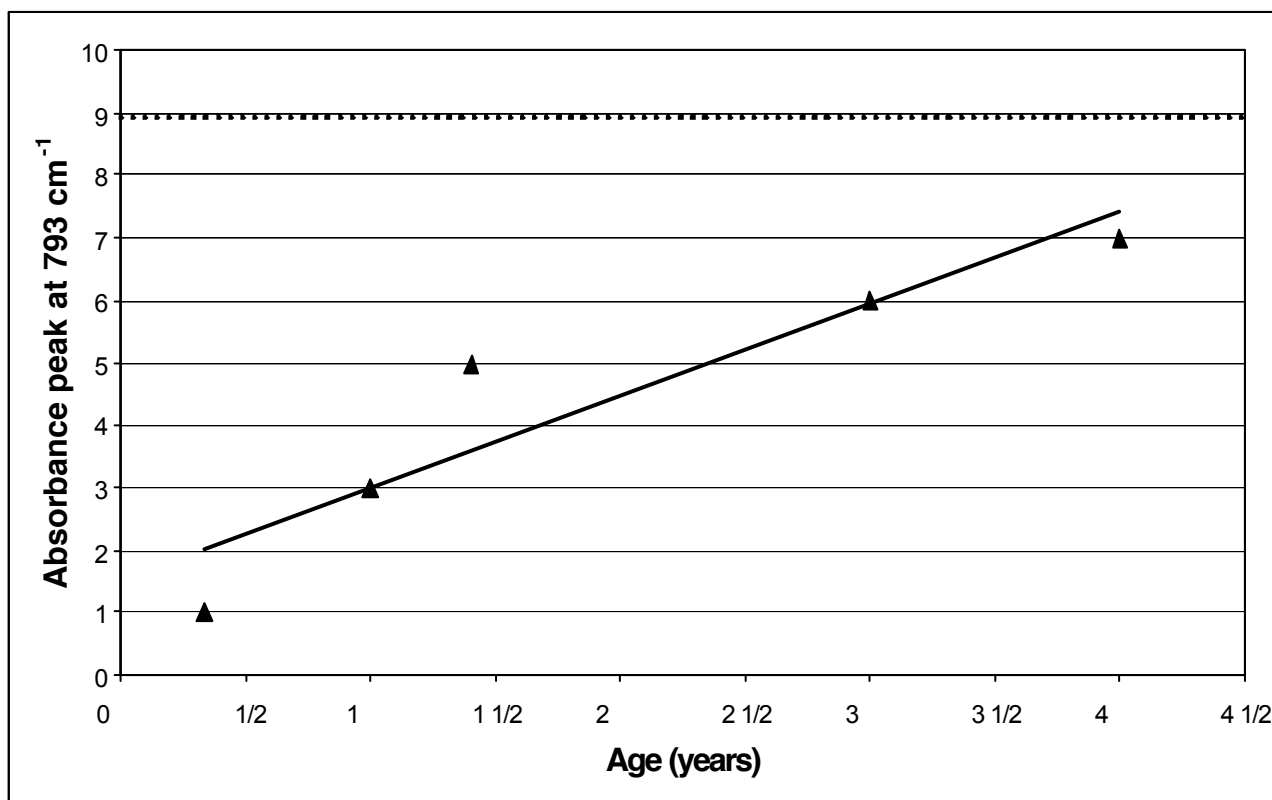


Figure 12. Semi-quantitative plot of peak height (mm) versus mine water sludge age. The horizontal dotted line indicates goethite.

FT-IR peak intensities varied with sludge water content in the spectral region 3000-3500 cm^{-1} . Fig. 13 shows a derived chart of peak height at 3400 cm^{-1} versus mode of mine water sludge conditioning. The peak height decreased in the order spontaneous sedimentation > polymer conditioning > freeze/thaw > centrifuging > accretion > oven drying. Centrifuging, as shown here, intensified spontaneous sedimentation (without specific sludge conditioning), and, of course, also gave decreased peak heights when used to intensify sedimentation with polymers, freeze/thaw or accretion. These results largely substantiated the water content and density measurements described earlier. They additionally indicated the proportion of water remaining in oven-dried material (about 5%). TGA results (not shown here) gave a detailed profile of how this water was removed at higher temperatures. In principle the spectra also facilitated an independent measure of composition, particularly iron:water ratio, but in practice precision was too low to be useful. There were minor or no discernable effects of crystallinity or particle size on densification, and therefore no significant effects of ageing other than from water loss by dewatering or drying. Similarly, there are unlikely to be significant effects of density on reactivity, other than related to increase in surface area available for leaching.

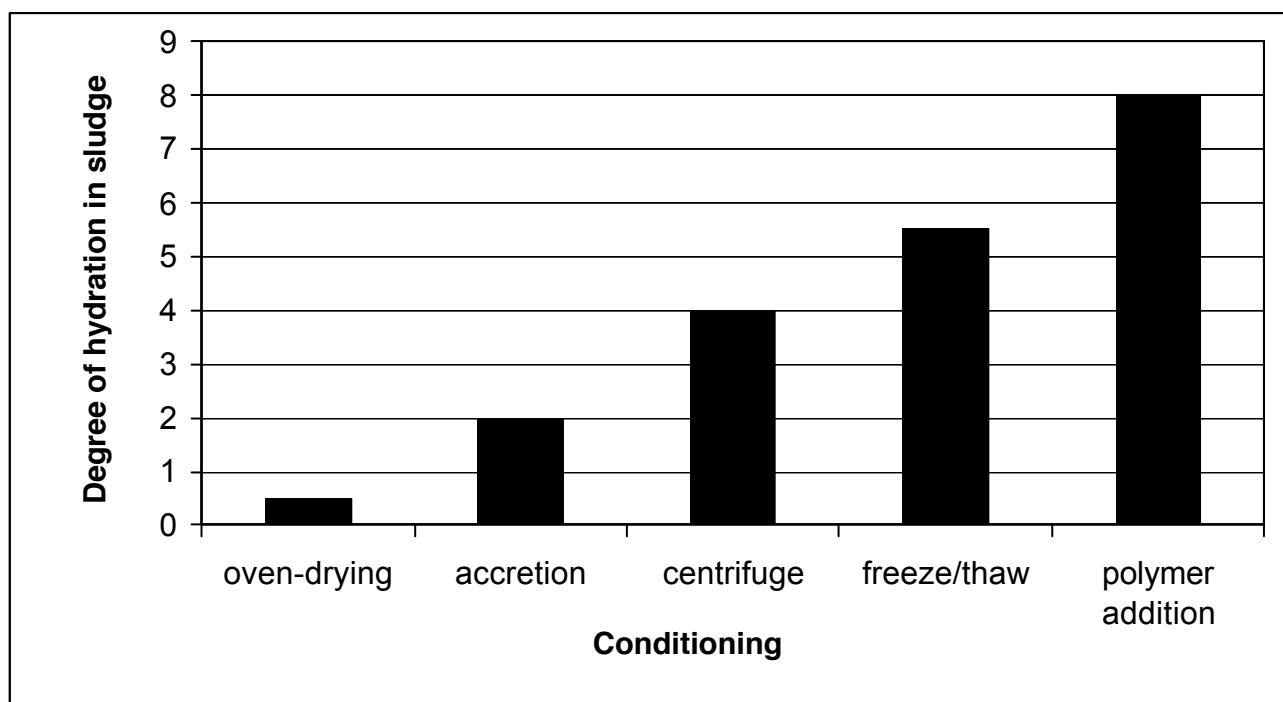


Figure 13. Chart showing FTIR-derived degree of hydration for different modes of sludge conditioning.

CONCLUSIONS

The results of this paper tested a hypothesis (Fig. 1) that correlations could be made between the structure, reactivity and density of iron rich sludge of different origin, composition, pretreatment and age. Owing to its industrial significance and the voluminous literature relating to such sludge, some of the present work was a substantiation of earlier results in a different context, particularly with regard to densification. The use of ion exchange resins as a means of controlling and comparing acid leaching processes and application of multi-instrument assessment, particularly with FT-IR, were substantially novel. The results were relevant to sludge from mine waters and water treatment plants employing iron coagulants.

A clear semi-quantitative correlation was established between sludge reactivity and age: reaction became slower over several years as the sludge expelled water and became structurally more ordered, i.e., altered from largely amorphous ferrihydrite towards crystalline goethite. This effect seemed to be additional to the more conventional correlation often made between reaction rate and particle size, although further confirmation would be helpful. The reaction was significantly retarded by surface-active reagents, particularly proprietary dispersants and flocculants - most evidently for freshly prepared sludge having the most surface-reactive sites. The practical implication is that, if sludge is leached in a recycling process, fresh material concentrated without the aid of surface-active agents is likely to be preferable.

Work on sludge density indicated the importance of water content and the relative insignificance of structural change. As expected, precipitation and initial sedimentation (recovering more than 90% of contained water) could be enhanced by flocculation. Densification in aqueous medium (typically facilitating sludge management) reduced the volume of the sludge to about 15 % of solids. This could be intensified variously by well-established surface chemical, chemical and physical means, but, unless specially co-accreted (Coulton, *et al.*, 2003), only to a maximum of about 20-25% of solids. Both physical and FT-IR assessment confirmed that the processes were all similarly limited by the fairly constant proportion of water weakly associated with the sludge particles and the limiting efficiency of particle packing. Physical separation of water from dense sludge could achieve 30-35% solids via dewatering processes (some 50% reduction in volume) and nearly 100% by drying (a further 60-70% volume reduction).

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